



**Variabilités des temps de résidence de l'eau et du débit
dans les rivières et les nappes phréatiques : implications
sur la qualité de l'eau : inférence, modélisation et
prédiction des temps de transit de l'eau dans les bassins
versants**

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Par

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Variabilités des temps de résidence de l'eau et du débit dans les rivières et les nappes phréatiques : implications sur la qualité de l'eau

Inférence, modélisation et prédiction des temps de transit de l'eau dans les bassins versants

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« Presque une canonnade.

*C'est pourquoi rieuses, réjouies, ravies ne convient
pas à ces eaux. Fougueuses, violentes [...] ;
fraîches, usées par rien, troublées par rien,
premières ; le plus étrange étant peut-être qu'elles
fussent à la fois l'image du temps le plus rapide (le
plus preste, le plus allègre) et hors du temps ou du
moins inaltérées par le temps. Les plus
désaltérantes d'être inaltérées. »*

Philippe Jaccottet, Après beaucoup d'année, « Au
col de Larche », ed. Gallimard (1994).

Table des matières

Préambule.....	7
Partie I Introduction Générale.....	9
Chapitre 1 Mesurer le temps de séjour dans les différents hydrosystèmes	10
1.1 Motivations : les temps de résidence et de transit, un concept unificateur pour appréhender les questions de qualité d'eau	10
1.2 Données géochimiques contraignant les temps de résidence et de transit de l'eau.....	14
1.3 Eaux vieilles versus eaux jeunes : le paradoxe du stock et du flux	19
Chapitre 2 Modéliser les temps de résidence et de transit à l'échelle du bassin versant.....	26
2.1 En hydrologie de surface, tour d'horizon des approches implicites classiquement développées pour inférer les temps de transit.....	26
2.2 En hydrogéologie, des approches explicites souvent privilégiées pour modéliser les temps de résidence	30
2.3 Introduction du travail de thèse	33
Partie II Inférence des temps de résidence dans les aquifères cristallins	36
Chapitre 1 Evaluer le contenu informationnel des traceurs atmosphériques pour inférer les distributions des temps de résidence	37
1.1 Introduction	37
1.2 Article: Inferring transit time distributions from atmospheric tracer data: Assessment of the predictive capacities of Lumped Parameter Models on a 3D crystalline aquifer model	38
1.3 Bilan	52
Chapitre 2 Développer des traceurs géochimiques pour déterminer les temps de résidence en aquifère cristallin.....	53
2.1 Introduction	53
2.2 Article: Dating groundwater with dissolved silica and CFC concentrations in crystalline aquifers	54
2.3 Bilan	68
Chapitre 3 Intégrer des traceurs atmosphériques dans des modèles hydrogéologiques	69
3.1 Introduction	69
3.2 Article: Coupling 3D groundwater modeling with CFC-based age dating to classify local groundwater circulation in an unconfined crystalline aquifer	69
3.3 Bilan	86
Partie III Stratégie de modélisation du flux et du transport à l'échelle du versant : un modèle à base physique parcimonieux.....	87
Chapitre 1 Modéliser le flux : Couplage des écoulements souterrains en aquifères avec les écoulements de proche subsurface dus à des processus de ruissellements.....	89
1.1 Introduction	89

1.2	Article: Dynamic coupling of subsurface and seepage flows solved within a regularized partition formulation.....	90
1.3	Bilan	103
Chapitre 2	Modéliser le transport : Développement d'un modèle parcimonieux semi-explicite à l'échelle du versant.....	104
2.1	Introduction	104
2.2	Article: Coupling hillslope transfers and biogeochemical reactivity within a parsimonious and physically-based catchment model.....	105
2.3	Bilan	141
Chapitre 3	Comprendre le partitionnement entre eaux jeunes et eaux vieilles dans les cours d'eau à l'aide de données en silice et d'un modèle à base physique.....	142
3.1	Introduction	142
3.2	Article : Partitioning young and old groundwater contributions to streams with integrated discharge and water quality data.....	143
3.3	Bilan	176
Partie IV	Discussions et perspectives	177
Chapitre 1	Comprendre les déterminants géomorphologiques du ruissellement à l'échelle du versant	178
1.1	Position du problème : prédire l'importance des écoulements rapides sur le débit en rivière	178
1.2	Méthodes : un laboratoire numérique permettant des expériences de synthèse basées sur un modèles physique pour réduire la complexité du réel	179
1.3	Résultats préliminaires : l'importance des propriétés de la zone riparienne	180
1.4	Perspectives : comment enrichir cette analyse et la tester sur des cas « réels »?	182
Chapitre 2	Rechercher des descripteurs géomorphologiques des distributions de temps de transit	184
2.1	Position du problème : est-il possible de prédire la forme de la distribution des temps de transit à partir de la topographie du versant ?.....	184
2.2	Résultats préliminaires : la distribution des volumes sur le versant est un facteur de contrôle clef de la distribution des temps de transit	185
2.3	Discussion : comment tester cela sur des cas réels ?.....	187
Chapitre 3	Modélisation des aquifères libres de proche subsurface à l'échelle régionale	189
3.1	Position du problème : disposer d'un système de modélisation sur le territoire cristallin breton	189
3.2	Approches de modélisation : à base de versants élémentaires représentatifs	189
3.3	Identification des propriétés hydrauliques des versants à l'échelle régionale	190
Chapitre 4	Une approche de la réactivité pour intégrer de nouveaux traceurs, révélateurs du fonctionnement de la zone critique.....	192

4.1	Position du problème : vers une description mécaniste de la réactivité à l'échelle du versant	192
4.2	Une nouvelle approche des bassins versants comme des réacteurs compartimentés	193
4.3	Comment informer la réactivité ? Exemple de données en nitrate sur des bassins versants bretons	196
4.4	Identification des compartiments d'intérêts, recherche d'une inférence ciblée à l'aide de traceurs spécifiques et intérêt de la haute fréquence pour le suivi de la qualité de l'eau en rivière	199
Chapitre 5	Vers une meilleure intégration des données et des modèles à base physique	202
5.1	Introduction	202
5.2	Abstract	202
5.3	Article: Prospective Interest of Deep Learning for Hydrological Inference	203
5.4	Bilan	209
Partie V	Conclusions générales	210
Références		214

Préambule

La seconde moitié du vingtième siècle a vu une accélération des changements globaux sur l'écosystème terrestre [Rockstrom et al., 2009; Steffen et al., 2015]. Ces changements sont imputables à l'activité humaine si bien qu'on a défini le terme d'anthropocène pour déterminer géologiquement la période de 1945 à nos jours [Crutzen, 2006; de Chardin, 1947; Vernadsky, 1945]. Ces changements ne se limitent pas aux changements climatiques en cours. Les limites de la planète ont été outrepassées dans un certain nombre de domaines, de l'érosion de la biodiversité aux grands cycles biogéochimiques, en passant par le climat et l'artificialisation des terres [Rockstrom et al., 2009; Vitousek et al., 1997a]. Au regard des grands cycles biogéochimiques, l'intensification de l'agriculture et l'ouverture des cycles de l'azote et du carbone grâce aux énergies fossiles ont conduit à une pollution de l'eau à l'échelle mondiale [Spalding and Exner, 1993; Vitousek et al., 1997b]. C'est ainsi que la majorité des pays de l'hémisphère nord ont des problèmes d'eutrophisation dans les cours d'eaux et dans les baies côtières [Pinay et al., 2017].

Pour comprendre les origines et évaluer les impacts de ces pollutions humaines, la communauté scientifique et les gestionnaires de l'environnement ont investi massivement dans des systèmes de collecte de données environnementales implantés sur des observatoires de l'environnement [Baatz et al., 2017; Brantley et al., 2017; White et al., 2015; Zacharias et al., 2011]. Que ce soit du suivi *in situ* ou de la caractérisation spatialisée via des données satellitaires ou des drones, de la mesure haute fréquence en rivière dans des observatoires environnementaux ou des mesures plus ponctuelles de suivi de qualité de l'eau dans les grands bassins versants, la mesure est partout [Floury et al., 2017; Le Phong and Kumar, 2014; 2017; Rode et al., 2016]. Cet investissement engendre une collecte de données sans précédent relative aux milieux aquatiques continentaux et aux structures géologiques traversées [Richter and Mobley, 2009; Vereecken et al., 2015]. Ces données permettent d'avancer vers une caractérisation structurelle, fonctionnelle et réactive de la zone critique [National Research Council, 2001]. La zone critique se définit en effet comme étant l'interface où se rencontrent la lithosphère, l'atmosphère, l'hydrosphère et la biosphère [Brantley et al., 2007; Chorover et al., 2007]. Elle s'étend de l'horizon non altéré des roches au sommet de la canopée [Guo and Lin, 2016; Riebe et al., 2016]. Cette zone est critique pour la vie des milieux continentaux et est, à ce titre, critique pour l'humanité [Lin, 2010].

Cependant, ces données se caractérisent aussi par leur nature hétérogène et par le fait qu'elles reflètent l'intégration et la coévolution de différents processus provenant de différentes disciplines (e.g. hydrologie, géologie, biologie) [Capell et al., 2012; Pelletier et al., 2013; Troch et al., 2009; Troch et al., 2015; Yoshida and Troch, 2016]. Les intégrer dans un exercice de modélisation renouvelé est impératif pour penser la zone critique, comprendre son fonctionnement, prédire son évolution future [Kirchner, 2006; Pinay et al., 2015] en intégrant les inflexions nécessaires à une protection et une sauvegarde de l'environnement.

Cette thèse s'inscrit dans le contexte de la forte augmentation du nombre de données environnementales disponibles pour mieux comprendre l'impact des activités humaines sur les écosystèmes aquatiques terrestres. C'est donc un travail visant à développer un cadre de modélisation adapté pour amorcer l'intégration de ces données en vue de mieux prédire l'évolution de la qualité de l'eau en rivière suite aux forçages de l'agriculture intensive. Pour comprendre comment se forme cette « qualité de l'eau en rivière », un concept clef est celui de temps de transit et de temps de résidence. En effet, le temps de

transit représente, pour les eaux constituant le débit d'une rivière, le temps qui a été nécessaire à cette eau pour « voyager » à travers les différentes parties de l'hydrosystème du bassin versant, de son entrée sous forme de pluie à sa sortie sous forme de débit à l'exutoire. Le temps de résidence caractérise, lui, pour l'eau stockée dans le bassin versant, le temps depuis lequel cette eau est stockée dans le bassin versant. La détermination de ces temps est essentielle pour estimer l'inertie des masses d'eau ainsi que le stock de nitrates qu'elles contiennent comme pour prédire le temps de réponse des systèmes hydrologiques à des changements de pratiques agricoles par exemple.

J'ai donc mené une réflexion sur le potentiel informatif d'un certain type de données, aussi bien spatiales (données topographiques, données sur les apports en fertilisants azotés, données de concentrations de silice, de nitrates ou de CFCs en puits) que temporelles (données de débit, de concentrations en silice ou en nitrates en rivières) pour comprendre et prédire l'évolution de la pollution azotée dans les masses d'eaux (rivières et aquifères) des bassins versants côtiers bretons. Cette réflexion vise à estimer les temps de résidence (pour les aquifères) ainsi que les temps de transit (pour les rivières) ainsi que leur variabilité temporelle. Pour contraindre et inférer ces temps caractéristiques de résidence et de circulation, deux connaissances sont fondamentales à développer : premièrement, une connaissance des volumes d'eaux stockés et de leur répartition dans le bassin versant ; deuxièmement, une connaissance des flux d'eaux qui traversent ces volumes et qui vont renouveler ces volumes stockés. En effet, comme on va le voir, le temps de résidence dépend du volume stocké et dépend inversement du flux qui le traverse.

Nous développons ensuite une stratégie de modélisation originale, articulée autour de la représentation de processus hydrologique clefs à l'échelle du versant, qui soit adaptée à un grand nombre de sites, pour décrire de manière quantitative ces concepts centraux et unificateurs que sont les temps de résidence et de transit. Ces processus visent à décrire comment le climat (les flux d'eau qui forcent la réponse du bassin versant) et l'humidité du bassin versant (i.e. les stocks d'eau qui varient suivant la saison) contrôlent la connectivité du versant, les chemins préférentiels des écoulements d'eau qui le traversent ainsi que leur vitesse de parcours. Cette démarche vise à progresser dans l'intégration de ces données à des modèles pour une meilleure compréhension des processus d'intérêts. Ces modèles sont à base physique, suffisamment simples pour demeurer informable grâce aux données disponibles mais suffisamment complexes pour relier et donner du sens à des données qui restent parcellaires face à l'inconnu que représentent les eaux continentales. En effet, les données collectées en hydrologie caractérisent massivement les milieux aquatiques continentaux directement accessibles à la mesure (e.g. rivières via des mesures en continu, sols via des mesures de télédétection) mais restent parcellaires vis-à-vis du milieu souterrain.

Partie I Introduction Générale

*« L'eau ainsi est le regard de la terre,
son appareil à regarder le temps. »*

Paul Claudel, *L'oiseau noir dans le soleil levant*

Cette partie est composée de deux sections. La première traite du concept de temps de résidence et de temps de transit de l'eau dans les hydrosystèmes, des moyens mis en œuvre par la communauté en hydrologie pour les mesurer ainsi que des problématiques qui se posent pour comprendre le fonctionnement des bassins versants à l'aide de ces données de temps de résidence / transit. La deuxième partie traite de la manière de développer des modèles à même d'intégrer l'information sur le temps de résidence contenue dans ces données géochimiques, ainsi que des approches de modélisation qui ont été développées en hydrologie de surface et en hydrogéologie.

Chapitre 1 Mesurer le temps de séjour dans les différents hydrosystèmes

1.1 Motivations : les temps de résidence et de transit, un concept unificateur pour appréhender les questions de qualité d'eau

Le temps de transit de l'eau est le temps que l'eau passe pendant son séjour dans le bassin versant depuis le moment où elle tombe sous forme de précipitation jusqu'à la fin de son parcours à l'exutoire de son bassin versant (Figure 1). Dû à l'hétérogénéité du bassin versant et à la variabilité des épisodes climatiques de recharge qui favorisent le mélange de l'eau dans le milieu souterrain, un échantillon d'eau prélevé en rivière ou dans l'aquifère ne contient pas un unique temps de résidence mais une distribution de temps de résidence [Bethke and Johnson, 2008; McGuire and McDonnell, 2006]. Cette distribution reflète la manière dont le bassin versant conserve et libère l'eau. Cette fonction est un descripteur fondamental pour appréhender les stocks d'eau du bassin versant et leur répartition ainsi que les flux d'eau qui le traversent [McDonnell et al., 2010].

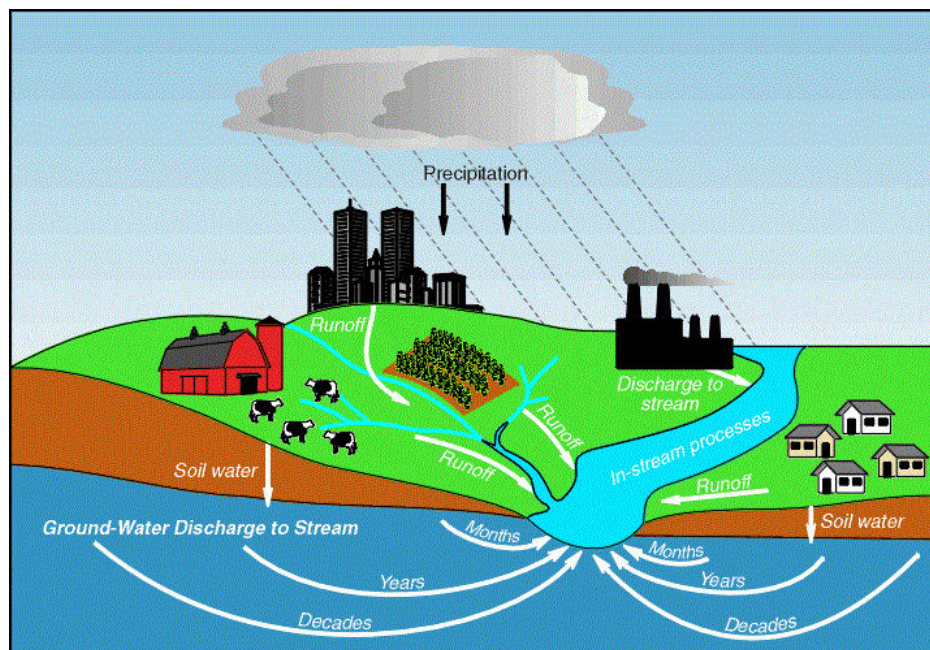


Figure 1: Illustration de la diversité des temps de résidence qui conduisent à la distribution des temps de résidence. Source (USGS).

La donnée de cette distribution de temps de transit est ainsi particulièrement importante à connaître pour estimer la vulnérabilité d'un bassin versant à des pollutions ponctuelles comme à des pollutions diffuses [Hrachowitz et al., 2016; Kirchner et al., 2000]. Dans le cas de pollutions ponctuelles, c'est les temps courts de la distribution qui intéressent car ces temps courts vont caractériser la vitesse à laquelle cette pollution va se propager. Le poids de la distribution sur ces temps courts va également définir la dilution qui va s'opérer, dilution à même de diminuer l'impact de cette pollution ponctuelle. Dans le cadre des pollutions diffuses, c'est l'intégralité de cette distribution qui va nous intéresser : la partie de la distribution centrée sur les eaux jeunes (qui représente généralement le pic de la distribution) ainsi que la partie de la distribution représentant les eaux âgées (la queue de la distribution). Le pic de la distribution nous permet d'évaluer quel peut être l'impact « immédiat » (i.e. de l'ordre de quelques années) de mesures de réduction d'intrants (en nitrates par exemple dans le cas de pollutions agricoles). D'autre part, la queue de la distribution va nous renseigner sur l'effet mémoire de notre bassin versant

[Hrachowitz *et al.*, 2015; Meter and Basu, 2017; Meter *et al.*, 2016]. A cette caractérisation purement physique du mélange de l'eau par cette distribution de temps de transit doit se rajouter une connaissance des zones biogéochimiquement actives ainsi que du temps que l'eau a passé en contact avec ces zones pour que des solutés réactifs comme les nitrates puissent être réduits (i.e. dénitrifiés) [McClain *et al.*, 2003].

Différence entre distribution de temps de résidence et distribution de temps de transit

Il convient de distinguer la notion de temps de résidence de celle de temps de transit (Figure 2). En effet, le temps de résidence se réfère à la distribution des temps de résidence, $p_S(\tau, t)$, qui caractérise, à un instant t (puisque cette distribution n'est pas fixe dans le temps mais au contraire, varie suivant les événements pluvieux, les saisons, les années), la proportion d'eaux ayant résidé dans le bassin versant pendant un temps de résidence τ . Cette distribution caractérise l'ensemble des âges τ des « parcelles » d'eau stockées dans le bassin versant depuis son entrée sous forme d'infiltration. Le temps de transit se réfère à la distribution des temps de transit $p_Q(\tau, t)$. Cette distribution reflète, à un instant donné t , l'ensemble des temps de parcours des « parcelles » d'eau qui alimentent la rivière depuis leur entrée. Ces temps de parcours se mesurent depuis le moment où ces parcelles entrent dans le bassin versant sous forme d'infiltration, lors d'événements pluvieux, jusqu'au moment où elles le quittent dans le débit de la rivière [Bolin and Rodhe, 1973; Rinaldo *et al.*, 2011]. Excepté dans le cas d'un réservoir parfaitement mélangé, ces deux distributions n'ont aucune raison d'être identique [Berghuijs and Kirchner, 2017]. Cependant, en régime permanent, il est possible de déduire l'une des distributions connaissant l'autre [Eriksson, 1961; Eriksson, 1971]. En régime transitoire, ces distributions et leurs variations sont spécialement mal caractérisées. Pourtant, l'étude conjointe des distributions des temps de résidence et des distributions de temps de transit ainsi que leur variation temporelle permet de caractériser la connectivité des différents compartiments des hydrosystèmes ainsi que la manière dont ils contribuent au débit en rivière [Rinaldo *et al.*, 2015].

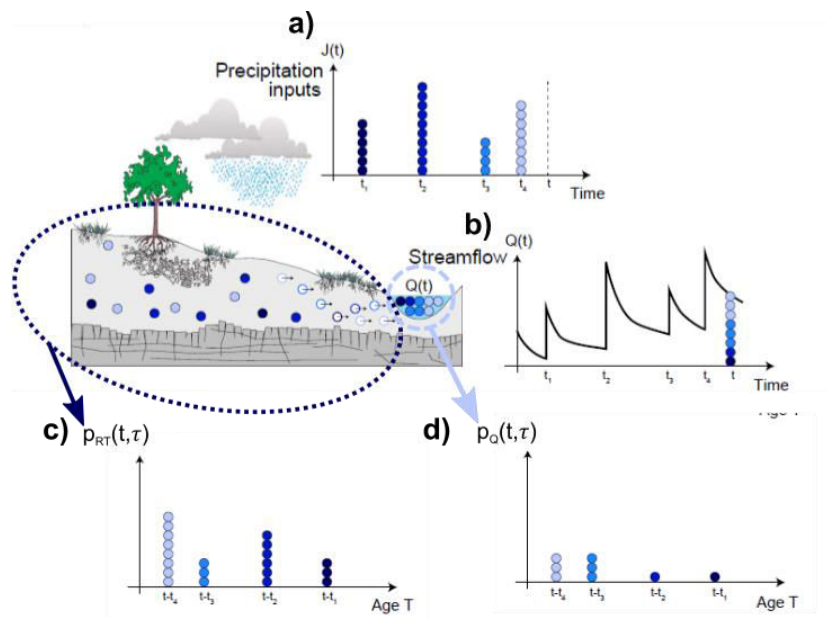


Figure 2: Illustration des différences entre distribution de temps de résidence (c) et distribution de temps de transit (d) suite aux forçages variables de précipitations (a). Alors que la distribution des temps de résidence représente la distribution d'âges des parcelles d'eau stockées dans le bassin versant, la distribution des temps de transit représente la distribution d'âges des parcelles alimentant le débit de la rivière (b) à un instant donné. D'après Benettin and Bertuzzo [2018].

Dans le cadre des problèmes d'eutrophisation que la Bretagne connaît, la connaissance de cette distribution des temps de résidence permet donc de comprendre quel est l'effet des pollutions agricoles passées sur la qualité de l'eau (teneur en nitrates par exemple) que nous observons aujourd'hui dans les rivières et dans les estuaires [Pinay *et al.*, 2015; Pinay *et al.*, 2017]. Cette connaissance de la distribution des temps de résidence est la première étape pour déconvoluer les apports successifs de l'agriculture passée à la qualité de l'eau présente avant de pouvoir spécifiquement évaluer la capacité du bassin versant à épurer l'eau qui le traverse via des processus de dénitrification par exemple. C'est aussi une première étape avant la réalisation de prédictions via des scénarios, pour évaluer l'impact des inflexions et des normes développées pour permettre une agriculture plus durable [Creed *et al.*, 2017; Directive, 2000; Meter and Basu, 2017; Meter *et al.*, 2016].

Évaluer l'intégralité de cette distribution de temps de transit est donc une première étape nécessaire pour prédire la qualité de l'eau en rivière. Cependant, il apparaît que cette distribution contient à la fois des eaux très jeunes qui séjournent peu dans le bassin versant mais aussi des eaux très anciennes qui sont stockées pendant longtemps dans les aquifères avant d'alimenter le débit des rivières. Ainsi, il y a des proportions significatives de l'eau dans les rivières qui ont un âge de moins de trois mois [Benettin *et al.*, 2017; Jasechko *et al.*, 2016] mais, lors d'un épisode pluvieux, les eaux ne contiennent que très peu d'eau provenant de l'épisode de pluie considéré [Bishop *et al.*, 2004; Botter *et al.*, 2010; Kirchner, 2003; McDonnell, 1990]. D'autre part, les aquifères qui alimentent ces rivières ont souvent des temps de résidence de l'ordre de la dizaine voire de la centaine d'années [Ayraud *et al.*, 2008; Gleeson *et al.*, 2015; Jasechko *et al.*, 2017; Kolbe *et al.*, 2016]. Cependant, les eaux de la rivière sont en général beaucoup plus jeunes que les eaux de l'aquifère qui participent à son alimentation [Gabrielli *et al.*, 2018]. Enfin, la variabilité temporelle de ces distributions en fonction des saisons et des années, sèches ou humides, est quelque chose de relativement mal contraint, les modèles de transport simulant les états transitoires étant lourds à développer et à caler [Birkel *et al.*, 2012]. Estimer la distribution des temps de transit, les différentes contributions des eaux jeunes contre les eaux âgées, ainsi leur variation temporelle, au gré des saisons, est nécessaire pour comprendre comment les circulations de l'eau dû à la physique des processus contrôlent l'évolution de la qualité de l'eau.

Certains climats arides permettent d'effectuer cette décorrélation entre eaux jeunes et eaux vieilles, dû à des phénomènes de recharge et à des épisodes de ruissellement bien déterminés temporellement [Desilets *et al.*, 2008]. D'autre part, certaines géologies sédimentaires permettent parfois de séparer le milieu souterrain en zones présentant des temps de résidence bien distincts du fait des structures géologiques étudiés [Lehmann *et al.*, 2003; Sturchio *et al.*, 2004] ou du fait de forçages topographiques rencontrés générant des circulations de différents types (locales, intermédiaires et régionales, Figure 3) [Toth, 1963; Wang *et al.*, 2016].

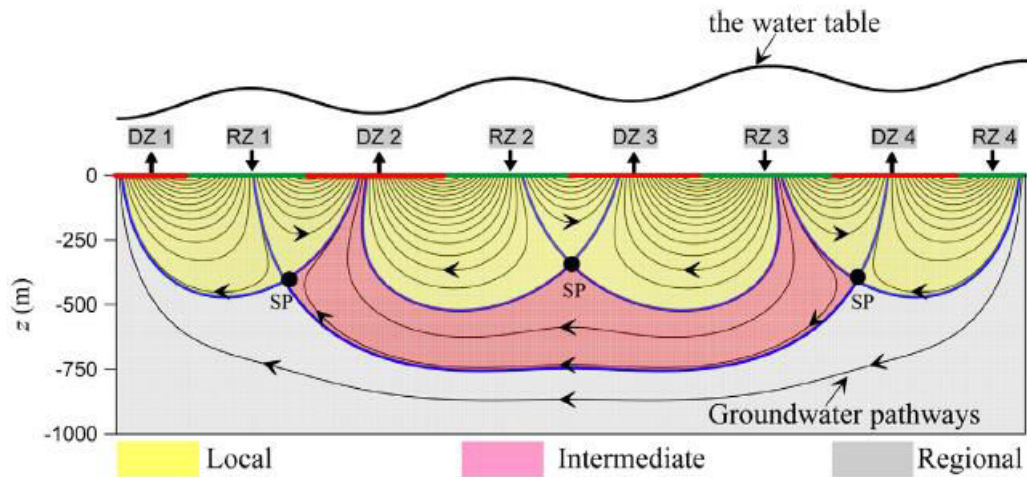


Figure 3: Organisation des écoulements en cellules d'écoulements locales, intermédiaires et régionales. D'après Wang et al. [2016] and originellement de Toth [1963].

Au contraire, la géologie cristalline de la Bretagne couplée à son climat tempéré océanique ne permet pas une telle décorrélation des temps de transit ; les bassins versants bretons présentent au contraire des interactions fortes entre subsurface et surface [Martin et al., 2004; Martin et al., 2006; Molenat and Gascuel-Oudou, 2002; Molenat et al., 2013; Rouxel et al., 2011; Ruiz et al., 2002]. Ces interactions accrues entre écoulements de nappe, écoulements de subsurface et écoulements de surface, rendent la distribution des temps de transit assez large avec des temps variant de quelques semaines à plusieurs dizaines d'années [Ayraud et al., 2008; de Montety et al., 2018; Kolbe et al., 2016; Leray et al., 2012]. En effet sa géologie est caractérisée par une géologie cristalline dont la fracturation diminue fortement avec la profondeur [Dewandel et al., 2006; Guiheneuf et al., 2014; Maréchal et al., 2004; Twidale, 1973], facilitant des circulations d'eaux aux contrastes de perméabilité [Freer et al., 2002; Tromp-van Meerveld and McDonnell, 2006a; b]. On conceptualise souvent le sous-sol breton très schématiquement comme étant constituée de 4 couches : le sol, la zone altérée, la zone fracturée et la roche saine (Figure 4) [Maréchal et al., 2004; Taylor and Howard, 2000; Wyns et al., 2004]. D'autre part, la variation saisonnière des précipitations et de l'évapotranspiration favorise une interaction qui varie selon les saisons. Cette interaction est principalement le fait du processus de battement de nappe qui affleure la surface en saison humide pour s'enfoncer en saison sèche (Figure 5) [Molenat et al., 2008].

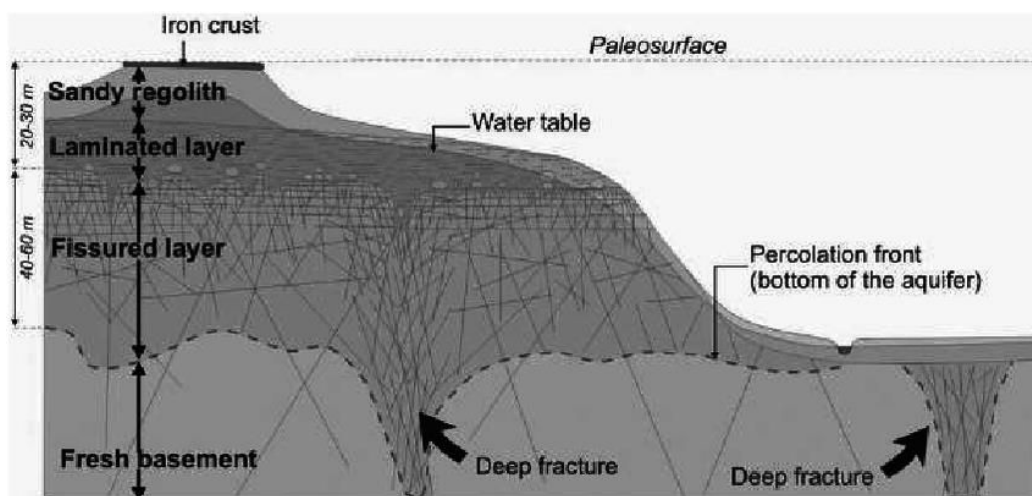


Figure 4: Schématisation de la succession de zones altérés en Bretagne. D'après Wyns et al. [2004].

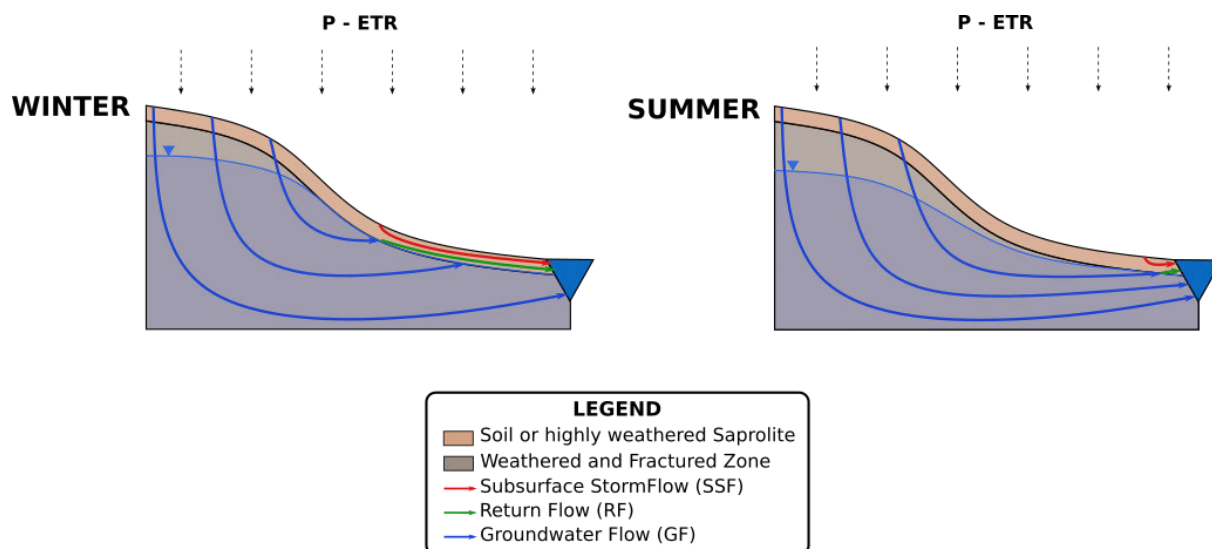


Figure 5: Variation saisonnière de la recharge et processus de battements de nappes en climat tempéré.

1.2 Données géochimiques contraignant les temps de résidence et de transit de l'eau

Pour contraindre cette distribution de temps de résidence (ou temps de transit en rivière), plusieurs observables ont été développées [Abbott *et al.*, 2016]. Elles permettent une estimation directe ou indirecte de l'âge moyen de l'eau mais sont dans les deux cas des agrégations de la fonction physique plus fondamentale mais non mesurable qui est la distribution de temps de transit (ou de résidence) [Ayraud *et al.*, 2008; Bethke and Johnson, 2002]. Nous détaillons dans un premier temps les traceurs géochimiques utilisés en hydrogéologie présentant l'avantage de pouvoir donner une estimation directe renseignant sur la distribution des temps de résidence. Puis nous détaillerons les approches développées en hydrologie, qui visent, à partir de chroniques isotopiques en $\delta^{18}\text{O}$ et $\delta^2\text{H}$ mesurées dans la pluie et en rivière, à obtenir une estimation indirecte du temps de transit. Cette relation se fait à partir de considération sur le filtrage de la chronique isotopique d'entrée par rapport à la chronique isotopique de sortie.

1.2.1 Mesure directe des temps de résidence en hydrogéologie : traceurs atmosphériques et radioactifs

Principe

Pour ces données, le principe est de mesurer la concentration d'un traceur contenue dans un échantillon d'eau et de relier cette concentration à la date à partir de laquelle l'échantillon d'eau a été isolé du reste de l'atmosphère. Du fait de ce principe, cette technique s'utilise à de rares exceptions près en aquifère et non en rivière. Relier la concentration mesurée à la date d'entrée de l'échantillon dans le système souterrain se fait grâce à différentes propriétés des traceurs atmosphériques ou radioactifs. S'ils sont atmosphériques, on relie la concentration mesurée à la date à laquelle l'atmosphère avait cette concentration en traceur après avoir pris en compte les phénomènes d'équilibration entre l'air et l'eau via un processus d'équilibre (loi de Henri, [Labasque *et al.*, 2006; Labasque *et al.*, 2014]). S'ils sont radioactifs, c'est directement la décroissance observée par rapport à la concentration initialement attendue qui renseigne sur le temps nécessaire à une telle dégradation. Cet âge obtenu n'est qu'un âge apparent, en d'autres termes, ce n'est rien de plus qu'une transcription sous forme d'une quantité plus facile à appréhender que la donnée de concentration initiale (une donnée d'âge en années à comparer à une donnée de concentrations en CFCs en pptv...) [Suckow, 2014]. Pour l'interpréter en terme de temps

de résidence, cela nécessite d'utiliser un modèle de temps de résidence implicite ou explicite (voir Partie I Chapitre 2) pour remonter, à partir de ces observables (les concentrations), aux distributions de temps de résidence.

Type de traceurs utilisés en hydrogéologie

CFCs et SF₆

Les CFCs et le SF₆ sont des traceurs atmosphériques dont la concentration atmosphérique renseigne sur la partie de la distribution des temps de résidence de l'eau comprise entre 0 et 70 ans [Busenberg and Plummer, 1992; Busenberg and Plummer, 2000; Cook et al., 1995]. En effet, ces traceurs ont commencé à être présent dans l'atmosphère après la seconde guerre mondiale (années 1940) et leur concentration atmosphérique a ensuite augmenté exponentiellement du fait de leur utilisation comme gaz réfrigérant (ou isolant électrique pour le SF₆). Ces traceurs sont donc un outil fondamental (bien qu'ils soient responsables de la destruction de la couche d'ozone...) pour évaluer les temps de résidence qui sont reliés à la période durant laquelle l'agriculture s'est intensifiée en France. Cependant, l'adoption du protocole de Montréal, interdisant l'usage de ces gaz réfrigérants du fait de leur rôle dans la destruction de la couche d'ozone, a induit l'apparition d'un plateau suivi d'une légère décroissance dans la chronique temporelle de l'évolution de leur concentration atmosphérique (Figure 6). Ceci a pour conséquence d'avoir une chronique atmosphérique d'entrée moins informative qu'auparavant sur les eaux rechargées récemment (<5 ans) et permet d'envisager qu'ils deviendront obsolètes dans le futur.

Il est à noter que le SF₆ peut être produit de manière terrigène par les roches cristallines. Il est donc peu souvent utilisé en Bretagne [Aquilina et al., 2011; Darling et al., 2012; Koh et al., 2006]. D'autre part, si ces traceurs sont considérés comme inerte et reflétant le transport uniquement conservatif de l'eau (leur concentration n'est que le fruit de la concentration atmosphérique initiale et du mélange s'opérant dans le milieu souterrain), ils peuvent subir 1/ des contaminations dues à des décharges qui voient des produits contenant des CFCs « contaminer » la nappe phréatique ; 2/ des dégradations par réaction biogéochimiques en milieu anoxique [Höhener et al., 2003; Plummer et al., 1998a; Plummer et al., 1998b; Sebol et al., 2007].

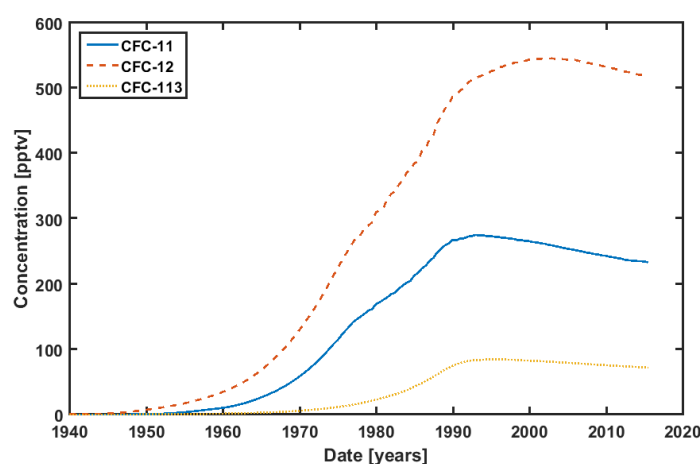


Figure 6: Illustration de l'évolution des concentrations atmosphériques en CFCs depuis la fin de la seconde guerre mondiale. Le SF₆ présente une évolution très similaire mais est rarement utilisé en Bretagne du fait d'une production terrigène des roches granitiques. D'après Marçais et al. [2018].

¹⁴C

Le carbone 14 est le traceur radioactif emblématique [Vogel, 1970]. L'eau qui se recharge dans la nappe a une concentration atmosphérique initiale en ¹⁴C. Cette concentration initiale dépend du moment de la

recharge puisque ses concentrations ont été influencées par les essais nucléaires dans les années 1950-1960. Le ^{14}C étant radioactif, cette concentration décroît ensuite vers 0 et c'est cela qui permet de l'utiliser pour la datation. Le temps de demi-vie du ^{14}C étant de 5730 ans environ, le ^{14}C permet de dater des eaux entre 1000 ans et 50000 ans. Ceci en fait un traceur pour les eaux anciennes, complémentaires aux mesures en CFCs (Figure 7). Il est à noter que ce traceur est influencé par de nombreux processus parmi lesquels les réactions d'oxydo-réduction, la précipitation et la dissolution de minéraux, surtout en présence de roches carbonatées dans les milieux sédimentaires. Ces réactions ont pour conséquence de vieillir artificiellement les échantillons d'eaux analysés [Bethke and Johnson, 2008]. C'est pourquoi une modélisation du transport réactif du ^{14}C dans l'aquifère, avec prise en compte des termes sources et des interactions eaux/roches, est souvent requise pour avoir accès à l'âge ^{14}C [Plummer et al., 1994].

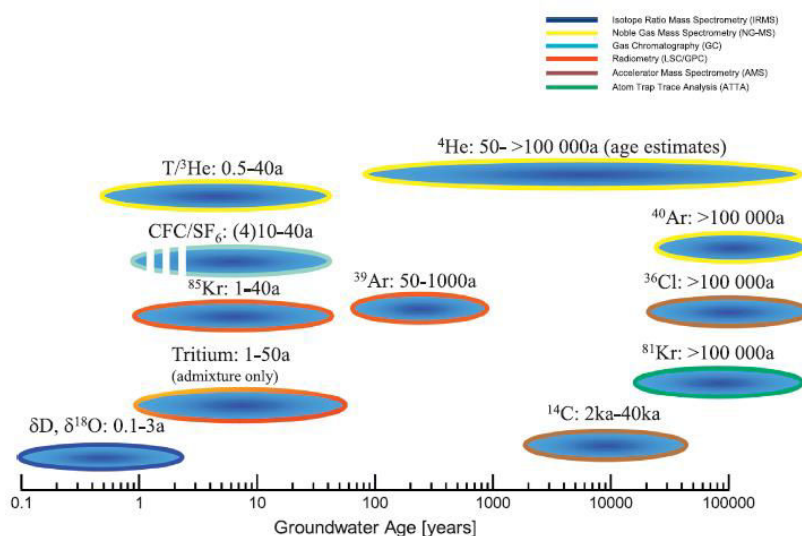


Figure 7: Différents traceurs utilisés en hydrogéologie ainsi que la gamme de temps accessible pour ces différents traceurs. D'après [Suckow, 2014].

$^3\text{H}/^3\text{He}$ et ^{85}Kr

Le tritium (^3H) est un traceur qui a été émis ponctuellement dans l'atmosphère durant les tests de bombes nucléaires (1950-1960) et est radioactif avec une demi-vie de 12 ans environ [Unterweger et al., 1980]. Sa demi-vie relativement courte combinée au fait que le pic atmosphérique observé a maintenant 70 ans fait qu'il est rarement utilisé seul. On mesure maintenant également son élément fils l'hélium 3 et leur rapport $^3\text{H}/^3\text{He}$ qui permet d'avoir une estimation absolue de son âge apparent [Schlosser et al., 1988; Weise and Moser, 1987].

Il est à noter que la première étape d'interprétation de ces concentrations en âge apparent est souvent difficile à réaliser car les concentrations de ^3H sont sensibles aux excès d'air et aux productions terrigènes (pour plus de détails, le lecteur pourra se référer à l'excellente introduction donnée par le laboratoire d'analyse de traceurs d'âge de l'eau de l'USGS de Reston : <https://water.usgs.gov/lab/3h3he/background/>).

Enfin la mesure en ^{85}Kr se fait sur le même principe que la mesure en tritium [Alvarado et al., 2007; Visser et al., 2013]. Le ^{85}Kr a un temps de demi-vie de 11 ans environ. Sa concentration atmosphérique a suivi la même tendance que celles de CFCs mais il présente l'avantage d'avoir une concentration qui augmente toujours dans l'atmosphère (Figure 8). La difficulté réside ici dans les concentrations extrêmement faibles qui nécessitent de prélever des quantités d'eau suffisamment importante pour récupérer des concentrations en ^{85}Kr mesurables [Du et al., 2003].

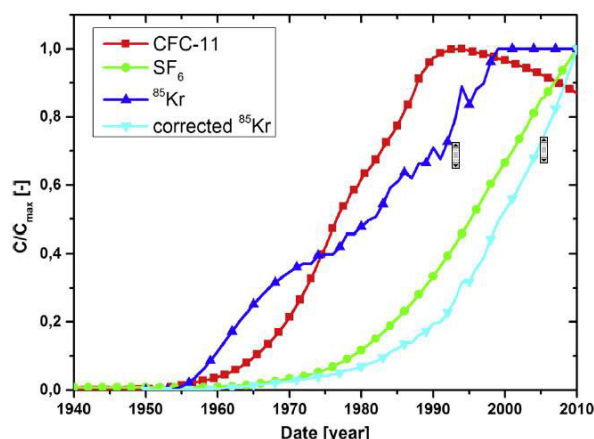


Figure 8: Evolution des concentrations atmosphériques en CFCs, SF_6 et en ^{85}Kr . Ces concentrations ont été normalisées par le maximum de concentration observé durant la période considérée. D'après Marçais et al. [2015].

Le besoin s'est donc fait sentir de développer de nouveaux traceurs des temps de résidence qui soit informatifs des temps intermédiaires, typiquement l'échelle de temps 0-100 ans. En parallèle du développement de nouveaux traceurs comme le ^{85}Kr , qui requiert des technologies avancées, une nouvelle dynamique se fait jour dans la communauté scientifique via le développement de traceurs géochimiques, qui soient à la fois, facile à mesurer et bon marché [Abbott et al., 2016; Beyer et al., 2016]. C'est dans ce contexte que nous nous intéresserons à l'utilisation de la silice en milieu cristallin pour dater les eaux intermédiaires (voir Partie II Chapitre 2).

1.2.2 Mesures indirectes du temps de transit en hydrologie : chroniques isotopiques ($\delta^{18}\text{O}$, $\delta^2\text{H}$) et en ions chlorures

En hydrologie, d'autres traceurs combinés à des méthodes différentes ont été utilisés pour dater le temps de transit en rivières. En effet, pour mesurer les temps de transit en rivières, les traceurs précédemment cités sont difficiles à utiliser (hormis le ^3H seul qui peut être utilisé en rivière) [Cook and Solomon, 1995; McGuire and McDonnell, 2006]. Si quelques études mentionnent l'utilisation de traceurs comme le CFCs pour dater les eaux en rivières, elles ne sont pas majoritairement utilisées [Sanford et al., 2015].

Ceci est dû au fait que la rivière n'est pas isolée de l'atmosphère et que par conséquent, les concentrations en gaz dissous comme les CFCs se « pollueraient » au contact de la concentration atmosphérique. Pour avoir une mesure du temps de transit en rivière, plusieurs méthodes ont été développés. Elles diffèrent par l'élément utilisé (^{18}O , ^2H) mais relèvent de la même méthodologie [Heidbüchel et al., 2012]. Cette méthodologie repose sur le monitoring régulier de la concentration de ces composés isotopiques dans l'eau de pluie (signal d'entrée) et en rivière (signal de sortie) [McDonnell et al., 2010]. Après plusieurs années de suivi à résolution hebdomadaire au moins, on obtient deux chroniques qu'il est aisé d'interpréter comme des signaux d'entrée et de sortie représentatifs du filtre opéré par le bassin versant (Figure 9). Le filtre opéré par le bassin versant est dû à l'effet de convolution opéré par la distribution des temps de transit. En effet, plus le bassin versant présente des distributions de temps de transit comportant des eaux vieilles, plus ce mélange viendra amortir le signal d'entrée et le déphaser.

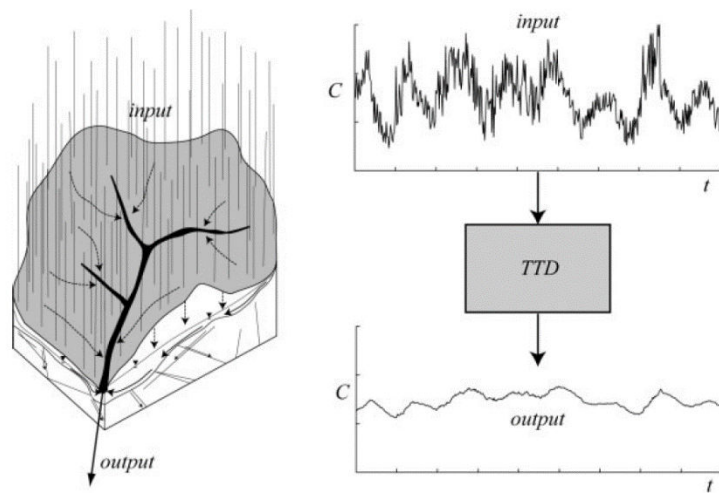


Figure 9: Schéma de principe illustrant la manière dont la pluie spatialement distribuée, porteuse d'un signal isotopique d'entrée, est filtrée par le bassin versant via sa distribution de temps de transit et aboutit à une chronique isotopique de sortie. D'après McDonnell et al. [2010].

On a aussi utilisé des chroniques en ions chlorures pour appliquer cette méthode, l'ion chlorure étant considéré comme un bon élément conservatif [Harman, 2015; Hrachowitz et al., 2010]. Cependant, il est à noter que ces méthodes sont utilisées dans des régions plutôt humides pour que le signal précipitation / débit ne soit pas trop amorti. Dans des régions plus arides, l'évapotranspiration concentre beaucoup les eaux en ions chlorures et devient le processus dominant rendant impossible l'interprétation d'une chronique en ions chlorures en sortie de bassin versant seulement à partir de la chronique présente dans la pluie. Certains travaux visent à dépasser ce problème en intégrant la représentation des processus d'évapotranspiration qui augmentent la concentration en ions chlorures dans le réservoir de l'aquifère.

1.2.3 Caractéristiques des temps de résidence mesurés en aquifère et des temps de transit mesurés dans les rivières

Temps de résidence en aquifère

Les temps de résidence en aquifère sont extrêmement variables suivant les systèmes hydrogéologiques. Il peuvent ainsi varier de l'année pour les nappes phréatiques connectées à la surface aux millénaires pour les grands systèmes aquifères [Castro et al., 1998; Gleeson et al., 2015; Guendouz and Michelot, 2006; Jasechko et al., 2017; Kenoyer and Bowser, 1992]. Cependant, si globalement, le temps de résidence d'un aquifère est corrélé à la profondeur de prélèvement de celui-ci [Ayraud et al., 2008; Vogel, 1967], il subsiste à l'intérieur même de ces aquifères un mélange extrêmement important des temps de résidence comme en attestent la présence de traceurs de gamme d'âges très différentes [Jasechko et al., 2017]. Ainsi, on a pu montrer que ces distributions de temps de résidence peuvent s'étendre sur des gammes allant de la dizaine d'années aux millénaires. Ceci est en partie dû à la dispersion qui y a lieu du fait de l'hétérogénéité des champs de vitesse (voir Partie III Chapitre 2) [Kirchner et al., 2001].

En Bretagne ces temps de résidence sont de l'ordre de quelques années à plusieurs décennies [Ayraud et al., 2008; Kolbe et al., 2016; Leray et al., 2012; Roques et al., 2014a]. Quelques aquifères profonds ont des temps de résidence bien plus anciens mais sont dans ce cas peu suspects d'être connectés activement au débit en rivière [Aquilina et al., 2015].

Temps de transit en rivière

En rivière, les temps de transit sont beaucoup plus courts souvent de l'ordre de quelques années [McGuire and McDonnell, 2006; Tetzlaff et al., 2009a]. Quelques cas mentionnent des temps de transit moyens plus importants de l'ordre de la décennie [Morgenstern et al., 2010; Peters et al., 2014]. Cependant contrairement à l'aquifère où l'on peut mesurer en un même endroit des traceurs représentatifs de différentes gammes d'âges, la quasi inexistence de traceurs mesurant les temps longs en rivière ne permet pas de caractériser la proportion d'eaux vieilles en rivière. C'est pourquoi la métrique communément utilisée aujourd'hui est de caractériser la proportion d'eaux de moins de trois mois en rivières [Benettin et al., 2017; Kirchner, 2016].

1.2.4 Conclusion

Une diversité de traceurs a été développée pour approcher soit la distribution des temps de résidence de l'eau stockée dans les aquifères, soit la distribution des temps de transit de l'eau circulant dans les rivières. Paradoxalement, à notre connaissance, peu d'études ont tenté d'approcher les temps de résidence et les temps de transit à l'aide de traceurs et d'une méthodologie commune. Nous proposons dans cette thèse des pistes pour avancer vers une conceptualisation commune informée grâce à des traceurs communs.

Cependant, cette courte bibliographie concernant les études sur les temps de transit et les temps de résidence montre une dichotomie entre les temps de transit obtenus d'une part, qui sont souvent de l'ordre de quelques années (1 à 5 ans) et les temps de résidence moyens qui sont souvent de l'ordre de la décennie à la centaine d'années. Nous allons voir qu'il y a plusieurs raisons invoquées à cela ; elles reposent sur la différence fondamentale entre stock et flux. Plus récemment des limites méthodologiques ont été avancées. Ces travaux démontrent l'inadéquation de la méthode utilisée pour déterminer les temps de transit moyen à l'aide de chroniques isotopiques. Ils suggèrent que le suivi des chroniques isotopiques ne permet d'estimer que la proportion d'eaux jeunes qui alimentent la rivière (i.e. la proportion d'eau qui a moins de 3 mois) et non pas le temps de transit moyen de ces eaux de rivière [Kirchner, 2016]. Néanmoins, si cette limite méthodologique est intéressante parce qu'elle met en garde contre la comparaison directe des temps moyen de transit (obtenus en rivière) et les temps moyens de résidence (obtenus en aquifère), elle ne permet pas de rendre compte du paradoxe des eaux vieilles observées en aquifère qui alimentent les rivières constituées d'eaux jeunes.

1.3 Eaux vieilles versus eaux jeunes : le paradoxe du stock et du flux

Dans cette partie, au travers de quelques cas analytiques simples, nous allons montrer quel type de conceptualisation pourrait permettre de rendre compte du paradoxe signalé précédemment : comment les eaux stockées dans le bassin versant qui sont vieilles peuvent conduire à libérer des eaux jeunes en rivière ? Dans un premier temps nous décrirons quelques cas simples en régime permanent. Puis nous évoquerons comment ces cas simples peuvent se comprendre en terme de processus. Enfin, nous évoquerons le cas du régime transitoire qui amène une complexité supplémentaire.

1.3.1 Le réservoir parfaitement mélangé : un cas simple où la distribution des temps de transit correspond à la distribution des temps de résidence

Avant de présenter des processus capables de lever ce paradoxe des eaux vieilles versus eaux jeunes, intéressons-nous à un cas simple, celui du réservoir linéaire parfaitement mélangé, illustrant un aquifère homogène (Figure 10). Le réservoir linéaire est un cas emblématique en hydrologie où l'on suppose que le débit Q sortant du bassin versant dépend linéairement du volume V stocké dans celui-ci via le coefficient de vidange k . Si l'on fait l'hypothèse que ce réservoir est de plus parfaitement mélangé, on

peut montrer qu'en régime permanent, la distribution des temps de transit équivaut à la distribution des temps de résidence et se ramène à une distribution exponentielle dont le temps moyen correspond à l'inverse du coefficient de vidange égal à $1/k$.

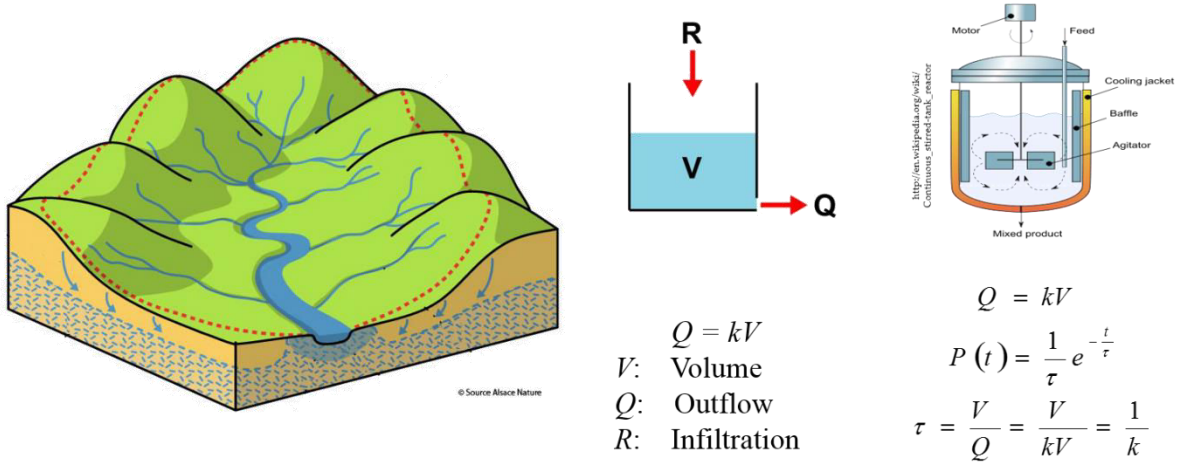


Figure 10: Illustration du concept de réservoir linéaire parfaitement mélangé auquel on peut assimiler un bassin versant homogène.

Ce cas-là mène donc à une conceptualisation du bassin versant où temps de résidence et temps de transit coïncident. Cette comparaison des distributions des temps de résidence et de transit peut se faire à l'aide de la « SAS function » ou « storage selection function » noté $\omega_Q(\tau)$ qui n'est rien d'autre que le ratio de ces deux distributions (pour la définition précise, voir Partie I2.1.3 et pour plus de détails, voir Partie III Chapitre 2). Cette « SAS function » ω_Q dépend du temps de résidence τ . Pour le cas du réservoir parfaitement mélangé, cette fonction est constante et égale à 1 puisque la distribution de temps de résidence et celle du temps de transit coïncident. De plus sa cumulée est directement la fonction linéaire correspondant à la première bissectrice (Figure 11). Cela illustre le fait que, pour alimenter le débit en rivière, le bassin versant sélectionne les particules d'eau stockées dans l'aquifère indifféremment de leur âge.

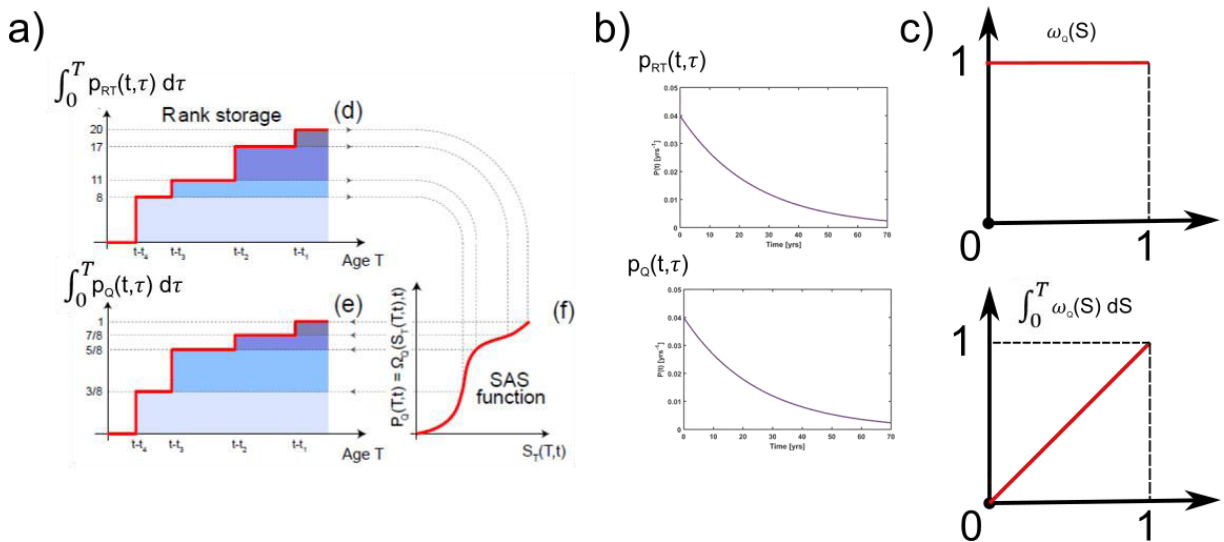


Figure 11: (a) Illustration de la construction de la « SAS function » à partir des distributions des temps de résidence et de transit (voir Partie I2.1.3) (b) Dans le cas du réservoir linéaire parfaitement mélangé, distributions de temps de résidence et de transit sont une distribution exponentielle. (c) C'est pourquoi la « SAS function » qui se définit mathématiquement comme le ratio de ces deux distributions.

le ratio de ces deux distributions est constante dans le cas d'un réservoir parfaitement mélangé. Cela illustre que ce type de réservoir relâche indifféremment des parcelles d'eau de tout âge dans la rivière. D'après Benettin et Bertuzzo (2018).

Ce modèle du réservoir linéaire parfaitement mélangé ne permet pas de rendre compte de la différence d'âges observée entre eaux stockées et flux d'eaux en rivière. Conceptuellement, il faut introduire de l'hétérogénéité pour avoir des différences significatives à même d'expliquer ces différences entre les eaux jeunes s'écoulant en rivière et les eaux vieilles stockées dans les aquifères.

1.3.2 La stratification de l'aquifère à l'origine de processus responsable d'une dichotomie entre distribution de temps de transit et distribution de temps de résidence.

On fait maintenant l'hypothèse que cet aquifère présente une hétérogénéité de perméabilité due à la stratification de cet aquifère en deux couches de même épaisseur et de même porosité ϕ avec deux perméabilités contrastées K_1 et K_2 , tels que $K_1 \gg K_2$ (Figure 12). Si l'on fait toujours l'hypothèse que l'écoulement est en régime permanent et que les deux couches de l'aquifère sont soumises au même gradient de charge, le flux sortant de chacune de ces couches sera proportionnel à leur perméabilité (puisque la vitesse du flux sera tel que : $v_i = \frac{K_i}{\phi} \Delta H / L$). De plus, l'âge de l'eau sortant de chacune de ces couches sera inversement proportionnel à la vitesse de flux et donc sera inversement proportionnel à leur perméabilité. Ces deux faits combinés conduisent au fait que la distribution des temps de transit de l'eau en rivière est majoritairement constituée d'eaux très jeunes provenant de la couche 1. Au contraire, le stock dans cet aquifère est majoritairement constitué d'eau stockée dans la couche 2 qui contient les eaux les plus âgées du fait de sa faible perméabilité (la couche 1 du fait de sa forte perméabilité ne retient qu'un faible stock d'eau jeune). La distribution des temps de résidence de l'eau stockée dans l'aquifère sera donc majoritairement constituée d'eaux vieilles contenues dans la couche 2 [Berghuijs and Kirchner, 2017].

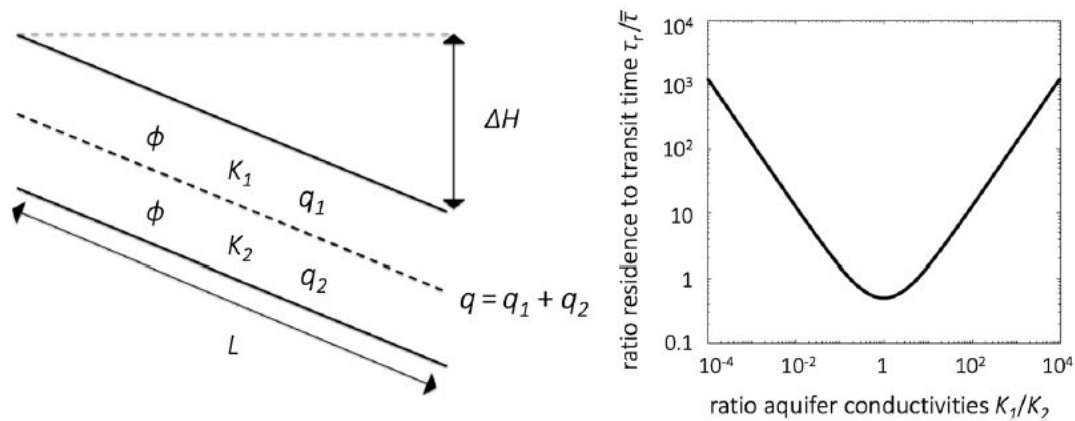


Figure 12: Illustration d'un aquifère hétérogène et de l'influence que cette stratification amène sur la différence entre temps de transit et temps de résidence. D'après Berghuijs and Kirchner [2017].

Une telle représentation de l'aquifère conduit donc à des distributions de temps de transit « piquées » sur les eaux jeunes et à des distributions de temps de résidence avec une queue de distribution « lourde ». Cela amène à des « SAS functions » typiquement piqués sur les stocks d'eaux jeunes qui alimentent préférentiellement le débit en rivière (cas b de la Figure 13).

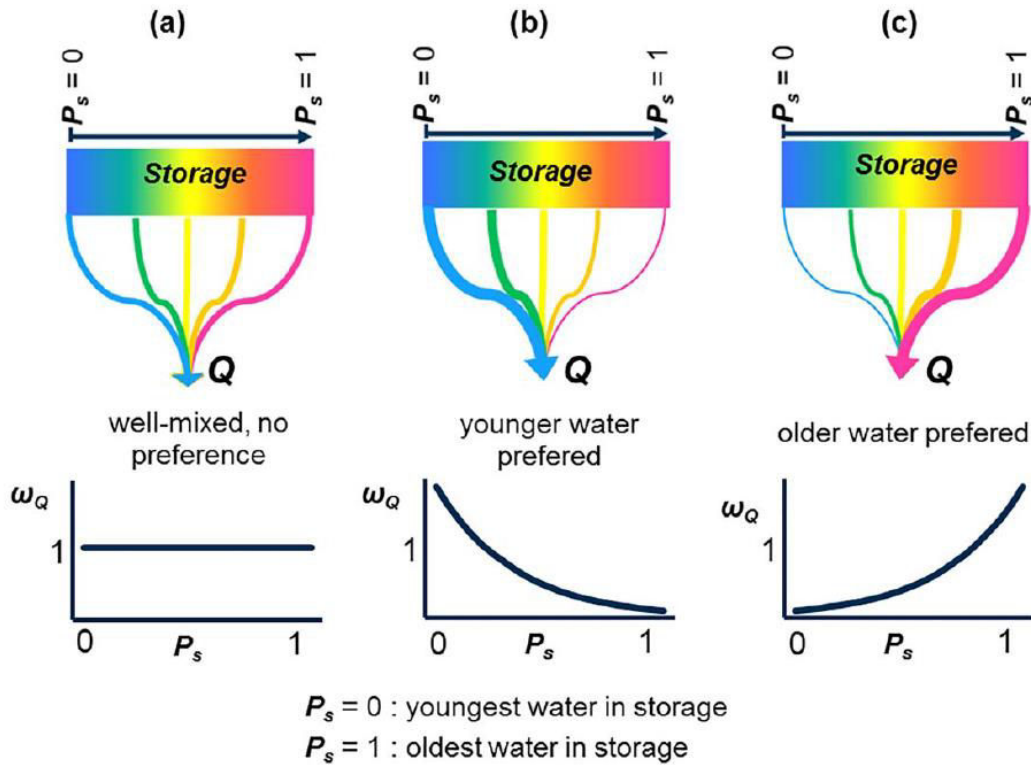


Figure 13: Illustration des différents types de « SAS functions » en fonction de la relation stock / débit. (a) Quand le réservoir est parfaitement mélangé, on retrouve le cas d'une « SAS function » constante, (b) quand le bassin versant présente une hétérogénéité importante, il relâche préférentiellement des eaux jeunes. (c) Enfin, un cas théorique intéressant est celui d'un système relâchant préférentiellement les eaux âgées. Ce cas se présente lorsqu'on considère un écoulement type « piston » puisque dans ce type d'écoulements, les parcelles d'eau alimentant le flux sont les plus anciennes puisque ce sont celles qui ont achevé leur trajet dans le bassin versant. D'après Yang et al. [2018], originellement de Harman [2015].

1.3.3 Autres processus pouvant expliquer ce paradoxe des eaux jeunes et vieilles

Nous avons donc vu que cette dichotomie entre eaux vieilles stockées et eaux jeunes s'écoulant en rivière peut s'interpréter comme étant la preuve du mélange imparfait qui a lieu dans l'aquifère où cohabiteraient des eaux jeunes, représentatives du cycle actif de l'eau et des eaux vieilles, stagnantes, représentatives des eaux de l'aquifère ne participant pas activement au cycle de l'eau mais étant stocké dans l'aquifère, comme présenté dans l'explication précédente.

Les processus de ruissellements

Tout d'abord, les différents processus de ruissellements (« runoffs ») peuvent expliquer cette dichotomie entre temps de transit et temps de résidence (Figure 14). En effet la présence d'écoulements de ruissellements favorise via des effets seuils des écoulements rapides qui retournent rapidement à la rivière sans compter pour une part importante des stocks d'eau présent sur le versant à un instant t . Ces processus de ruissellements sont classiquement distingués entre plusieurs types selon qu'ils sont de surface (« saturation excess overland flow » ou « infiltration excess overland flow ») ou de subsurface (« lateral flow », « subsurface stormflow »). Toute cette littérature des processus de ruissellement a débuté avec le processus hortonien par excès d'infiltration [Horton, 1933], en passant par le concept d'aire saturée variable (Figure 15) [Hewlett and Hibbert, 1967]. Les derniers « progrès » accomplis dans la compréhension de ces processus ont eu lieu avec la disponibilité des mesures isotopiques en rivière qui ont révélées le paradoxe de l'eau vieille (« old water paradox »). Ce paradoxe peut se formuler ainsi : comment le débit d'un bassin versant peut répondre de manière quasi instantanée aux précipitations tout en étant constituée d'eaux plus vieilles que l'évènement pluvieux ? [Bishop et al., 2004; Kendall et al., 1999; Kirchner, 2003; Klaus and McDonnell, 2013; McDonnell, 1990].

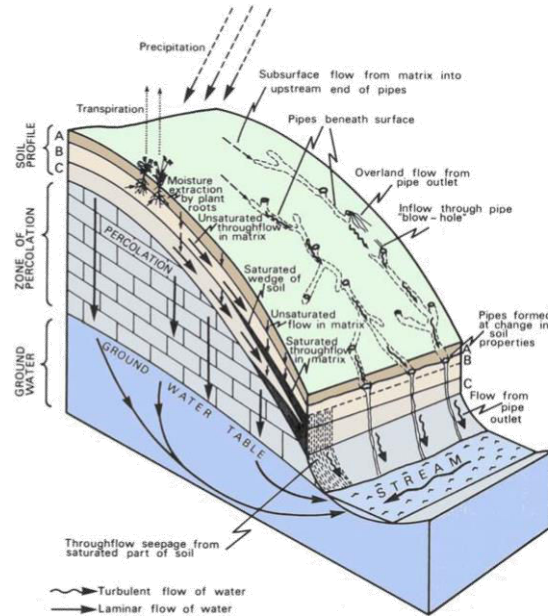


Figure 14: Illustration des différents processus d'écoulements à l'échelle du versant avec un accent sur les processus de ruissellements. D'après Kirkby [1985].

Au-delà de la description détaillée de tous ces processus, il semble que l'on puisse les classer en fonction du type d'effets de seuils, soit dus à des effets « *top down* » comme des seuils de précipitation (« *infiltration excess overland flow* »), soit dus à des effets « *bottom up* » comme le fait que la saturation de l'aquifère arrive au niveau de la surface (« *saturation excess overland flow* »). Pour le ruissellement de subsurface une même distinction peut être opérée selon que l'on considère du ruissellement ayant lieu aux contrastes de perméabilité du milieu souterrain (interface sol / roches par exemple) ou à cause d'effets appelés souvent « *transmissivity feedbacks* » qui résultent de la forte augmentation de la transmissivité avec la hauteur d'eau dans l'aquifère [Bishop *et al.*, 2011; Kendall *et al.*, 1999; McDonnell, 2013; Tromp-van Meerveld and McDonnell, 2006a; b]. Cette augmentation de la transmissivité avec la hauteur d'eau dans l'aquifère se réalise : (1) mécaniquement par l'augmentation de la hauteur sur lequel le flux peut circuler mais aussi (2) par le fait que la perméabilité croît exponentiellement lorsqu'on s'approche de la surface facilitant ainsi les écoulements de subsurface.

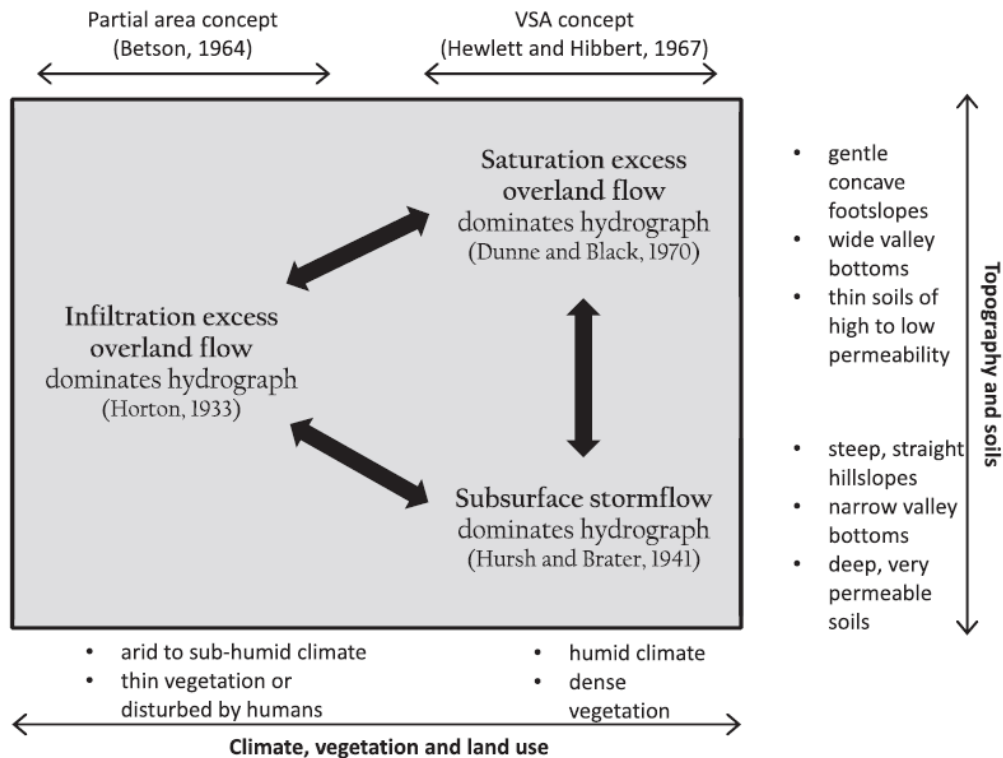


Figure 15: Classification classique des processus de ruissellements. Selon le climat et la topographie de la zone considérée, cette classification prévoit différents types de processus de ruissellements. La dernière classe d'écoulements de subsurface (« subsurface stormflow ») peut elle-même être subdivisée en deux en différenciant les processus de ruissellements générés aux interfaces de perméabilité contre ceux qui prennent naissance du fait de la remontée la nappe dans des zones plus perméables. D'après [McDonnell, 2013].

L'effet de réservoirs à double porosité

D'autre part, la présence dans l'aquifère, d'une double porosité peut aussi rendre compte de ce paradoxe. En effet, la porosité importante de l'aquifère facilite la connectivité des pores et lie les écoulements à l'échelle du versant de l'aquifère à la rivière. L'autre porosité étant faiblement connectée, retient l'eau dans des poches et engendre une eau stockée d'âge important. Cette conceptualisation est à la base de la théorie du transport anormal [Babey et al., 2014; Babey et al., 2017; de Dreuzzy et al., 2013; Haggerty, 2001; Haggerty and Gorelick, 1995; Haggerty et al., 2000].

Conclusion

Tous ces mécanismes ont en commun qu'ils reposent sur une conceptualisation unique de la subsurface : celle de l'existence d'une très forte hétérogénéité des chemins de l'eau en terme de vitesse de circulation qui permet à la fois d'avoir un volume important d'eau stocké dans l'aquifère et des chemins préférentiels rapides qui alimentent la rivière. Les volumes importants stockés dans l'aquifère engendrent des eaux anciennes, tandis que l'eau présente dans la rivière présente une part importante d'eaux jeunes provenant de l'existence de chemins préférentiels rapides.

1.3.4 Questions ouvertes sur la variabilité temporelle de ces temps de transit

Enfin, il est nécessaire d'examiner la variabilité temporelle de ces temps de transit à l'échelle interannuelle, à l'échelle saisonnière ou à l'échelle de la crue. En effet, ce qu'on a détaillé dans la partie précédente à savoir la préférence qu'a un bassin versant de relâcher en rivière des eaux jeunes ou des eaux plus âgées varie en fonction des conditions climatiques. Quand le bassin versant est très sec, il aura, intuitivement, plutôt tendance à relâcher des eaux vieilles. A contrario, quand le bassin versant est fortement saturé, il aura, intuitivement, tendance à relâcher des eaux jeunes. Cette variabilité temporelle

est mal contrainte mais est pourtant centrale pour expliquer les variations de solutés en rivière [Kirchner *et al.*, 2000]. En effet, à ce jour, ce sont majoritairement des stratégies implicites ou conceptuelles qui modélisent les variations temporelles de soluté en rivière [Benettin *et al.*, 2017; Benettin *et al.*, 2015; Harman, 2015]. Ces stratégies permettent d'expliquer ces variations temporelles de solutés par des variations temporelles des temps de transit mesurées en rivières. Cependant, ces approches ne permettent pas d'explicitier des processus responsables de ces variations aux différentes échelles de temps. C'est donc l'objet de ce second chapitre que d'introduire les différentes stratégies actuelles de modélisation développées en hydrologie et en hydrogéologie pour appréhender les temps de transit et de résidence dans les bassins versants ainsi que leur variabilité.

Chapitre 2 Modéliser les temps de résidence et de transit à l'échelle du bassin versant

Dans ce chapitre, nous faisons l'inventaire des différentes approches utilisés en hydrologie pour modéliser les temps de résidence et de transit à l'échelle du bassin versant. De cette étude bibliographique, il ressort que les approches utilisées varient en fonction de la communauté scientifique. En hydrologie de surface, les méthodes sont majoritairement implicites, reposant sur une intégration importante de données en rivière (« *data-driven modeling* »). En hydrogéologie, la modélisation explicite est majoritairement appliquée, traduction des processus existants dans le milieu souterrain (« *physically-based modeling* »). Entre les deux, relativement peu d'approches sont développées mis à part le développement de modèles explicites intégrant l'ensemble des processus à l'échelle du bassin versant, maillé et discrétisé. Ces modèles demandent cependant un investissement extrêmement important pour intégrer des données réelles à ces modèles physiques. Il existe aussi des approches conceptuelles, spécifiquement développées pour dépasser le paradoxe des temps de résidence versus temps de transit. Ces modèles permettent de gagner en intuition sur certaines propriétés clefs des bassins versants, du fait du grand nombre de données intégrées, mais ne permettent pas de fournir un schéma de compréhension avancée à même d'être testé et utilisé pour la prédiction de l'évolution de la qualité de l'eau en rivière et pour l'intégration de nouveaux processus (réactivité ou processus biologiques par exemple).

2.1 En hydrologie de surface, tour d'horizon des approches implicites classiquement développées pour inférer les temps de transit

Ces approches ont été en partie esquissées dans la partie précédente tant les données collectées (chroniques de solutés en rivières ou chroniques isotopiques) ne sont qu'indirectement reliées au temps de transit. Ces approches visent à déterminer les temps de transit à l'échelle du bassin versant via une intégration des chroniques isotopiques ou de solutés résultant du suivi en rivières. Dans cette partie, nous approfondissons la description de ces méthodes. On peut en effet distinguer classiquement trois types de méthodes : la méthode fréquentielle, la méthode « *sine wave* » en mesurant déphasage et amortissement des signaux de forçages et la méthode reposant sur les « *storage selection functions* ».

2.1.1 La méthode fréquentielle

Cette méthode repose sur l'analyse du contenu fréquentiel des chroniques en solutés. Cette analyse révèle en effet que la densité spectrale de puissance de ces chroniques varie en $1/f$ ou f est la fréquence considérée (Figure 16) [Kirchner *et al.*, 2000]. Cette décroissance est relativement faible, sans pour autant être un bruit blanc (spectre pour lequel la densité spectrale est constante pour toutes les fréquences de la bande passante). Cette décroissance a maintenant été observée sur un grand nombre de bassins versants si bien qu'on a pu dire que c'était une propriété universelle des bassins versants due à leur nature de filtre leur donnant une capacité à mélanger imparfaitement les eaux qui circulent dans ce bassin versant [Godsey *et al.*, 2010; Hrachowitz *et al.*, 2015; Kirchner and Neal, 2013]. En particulier, on parle pour décrire fréquentiellement ces chroniques de bruit rose, le bruit rose ayant pour propriété de posséder une énergie constante sur chaque ordre de grandeur ($\int_a^b \frac{df}{f} = \log b/a$). Cette propriété ne peut s'expliquer que par le fait que les distributions de temps de transit ont une proportion importante d'eaux jeunes, plus forte que celle la distribution exponentielle [Godsey *et al.*, 2010]. En supposant que la distribution des temps de transit suit une forme paramétrée (distribution gamma par exemple), on peut via l'analyse fréquentielle remonter aux paramètres de cette distribution et, *in fine*, estimer le temps moyen et le paramètre de forme de cette distribution [McGuire and McDonnell, 2006]. En hydrologie,

le *prior* de la forme paramétrée de la distribution se fait souvent avec une distribution gamma, étant donné que celle-ci est relativement flexible et a une queue de distribution exponentielle [Hrachowitz *et al.*, 2010; Kirchner, 2016]. Plusieurs travaux ont montré que les paramètres de cette distribution gamma pouvaient s'interpréter physiquement [Hrachowitz *et al.*, 2010], par exemple comme le résultat d'une convolution spatiale d'inverses gaussiennes générées par un processus d'advection dispersion [Kirchner *et al.*, 2001], et ce, bien que la distribution gamma ne soit pas la solution de l'équation classique d'advection diffusion. Bien entendu, ce choix de distribution peut aussi se faire à l'aide de distributions plus classiques (e.g. exponentielles, exponentielles « *shiftées* », inverse gaussienne) mais des travaux ont montré que ces distributions ne menaient pas à une décroissance exponentielle en $1/f$ [Godsey *et al.*, 2010].

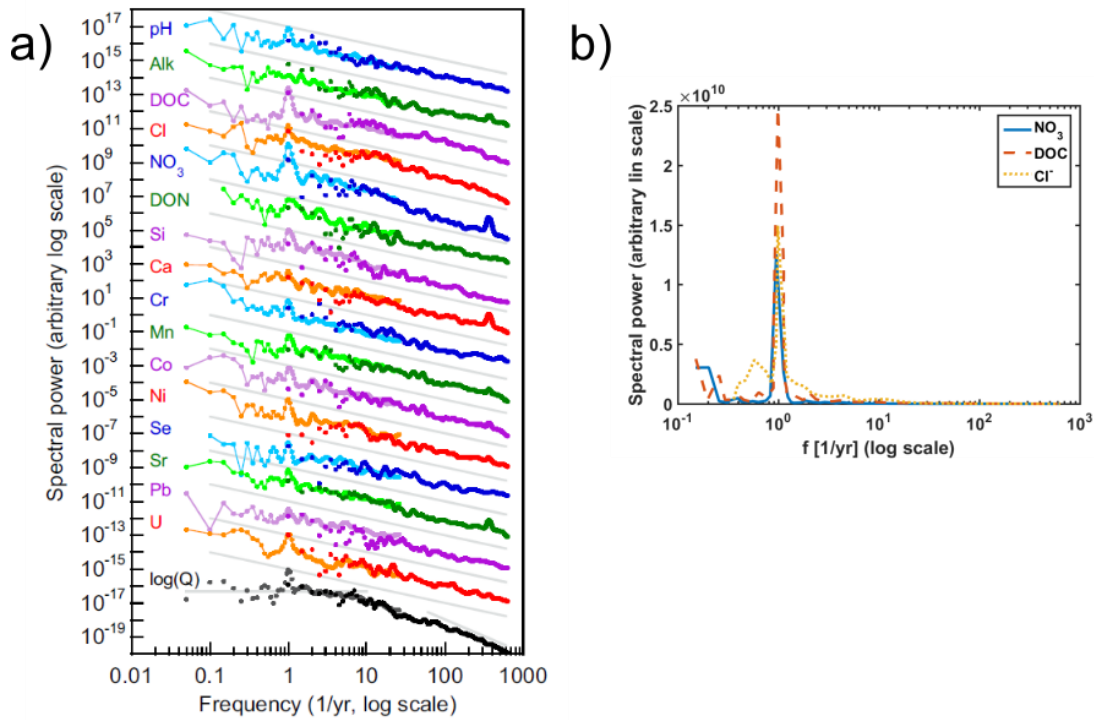


Figure 16: (a) Puissance spectrale de différentes chroniques temporelles en soluté obtenues sur le site de Plynlimon (Pays de Galles). Toutes ces puissances spectrales varient en $1/f$ ce qui n'est pas le cas de la chronique temporelle de débit représentée en bas de la figure. (b) Même représentation pour les nitrates, le carbone organique dissous et le chlore en échelles linéaires pour la puissance spectrale. Noter comment ces puissances spectrales sont toutes extrêmement piquées sur la fréquence annuelle caractéristique des variations saisonnières lorsqu'on les représente en échelle linéaire. Pris et adapté de Kirchner and Neal [2013].

2.1.2 La méthode « *sine-wave* »

Une autre approche communément utilisée en hydrologie pour tirer l'information du temps de transit moyen de chroniques isotopiques en rivière et dans la pluie est la méthode « *sine-wave* ». Cette méthode vise à expliquer le déphasage et l'atténuation qu'on observe lorsqu'on compare les signaux isotopiques en $\delta^{18}\text{O}$ ou $\delta^2\text{H}$ contenus dans la pluie tombant sur le bassin versant et dans le cours d'eau mesuré à l'exutoire du bassin versant en faisant l'hypothèse que ces variations saisonnières peuvent être assimilées à des variations sinusoïdales (Figure 17) [McGuire and McDonnell, 2006]. On fait l'hypothèse que la distribution des temps de transit peut être décrite à l'aide d'une distribution paramétrique supposée *a priori* et que ces distributions paramétriques permettent une estimation analytique du déphasage et de l'amortissement, qu'il suffit de « caler » aux signaux sinusoïdaux. Cette méthode ne peut s'utiliser que pour les chroniques isotopiques considérés comme un traceur « parfait »

puisque ces isotopes font partie intégrante de l'eau transportée dans les versants. Ces traceurs sont par contre des traceurs indirects du temps de transit puisque c'est leurs variations saisonnières et leur atténuation qui s'opère lors de leur transit dans le bassin versant qui renseigne sur la distribution des temps de transit.

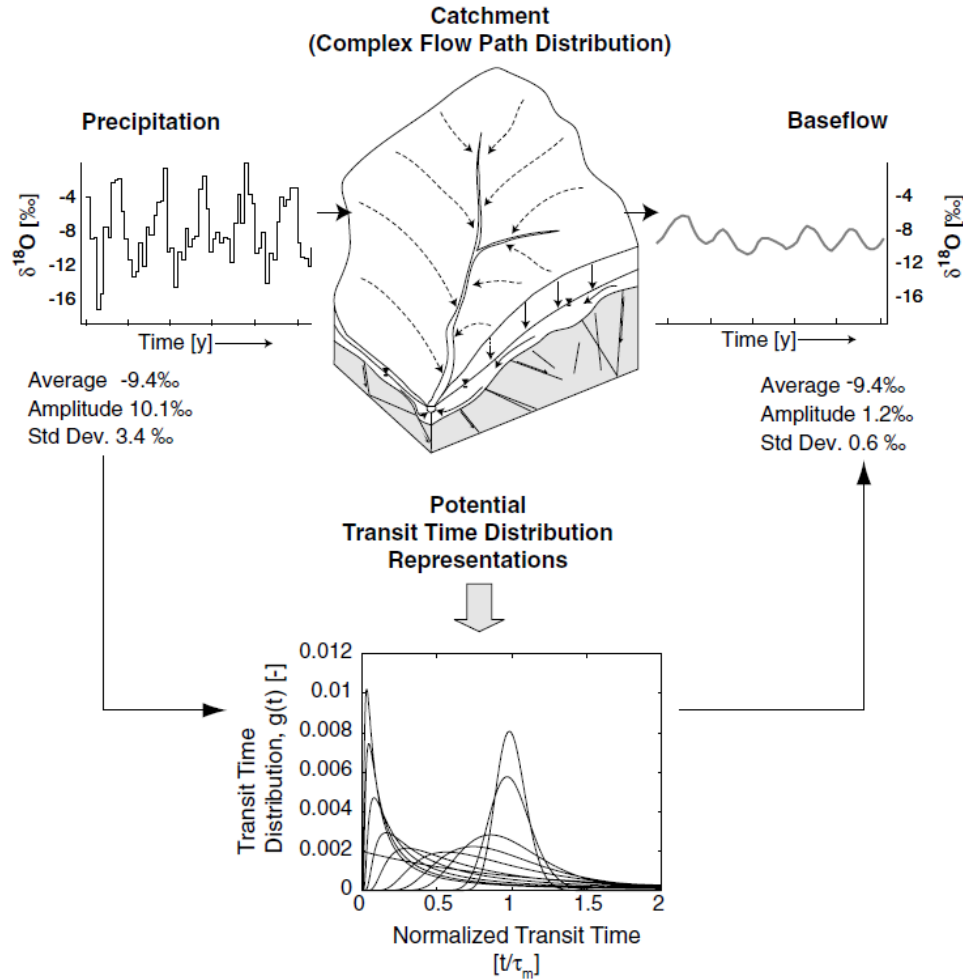


Figure 17: Illustration de la méthode « sine wave » qui vise à tirer du déphasage et de l'amortissement des variations isotopiques mesurées dans la pluie et le débit à l'aide de distributions de temps de transit dont la forme est supposée au préalable. D'après McGuire and McDonnell [2006].

2.1.3 Développement d'un nouveau formalisme : équation maîtresse et « SAS fonction »

Enfin, plus récemment, de nouvelles méthodes développant un nouveau formalisme visent à approcher la nature intrinsèquement variable des distributions de temps de transit et des temps de résidence [Botter, 2012; Botter et al., 2010; 2011; Rinaldo et al., 2015; van der Velde et al., 2012]. Cette variabilité est due aux forçages hydrologiques qui sont éminemment variables temporellement (pluie et évapotranspiration). Cette méthode repose sur une équation maîtresse qui décrit l'évolution temporelle du « système » bassin versant sous la forme d'une équation liant les distributions de temps de transit aux distributions de temps de résidence [Botter et al., 2011]. Cette équation se base sur l'équation de continuité, décrite à l'échelle du versant et sur la considération que l'évolution temporelle des temps de résidence dépend du temps qui s'écoule, des forçages externes qui s'appliquent (précipitation, évapotranspiration, débit) modifiant la quantité d'eau stockée. Cette méthode a été appliquée avec succès à différents bassins versants et permet de rendre compte de la variabilité du temps de transit

moyen en fonction du temps reflété par la variabilité de la concentration de solutés en rivière [Benettin et al., 2015]. Ces méthodes reposent sur le développement de modèles compartimentés qui représentent chacun les flux et le stockage dans différentes parties de l'hydrosystème (sols, aquifère). Cependant ces méthodes se heurtent à une paramétrisation importante pour un modèle conceptuel (9-10 paramètres) et ne rendent compte que des eaux relativement jeunes [Benettin et al., 2017; Benettin et al., 2015; Botter, 2017].

Ce formalisme repose également sur l'inférence de « *storage selection functions* » ou « *SAS functions* » $\omega_Q(\tau, t)$ qui mathématiquement se définissent comme étant le ratio de la distribution des temps de transit $p_Q(\tau, t)$ sur la distribution des temps de résidence $p_S(\tau, t)$, où t est le temps auquel se fait la mesure et τ est le temps de résidence ou de transit [Rinaldo et al., 2015] :

$$\omega_Q(\tau, t) = \frac{p_Q(\tau, t)}{p_S(\tau, t)}. \quad (1)$$

Via un changement de variable adéquat, ce ratio peut ensuite s'exprimer en fonction du volume stocké et adimensionnée, ordonné par temps de résidence croissant :

$$S(\tau, t) = \int_0^\tau p_S(u, t) du. \quad (2)$$

On obtient ainsi une distribution $\omega_Q(S, t)$ (d'intégrale 1) qui caractérise la préférence du bassin versant pour libérer les eaux jeunes ou vieilles selon la forme de la fonction (Figure 18). Méthodologiquement, les travaux qui ont utilisés la « *SAS function* » se limitent à supposer une forme fonctionnelle pour la « *SAS function* », comme une forme en loi de puissance, et à caler les valeurs des paramètres via une calibration aux données de qualité acquises en rivière [Benettin et al., 2017].

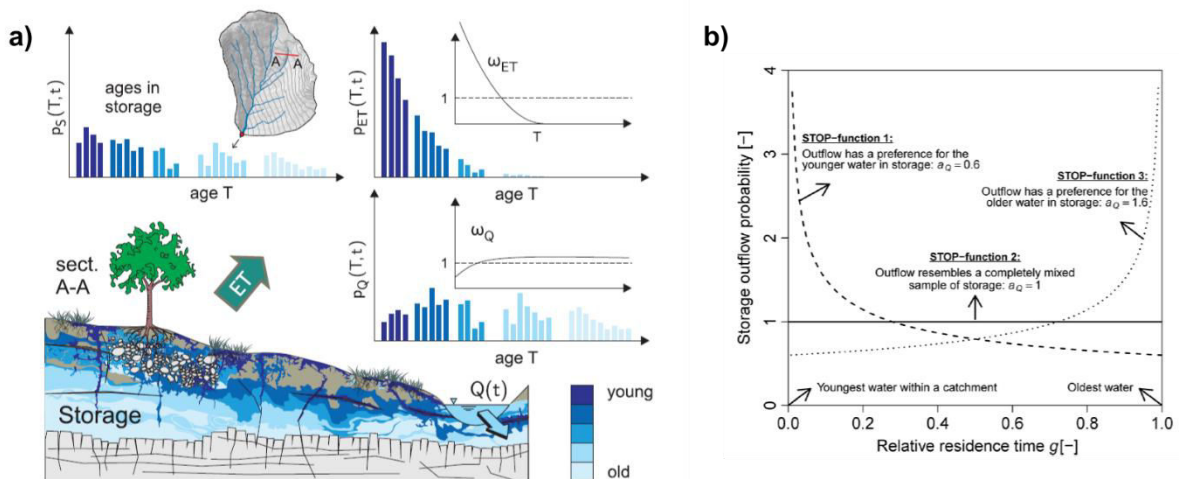


Figure 18: a) Illustration du concept de la « storage selection function » qui synthétise les différences entre la distribution de temps de transit des eaux sortant du système (par évapotranspiration $p_{ET}(\tau, t)$ ou dans le débit de la rivière $p_Q(\tau, t)$) par rapport à la distribution des temps de résidence des eaux stockées dans le bassin versant $p_S(\tau, t)$. Cela permet de synthétiser l'information pour répondre à la question : quels sont les eaux stockées dans le bassin versant qui participent aux écoulements ? D'après Rinaldo et al. [2015]. b) Illustration des différentes formes que peuvent avoir les « storage selection

functions » suivant qu'elle caractérise un bassin versant qui, à un instant donné, relâche en rivière les eaux stockées, jeunes ou au contraire, les eaux les plus vieilles. D'après van der Velde et al. [2012].

2.1.4 Conclusion des approches développées en hydrologie et perspectives

Récemment, *Kirchner* [2016] a montré que certaines de ces méthodes (analyses fréquentielles ou méthode « *sine-wave* ») ne pouvaient prétendre à informer que la partie d'eaux jeunes de la distribution. Cette étude développe ainsi un cadre théorique qui permet à partir de ces données de caractériser la proportion d'eaux de moins de 3 mois dans le débit observé en cours d'eau. Cette étude montre en particulier qu'on ne contraint que très mal les eaux vieilles (âges supérieurs à 1 an) qui transitent dans le bassin versant. Or ces eaux vieilles fournissent une importante proportion des débits en rivière (paradoxe de l'eau vieille) [*Bishop et al.*, 2004; *Botter et al.*, 2010; *McDonnell et al.*, 2010] De même, si le formalisme introduit récemment via une équation maîtresse et les « *SAS functions* » permet de rendre compte de la variabilité temporelle des temps de résidence, elle semble sous-estimer de manière importante l'âge et le volume de l'eau stockée dans les aquifères [*Botter*, 2017; *Evaristo et al.*, 2015; *McDonnell*, 2014].

De plus, toutes ces approches ne sont pas basées sur la physique des processus, rendant difficile la compréhension complète des processus de transport et de stockage des éléments. En particulier, la forme de distributions de temps de transit la plus classique est la distribution gamma alors même qu'elle ne semble pas basée sur des concepts physiques très robuste contrairement à l'inverse gaussienne qui, si elle est basée sur des considérations physiques (solution de l'équation d'advection dispersion), ne rend pas compte de manière satisfaisante des données observées (par exemple de la décroissance des puissances spectrales en $1/f$). Quelques récents travaux mentionnés plus en détail à la fin de la section suivante (voir Partie I2.2.3) tentent d'appréhender ce problème en partant de modèles hydrologiques intégrés à base physique. Ces travaux s'inscrivent pleinement dans la problématique de cette thèse qui vise à aborder ces questions sous l'angle d'une modélisation parcimonieuse à base physique.

2.2 En hydrogéologie, des approches explicites souvent privilégiées pour modéliser les temps de résidence

La communauté des hydrogéologues a majoritairement développé des approches physiques décrivant de manière explicite l'évolution des temps de résidence. Ces approches se basent sur une description mécaniste des écoulements dans un modèle maillé. La modélisation de l'évolution de l'âge de l'eau peut ainsi être décrit de manière lagrangienne ou eulérienne suivant les approches choisies. Ensuite, la méthode de choix pour informer le modèle à l'aide des données en traceurs géochimiques collectés reste toujours la calibration des paramètres du modèle via la méthode du problème inverse [*Certes and de Marsily*, 1991; *Zimmerman et al.*, 1998]. Dans cette section, on distingue donc ces deux types d'approches explicites (lagrangiennes ou eulériennes), de méthode semi-implicites reposant sur l'utilisation de modèles « boîtes noires », les « *Lumped Parameter Models* » (LPMs). Enfin, on évoquera les modèles hydrologiques intégrées qui se développent même s'ils sont rarement calibrés à des données d'âge de l'eau.

2.2.1 Modélisation explicite, approche lagrangienne versus approche eulérienne

Ces approches consistent à modéliser directement les temps de résidence en aquifère de manière mécaniste. La méthode la plus naturelle pour modéliser cette évolution des temps de résidence consiste à adopter une approche lagrangienne puisque cette approche vise justement à décrire la trajectoire des particules d'eau en milieu souterrain [*Erhel et al.*, 2009]. On solutionne ainsi l'évolution des trajectoires,

via une méthode de suivi particulaire (« *particle tracking* »), $\mathbf{x}(\xi, t) = \begin{cases} x(\xi, t) \\ y(\xi, t) \\ z(\xi, t) \end{cases}$, en se donnant la

position initiale de la parcelle d'eau ξ considérée, $\mathbf{x}_0(\xi, t_0) = \begin{cases} x_0 \\ y_0 \\ z_0 \end{cases}$ et grâce à un système d'équations

différentielles qui régit l'évolution de la trajectoire $\frac{d\mathbf{x}}{dt}$. La méthode de *particle tracking* permet ainsi de générer des trajectoires par différentes stratégies (« *forward* » ou « *backward* ») selon que l'on solutionne la trajectoire dans le sens de l'écoulement ou « en remontant » le temps [Cornaton and Perrochet, 2006]. Chacune des méthodes présente des inconvénients et des avantages. On retiendra que sans modélisation effective de la diffusion, la méthode « *forward* » est à privilégier pour échantillonner un nombre suffisamment différent de lignes de flux. Dans le cas de méthode « *forward* » de « *particle tracking* », on choisit généralement d'injecter l'ensemble des particules $\{\xi_i, i \in \llbracket 1, N_p \rrbracket\}$ proportionnellement au flux d'entrée, qui est généralement l'infiltration ou la pluie forçant la réponse du bassin versant (N_p étant le nombre de particules injectées).

Le cas de la description de l'âge de parcelles d'eau dans un formalisme eulérien a été solutionné par Goode [1996]. Elle vise à traduire l'évolution de l'âge de l'eau de la même manière que l'évolution de champs de concentration en milieu souterrain, à l'aide d'une équation d'advection dispersion classique :

$$\frac{\partial A}{\partial t} = 1 - \nabla \left(\frac{q}{\theta} A \right) + \nabla (D \nabla(A)). \quad (3)$$

Cette équation présente cependant une petite différence par rapport à l'équation d'advection dispersion classique qui tient en l'ajout d'un facteur constant 1 dans le terme droit de l'équation aux dérivées partielles. Ce terme traduit le fait que l'eau prend de l'âge au cours du temps à la même vitesse que l'évolution du temps elle-même ! Cette approche modélise donc directement l'évolution de l'âge moyen en tout point du domaine. Il ne permet cependant pas de remonter à la distribution des temps de résidence en tout point. D'autre part, cette modélisation directe fait appel à la résolution d'une équation d'advection dispersion qui pose des problèmes de stabilité numériques puisqu'elle contient des opérateurs aux propriétés très différentes (opérateur advectif versus opérateur dispersif). Pour ces deux raisons, cette équation est assez peu utilisée pratiquement bien qu'elle ait fait l'objet de nombreuses études théoriques pour préciser le rôle des opérateurs d'advection dispersion dans l'évolution de l'âge moyen en milieu souterrain [Cornaton et al., 2011; Ginn et al., 2009; Varni and Carrera, 1998].

Au contraire, les approches lagrangiennes de « *particle tracking* » peuvent mener à la modélisation directe des distributions de temps de résidence soit en ajoutant directement le terme de diffusion / dispersion dans le calcul des trajectoires des lignes de flux, soit en modélisant *ex post* la modélisation de la dispersion à l'aide d'un moyen adapté [Engdahl and Maxwell, 2014]. Quoiqu'il en soit, pour estimer cette distribution, il convient d'échantillonner ces lignes de flux sur un volume représentatif du milieu souterrain capables de contenir un nombre suffisant de particules [Leray et al., 2013; Leray et al., 2012]. Dans la suite de ce travail, on privilégiera donc les approches lagrangiennes de description des temps de résidence et de temps de transit (Partie III Chapitre 2).

2.2.2 Approches semi implicites : les « *Lumped Parameter Models* »

Parallèlement à ces approches mécanistes et explicites, une approche souvent utilisée pour inférer les distributions de temps de résidence à l'aide de données géochimiques tels que celles détaillées dans le chapitre précédent (Partie I 1.2) consistent à présupposer une forme paramétrique de distribution a priori

en considérant le type de structure géologique et de processus d'écoulements ayant lieu dans le milieu souterrain [Maloszewski and Zuber, 1996]. Ces distributions s'appellent des « *Lumped Parameter Models* » (voir Partie II Chapitre 1) et ont des formes paramétriques classiques, exponentielle, dirac, inverse gaussienne, gamma, voire une combinaison de ces distributions [Leray et al., 2016].

N	LPM's name	Expression
1	Dirac (<i>Piston Flow</i>)	$f_T(t) = \delta(t - T)$
	Exponential (<i>Exponential</i>)	$f_T(t) = \frac{1}{T} \exp\left(-\frac{t}{T}\right)$
2	Inverse Gaussian (<i>Dispersion</i>)	$f_{(T,Pe)}(t) = \left(\frac{Pe}{2\pi t^3}\right)^{0.5} \exp\left(-\frac{Pe(t-T)^2}{2t}\right)$
	Shifted Exponential (<i>Exponential Piston Flow</i>)	$f_{(T,t_0)}(t) = \begin{cases} \frac{1}{t_0} \exp\left(-\frac{t-(T-t_0)}{t_0}\right) & \text{for } t \geq T - t_0, \\ 0 & \text{otherwise.} \end{cases}$
	Uniform (<i>Linear Piston Flow</i>)	$f_{(T,\varepsilon)}(t) = \begin{cases} \frac{1}{\varepsilon} & \text{for } T - \frac{\varepsilon}{2} \leq t < T + \frac{\varepsilon}{2}, \\ 0 & \text{otherwise.} \end{cases}$
	Weighted sum of Diracs	$f_{(t_0, t_1, \omega)}(t) = \omega \delta(t - t_0) + (1 - \omega) \delta(t - t_1)$
3	Shifted Inverse Gaussian	$f_{(T,Pe,t_0)}(t) = \begin{cases} \left(\frac{Pe(t-t_0)}{2\pi(t-t_0)^3}\right)^{0.5} \exp\left(-\frac{Pe(t-T)^2}{2(t-t_0)(t-t_0)}\right) & \text{for } t \geq t_0, \\ 0 & \text{otherwise.} \end{cases}$

Tableau 1: Exemple de LPMs classiquement utilisés en hydrogéologie. D'après Marçais et al. [2015].

Chacun de ces « *Lumped Parameter Models* » présupposent une connaissance *a priori* des écoulements en milieu souterrain, traduite implicitement dans le choix de la distribution. La distribution dirac fait ainsi appel au présupposé que l'écoulement est uniquement advectif (non dispersif) et que par conséquent, l'écoulement est de type piston. Au contraire, l'inverse gaussienne trouve son origine dans le fait qu'elle est une solution de l'équation d'advection dispersion. Ces distributions LPMs ont des paramètres tel que la moyenne de la distribution assimilée au temps moyen de résidence. Ces paramètres sont ensuite informés à l'aide des données en traceurs en solutionnant par exemple l'équation de convolution suivante pour un traceur atmosphérique :

$$C_{mes}^A(t) = \int_0^{+\infty} C_{in}^A(t - \tau) \cdot p_S(\tau) d\tau, \quad (4)$$

où $C_{mes}^A(t)$ est la concentration en traceurs mesurée à la date d'échantillonnage t , $C_{in}^A(t - \tau)$ est la concentration d'entrée du traceurs atmosphérique à la date $t - \tau$ et $p_S(\tau)$ est la distribution de temps de résidence, supposée stationnaire (i.e. ne dépendant pas de la date d'échantillonnage t). L'intégrale traduit le fait qu'on mélange toutes les concentrations possibles s'étant rechargées dans l'aquifère par le passé, proportionnellement à leur importance relative dans le volume total.

Ces modèles implicites, ou plus exactement semi-implicites puisqu'ils font l'hypothèse d'un concept de circulation, sont faciles à utiliser pour inférer les valeurs de temps de résidence moyen ainsi que pour avoir une idée de la dispersion de la distribution de temps de résidence. Cependant leur aptitude n'a été que rarement évaluée via des expériences numériques sur des aquifères synthétiques [Eberts et al., 2012]. C'est donc l'un des objets du Chapitre 1 de la Partie II que d'évaluer la capacité prédictive de ces LPMs pour prédire les temps de renouvellement des eaux dans un aquifère (voir Partie II Chapitre 1Partie IIChapitre 1).

2.2.3 Les modèles hydrologiques explicites intégrés

Enfin, on peut signaler un troisième type de modèles qui vise à modéliser l'intégralité des processus d'écoulement ayant lieu dans un bassin versant. Ce type de modélisation modélise ainsi le flux et le transport dans la zone non saturée, dans l'aquifère ainsi que les processus d'écoulements en rivière et dû au ruissellement [Fatichi et al., 2016]. Plusieurs modèles concurrents sont actuellement développés parmi lesquels ParFlow [Ashby and Falgout, 1996; Kollet and Maxwell, 2006; Maxwell, 2013] ou HydroGeoSphere [Brunner and Simmons, 2012; Therrien and Sudicky, 1996].

Ces modèles extrêmement complexes ont ainsi été utilisés pour modéliser les distributions de temps de résidence à l'échelle des Etats-Unis (réalisé avec ParFlow, Figure 19) [Maxwell *et al.*, 2015]. Ces modèles n'ont pas été calés à proprement parler mais comparés à des données en puits et en rivière. De manière plus classique, ce type de modèles a été calibré puis utilisé pour comprendre l'évolution des temps de transit et des temps de résidence à l'échelle de petit bassin versant (réalisé avec HydroGeoSphere [Yang *et al.*, 2018]).

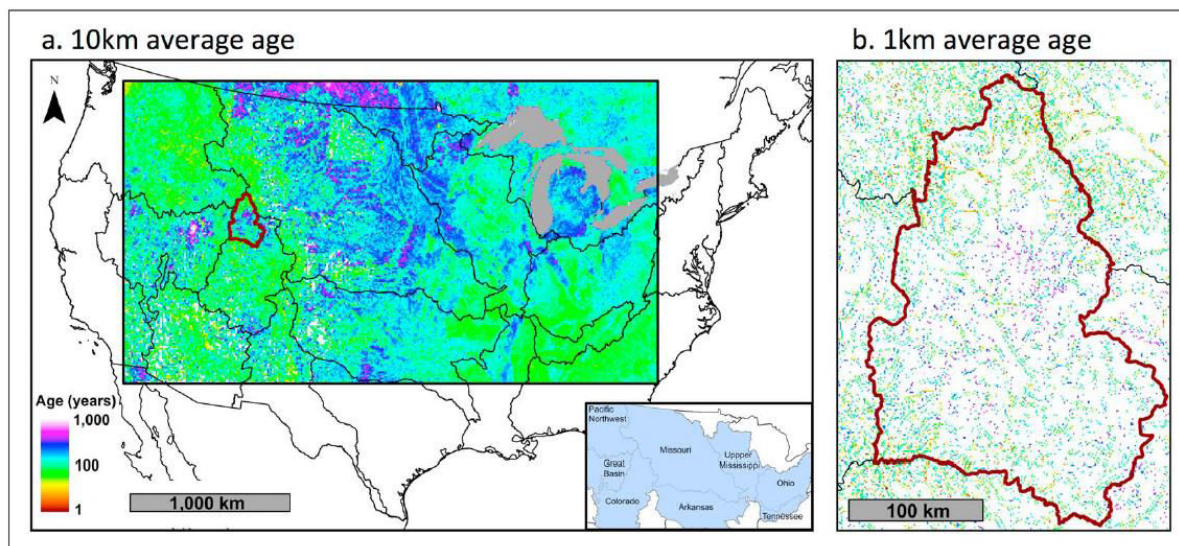


Figure 19: Représentation spatialisée du temps de résidence moyen à l'échelle des Etats-Unis et d'un bassin versant à l'aide d'un modèle explicite intégré. D'après Maxwell *et al.* [2015].

Ces modèles explicites intégrés présentent l'énorme avantage de représenter l'intégralité des processus d'écoulements et de transport dans les bassins versants. Ce faisant, ils permettent de modéliser les distributions de temps de résidence dans les différents compartiments du bassin versant ainsi que les distributions de temps de transit en rivière, et ce de manière transitoire [Danesh-Yazdi *et al.*, 2018]. Cependant, l'extrême complexité induite par la représentation de l'ensemble de ces processus à l'échelle de volumes élémentaires discrétisant l'ensemble du bassin versant les rend difficiles à informer à l'aide de données hétérogènes. C'est pourquoi dans cette thèse, on s'intéresse au développement de stratégie de modélisation intermédiaire à même de rendre compte de manière mécaniste de l'évolution de solutés en puits ou en rivière.

2.3 Introduction du travail de thèse

Cette première partie d'introduction générale a précisé les connaissances acquises sur les temps de résidence et de transit des eaux dans les hydrosystèmes, en s'attachant à décrire les questions ouvertes qui subsistent. Celles-ci peuvent être résumées en trois différents points : 1. la difficulté d'inférer les distributions de temps de transit et de temps de résidence en rivières et en aquifère ; 2. le paradoxe sur les différences importantes entre temps de résidence en aquifère et temps de transit en rivière (comment des eaux vieilles stockées dans les aquifères peuvent alimenter des rivières constituées d'eaux jeunes ?) ainsi que 3. la méconnaissance qui existe sur leur variabilité temporelle et sur les processus capables de rendre compte de cela.

Dans cette thèse, je m'attacherai donc à décrire différents moyens d'inférer des temps de résidence dans les aquifères à partir de données d'âge de l'eau et de données géochimiques (Partie II). Que ce soit pour prédire, à l'échelle du site, les temps de renouvellements dans un aquifère cristallin (Partie II Chapitre 1), pour évaluer le potentiel des produits issus de l'altération (comme la silice dissoute) comme proxys

des temps de résidence à l'échelle régionale (Partie II Chapitre 2) ou pour comprendre les facteurs de contrôles des circulations souterraines (Partie II Chapitre 3), les données d'âges de l'eau peuvent être utilisées dans différentes stratégies de modélisation (Figure 20: Différentes stratégies de modélisation). Ces stratégies, qu'elles soient implicites, semi-explicites ou explicites dépendent des objectifs poursuivis. Ces approches permettent donc de mieux caractériser les temps de résidence en aquifère à l'aide de données géochimiques et de comprendre comment ces temps de résidence sont impactés par la topographie, le climat et la géologie. Cependant, ces approches ne permettent pas d'intégrer le gisement de données en rivière. Ces données requièrent en effet des approches de modélisation du cycle hydrologique, intégrées à l'échelle du bassin versant.

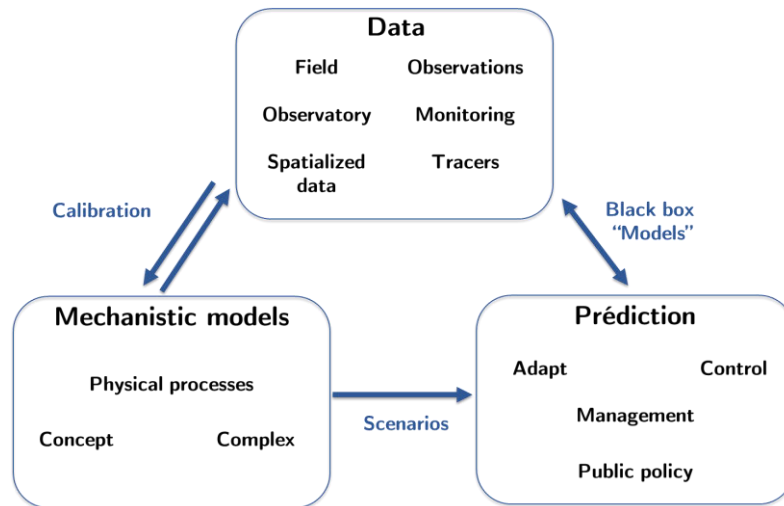


Figure 20: Différentes stratégies de modélisation pour coupler données et modèles suivant les objectifs poursuivis.

C'est pourquoi, dans la Partie III, nous développons un cadre original de modélisation parcimonieuse à base physique, capable de représenter la variabilité saisonnière et interannuelle des débits et des flux, des temps de transit et des temps de résidence, en rivière comme dans les aquifères. Ce modèle représente en effet le processus de battements de nappe et son interaction avec les couches perméables du sol qui mène à une génération variable de ruissellement. Ce processus est à même d'expliquer les fluctuations saisonnières de la qualité de l'eau en rivière. Nous adoptons donc une description des écoulements souterrains à l'aide de la théorie de Boussinesq, en prenant en compte les interactions entre le toit de la nappe et la topographie qui conduisent à la génération de ruissellement (Partie III Chapitre 1). Nous complétons cette représentation des flux par une méthode lagrangienne de transport capable de représenter la variabilité temporelle des distributions de temps de transit et des distributions des temps de résidence (Partie III Chapitre 2). Cette méthode de transport ouvre à la voie au développement d'un cadre de modélisation de la réactivité à l'échelle du versant. Enfin, nous montrons comment ce modèle permet, via une intégration adaptée de données de qualité de l'eau disponibles en rivière, de rendre compte des variations temporelles des temps de transit en rivière (Partie III Chapitre 3).

Enfin, nous esquisserons les perspectives à donner à ce travail de recherche (Partie IV), que l'on peut classer en trois parties. Tout d'abord, l'exploitation du modèle développé permet, par des expériences synthétiques, de mettre en lumière un certain nombre de processus suspectés de jouer un rôle dans la construction de la qualité de l'eau à l'échelle des versants (Partie IV Chapitre 1 et Partie IV Chapitre 2). Cette compréhension nous permet d'envisager une stratégie de modélisation cohérente des aquifères libres de proche subsurface, à l'échelle régionale (Partie IV Chapitre 3). Cette stratégie de modélisation vise à être informée par des données en rivière. Deuxièmement, nous esquissons une description de la réactivité visant à intégrer les différentes données géochimiques

acquises en continu en rivières dans différents observatoires de la zone critique (Partie IV Chapitre 4). En effet, si ces données sont autant de traceurs potentiels de la structure géologique et des compartiments hydrologiques de la zone critique, ils nécessitent pour être intégrés au modèle de disposer d'une description des processus de réactivité adaptés à l'échelle du bassin versant. Troisièmement et de manière plus prospective, l'émergence de nouvelles techniques implicites de modélisation issues de l'intelligence artificielle nous semblent être une opportunité pour la communauté des hydrologues si ces techniques sont capables de s'articuler à des méthodes explicites (Partie IV Chapitre 5). En effet, si l'acquisition des données environnementales progressent considérablement, la spécificité de l'hydrologie est de ne pas avoir d'accès direct au milieu souterrain hétérogène excepté de manière fragmentée (via quelques forages). Cette caractéristique semble nécessiter le couplage des méthodes d'apprentissage statistique avec des méthodes explicites.

Partie II Inférence des temps de résidence dans les aquifères cristallins

Inférer le temps de résidence dans les aquifères est clef pour renseigner sur quantifier et prédire les effets de l'agriculture intensive passée sur la qualité de l'eau en rivière présente et future. Ces temps de résidence, du fait de l'échelle de temps mis en jeu (plusieurs années à quelques siècles) et du fait de la nature du bassin versant qui mélange ces eaux, ne peuvent être inférés que de manière indirecte grâce à l'existence de traceurs géochimiques. La présence de ces traceurs et leurs concentrations permettent de tirer des informations quantitatives sur le temps qui s'est écoulé depuis la recharge de ces eaux dans l'aquifère et sur la diversité des temps de résidence des eaux au sein d'un même aquifère. Dans une première partie nous nous intéresserons à quantifier l'apport informatif de traceurs classiquement utilisés (CFCs) pour déterminer la distribution des temps de résidence. Dans une seconde partie, nous nous intéresserons au développement d'un proxy géochimique « bon marché » des temps de résidence : la silice. Enfin nous verrons comment l'intégration de ces informations est classiquement réalisée dans la modélisation en hydrologie via le paradigme du problème inverse, c'est-à-dire d'une calibration directe des données par le modèle. C'est ce type de modélisation qui permet en effet de comprendre comment les différents contrôles (climatiques, topographiques, géologiques et anthropiques) agissent pour former la distribution des temps de résidence.

Chapitre 1 Evaluer le contenu informationnel des traceurs atmosphériques pour inférer les distributions des temps de résidence

1.1 Introduction

Les traceurs atmosphériques en CFCs sont souvent utilisés pour donner un âge apparent de recharge des eaux dans le système aquifère d'étude. En effet, les CFCs sont des gaz dissous présent dans l'atmosphère depuis les années 1940, suite à leur utilisation comme gaz réfrigérant (Figure 21). Cette concentration qui a augmenté des années 1940 aux années 2000, permet via la connaissance du processus d'équilibration entre la concentration atmosphérique de CFCs dans l'air et la concentration en CFCs soluble dans l'eau, de déterminer un âge apparent reflétant l'âge à laquelle l'eau s'est rechargée dans l'aquifère. Les CFCs mesurent donc le temps depuis lequel l'eau souterraine s'est isolée de tout contact avec l'atmosphère. Cet âge est en fait le reflet d'une distribution de temps de résidence qui est caractéristique des eaux de l'aquifère qui se sont mélangées au fur et à mesure des recharges successives. Cet âge apparent est aussi sensible à la chronique atmosphérique d'entrée qui vient pondérer de différentes manières les temps de résidence. Typiquement, les CFCs ne pondèrent que les eaux jeunes (et ce d'autant plus qu'elles sont plus jeunes) mais sont « aveugles » sur les eaux plus vieilles que 80 ans (pas de présence de CFCs avant 1940) (Figure 21).

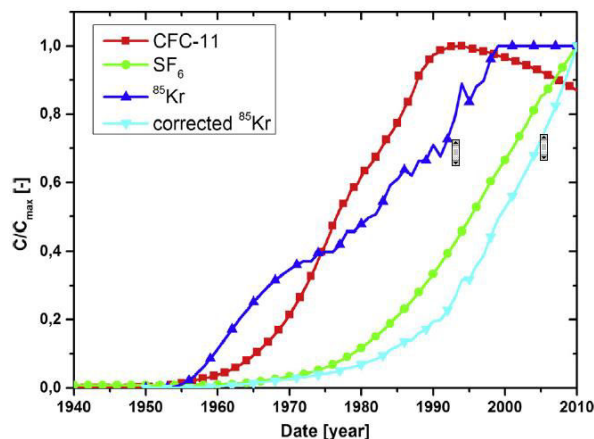
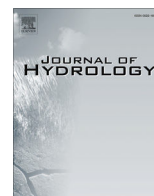


Figure 21: Chroniques atmosphériques normalisées en CFCs, SF₆ et ⁸⁵Kr pour la période de 1940 à nos jours. La chronique en ⁸⁵Kr est doublée d'une chronique apparente, une fois l'effet de la décroissance radioactive pris en compte.

Dans ce contexte, ce travail s'intéresse à quantifier la capacité qu'ont les données en CFCs pour caractériser la distribution des temps de résidence et, plus particulièrement, pour réaliser des prédictions sur le temps nécessaire au renouvellement d'un certain pourcentage de l'eau souterraine de l'aquifère. Nous évaluons donc le nombre de données en traceurs nécessaires pour caractériser la distribution de temps de résidence sur la période 0 – 70 ans. Pour faire cela, nous avons besoin de supposer, *ex ante*, une distribution de temps de résidence paramétrée (e.g. distribution exponentielle, inverse gaussienne, dirac) sur lequel on évaluera le contenu informationnel des CFCs. Nous évaluons donc à la fois le contenu informationnel des données en CFCs et le réalisme des distributions paramétrées que nous avons supposé. Cette évaluation n'est donc pas sans rappeler le cadre bayésien, via le renseignement d'un *prior* suffisamment bien choisi (le type de distribution) auquel s'ajoute une information exogène provenant des données (données en CFCs).

Méthodologiquement, ce travail se base sur des expériences numériques (*in silico*) qui permettent d'avoir accès à des distributions de temps de résidence synthétiques issues d'un modèle. En effet, les distributions de temps de résidence ne sont pas accessibles sur le terrain ! Le modèle mécaniste de Ploemeur précédemment développé [Leray *et al.*, 2013] joue ainsi le rôle de réalité virtuelle [Thomas *et al.*, 2016] sur lequel on va tester quel est la capacité informative des données en CFCs et en ^{85}Kr pour prédire des temps de renouvellement dans l'aquifère de Ploemeur. En effet, les distributions de temps de résidence obtenues avec ce modèle permettent d'avoir accès à 1. Des observables numériques, i.e. des concentrations (synthétiques) en CFCs et en ^{85}Kr en effectuant la convolution classique de la chronique d'entrée pondérée par la distribution des temps de résidence ; 2. Des prédictions numériques sur le temps de renouvellement des eaux de l'aquifère qui ne sont rien d'autre que des prédictions sur la cumulée de la distribution des temps de résidence. On évalue alors le pouvoir informationnel des données en CFCs et en ^{85}Kr à partir des observables synthétiques obtenues (les concentrations en traceurs issues du modèle). Ces concentrations sont utilisées pour caler des distributions de temps de résidence paramétrées (les « *Lumped Parameters Models* ») et pour ensuite réaliser des prédictions sur les temps de renouvellement des eaux dans l'aquifère de Ploemeur. Ces prédictions sont ensuite comparées à celles du modèle initial, permettant ainsi d'évaluer le contenu informationnel contenu dans ces traceurs ainsi que le choix de la distribution choisie.

1.2 Article: Inferring transit time distributions from atmospheric tracer data: Assessment of the predictive capacities of Lumped Parameter Models on a 3D crystalline aquifer model



Inferring transit time distributions from atmospheric tracer data: Assessment of the predictive capacities of Lumped Parameter Models on a 3D crystalline aquifer model



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SUMMARY

While central in groundwater resources and contaminant fate, Transit Time Distributions (TTDs) are never directly accessible from field measurements but always deduced from a combination of tracer data and more or less involved models. We evaluate the predictive capabilities of approximate distributions (Lumped Parameter Models abbreviated as LPMs) instead of fully developed aquifer models. We develop a generic assessment methodology based on synthetic aquifer models to establish references for observable quantities as tracer concentrations and prediction targets as groundwater renewal times. Candidate LPMs are calibrated on the observable tracer concentrations and used to infer renewal time predictions, which are compared with the reference ones. This methodology is applied to the produced crystalline aquifer of Plœmeur (Brittany, France) where flows leak through a micascists aquitard to reach a sloping aquifer where they radially converge to the producing well, issuing broad rather than multi-modal TTDs. One, two and three parameters LPMs were calibrated to a corresponding number of simulated reference anthropogenic tracer concentrations (CFC-11, ⁸⁵Kr and SF₆). Extensive statistical analysis over the aquifer shows that a good fit of the anthropogenic tracer concentrations is neither a necessary nor a sufficient condition to reach acceptable predictive capability. Prediction accuracy is however strongly conditioned by the use of a priori relevant LPMs. Only adequate LPM shapes yield unbiased estimations. In the case of Plœmeur, relevant LPMs should have two parameters to capture the mean and the standard deviation of the residence times and cover the first few decades [0; 50 years]. Inverse Gaussian and shifted exponential performed equally well for the wide variety of the reference TTDs from strongly peaked in recharge zones where flows are diverging to broadly distributed in more converging zones. When using two sufficiently different atmospheric tracers like CFC-11 and ⁸⁵Kr, groundwater renewal time predictions are accurate at 1–5 years for estimating mean transit times of some decades (10–50 years). 1-parameter LPMs calibrated on a single atmospheric tracer lead to substantially larger errors of the order of 10 years, while 3-parameter LPMs calibrated with a third atmospheric tracers (SF₆) do not improve the prediction capabilities. Based on a specific site, this study highlights the high predictive capacities of two atmospheric tracers on the same time range with sufficiently different atmospheric concentration chronicles.

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1. Introduction

Transit times in groundwater flow systems result from local-scale advective and dispersive processes (Bellin and Tonina, 2007; Dagan et al., 1992; Dentz, 2012; Maloszewski and Zuber,

1996; Simmons, 1982), as well as from global-scale watershed and geological structures (Eberts et al., 2012; Goderniaux et al., 2013; McGuire and McDonnell, 2006; Rinaldo et al., 2011). Hence Transit Time Distributions (TTDs) are most generally broad, mixing times of different flow lines (Engdahl and Maxwell, 2014; Ginn, 1999) potentially acquired from various recharge areas (Weissmann et al., 2002), within a succession of aquifers and aquitards (Castro and Goblet, 2005; Phillips and Castro, 2003; Zinn and Konikow, 2007), or through exchanges between high-flow zones

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like fractures and large diffusive zones like the matrix (Cook et al., 2005; Haggerty and Gorelick, 1995; Varni and Carrera, 1998). With only scarce observations, it is out of reach to identify accurately which processes intervene where and how multiscale complexity of the flow structures generate the TTD. Nevertheless some characteristics of the TTD, also called “groundwater age distribution” (Ginn, 1999) or “groundwater residence time distribution” (McCallum et al., 2014) may be inferred from measurements of isotopic tracer concentrations in the groundwater (McCallum et al., 2014; Massoudieh et al., 2012; Massoudieh and Ginn, 2011; Newman et al., 2010). We refer to these data as “groundwater age data.” Moreover classical renewal and flushing time applications can directly be derived from the TTD without going back to the transport processes (Bohlke, 2002; Katz et al., 2001; Lerner and Papatolios, 1993; Pinay et al., accepted for publication; Sebilo et al., 2013).

In this framework the model for the TTD takes the critical role of translating groundwater age data to renewal or flushing predictions, that with any principle of parsimony should be simple enough to be fully determined by the scarce information available. It should also be representative in a broad sense of the underlying transport processes. This has promoted the development of simple TTD models known as Lumped Parameter Models (LPMs) that represent the multi-scale multi-factor dispersive processes all together in a parsimonious “lumped” way (Cook and Herczeg, 2000; Maloszewski and Zuber, 1996). Numerous LPMs have been proposed following different primary objectives. Some have been developed to efficiently fit observed groundwater ages like the mono- or multi-modal Dirac distributions corresponding to one or several piston flow models (Begemann and Libby, 1957), or flexible generalized Gamma distributions (Cvetkovic, 2012). Others are analytical solutions of simplified problems. This is the case of the Inverse Gaussian distribution solution to the 1D advection–dispersion equation (Ginn et al., 2009), of the exponential model taken from chemistry of continuous stirred tank reactors (Eriksson, 1958; Haitjema, 1995; Kaufman and Libby, 1954), and of some more complex semi-analytical distributions for gently sloping aquifers (Etcheverry and Perrochet, 2000) or dipole flow configurations (Luo and Kitanidis, 2004). Increasing their complexity to three or more parameters has been proposed by composing some of the previous distributions (Ozyurt and Bayari, 2003; Ozyurt and Bayari, 2005). Globally, LPMs have been proposed following Bayes spirit either by favoring the goodness of fit of the groundwater ages (likelihood in Bayes theory) like for the multi-modal Dirac distributions, or by favoring some consistency with the a priori flow pattern (prior in Bayes theory) such as for the Inverse Gaussian or exponential models. LPMs are still extending to “shape-free” distributions precisely designed to find an optimal balance of the likelihood and prior terms within a Bayesian framework (Massoudieh et al., 2012, 2013).

Lumped Parameter Models are highly attractive as they offer predictive capacities at limited observation and modeling costs. However, they raise a number of questions that should be carefully assessed: is the LPM approach appropriate for 3D complex aquifers? How should the LPM distribution be chosen? Is there any a priori more relevant LPM among the existing analytical solutions? When is the information content of the groundwater age data enough for establishing the targeted predictions like the renewal or flushing times?

Assessment studies have been undertaken on sampling zones located preferentially in the downstream convergence zones (Eberts et al., 2012; Leray et al., 2012), using extensively geographical information with simple transport solutions (Basu et al., 2012), or with two parameters widely varying LPMs under a broad panel of observation and tracer scenarios (Green et al., 2014). In this article, we analyze the predictive capacities of LPMs against

evolving quantity of tracer information. We adapt the LPM complexity through the number of its parameters to the informational content of the tracer data, in order to determine the relation between the informational content of the tracer data and the quality of the predictions. While our analysis is centered on LPMs, LPMs just appear as the necessary step to extract from the tracer data the information needed to establish predictions. We first propose a methodology for a spatially extensive assessment of the LPMs (Section 2). It is illustrated on a 3D crystalline aquifer model under steady-state convergent flow (Section 3). Seven LPMs are compared at 73 locations of the crystalline aquifers (Section 4). Results are further discussed in Section 5 to determine the quantity of information required to establish accurate renewal time predictions.

2. Methodology: assessing LPMs on in silico aquifers

We detail the methods for determining the predictive capacities of Lumped Parameter Models (LPMs) based on groundwater age information derived from tracer concentrations on in silico aquifers. In-silico aquifers, also generally called synthetic aquifer models, are essential since the assessment procedure requires the knowledge of the true Transit Time Distributions (TTDs). As TTDs cannot be obtained in the field from any measurement at the watershed scale, we access it through aquifer modeling. Both 2D and 3D theoretical models have brought up key issues (Massoudieh et al., 2012; Park et al., 2002; Varni and Carrera, 1998; Weissmann et al., 2002; Zhang, 2004; Zinn and Konikow, 2007), as has direct modeling of age distributions in real 2D aquifer case (Woolfenden and Ginn, 2009). The most relevant aquifer models are however those closer to the 3D real aquifer cases calibrated using both hydraulic and atmospheric tracer information (Eberts et al., 2012; Green et al., 2014; Leray et al., 2013).

In this section, we assume that transport simulations have previously been performed and that the necessary results are available. These results can take the form of particle paths or concentration fields depending on the numerical method chosen for solving the advective–dispersive equation (Bear, 1973). When using random walk methods (Delay et al., 2005; Kinzelbach, 1988; Thompson and Gelhar, 1990), results are particle paths derived from forward or backward simulations (Neupauer and Wilson, 2002). For a straightforward derivation of concentrations from particle densities under forward tracking, particles must be injected at densities proportional to the inflow boundary fluxes. In recharge and pumping cases, the density of injected particles must be weighted by flows entering the aquifer either by the recharge zones in forward studies or by the sampling areas in backward studies (Leray et al., 2012). The method is general in the sense that it can be applied to any aquifer model with adequate transport simulation and injection conditions. In this article, it will be applied to the crystalline aquifer model of Plœmeur described in Section 3. We discuss application to other sites in Section 5. Methods are organized in 5 steps. In the two first steps, the transit time distributions (TTDs) are used to establish the reference atmospheric tracer concentrations often displayed as groundwater ages and the reference predictions. The third step consists in defining the candidate LPMs. Several LPMs are concurrently considered. In this article, we consider seven LPMs with evolving number of parameters. This is a key point of our methodology for studying the evolution of the prediction capacities according to the quantity of available information in the atmospheric tracer concentrations. The number of informative parameters will be taken as a measure of the available information. We then calibrate the LPMs on the reference atmospheric concentrations and compare their predictions with the reference ones. This procedure is consistent with a field

observation methodology where only atmospheric concentrations can be measured. There is no fitting of the TTD obtained from the numerical simulations by the candidate LPMs.

This assessment methodology is not only practically appropriate but also conceptually relevant. In fact, LPMs are not designed to reproduce all the details of the TTD and underlying transport processes but capture them globally to be both consistent with the available data and effective in terms of predictions. They should be somehow statistically similar but not identical. In the same spirit, LPMs are not thought to be excellent on every sampling zone of the aquifer, but should be good on average. It thus requires an extensive spatial assessment. We underline that, even if we eventually compare the performances of the LPMs at different sampling zones, the procedure to estimate the LPMs is always made point by point and never accounts simultaneously for observations coming from different sampling zones.

2.1. In-silico modeling approach

2.1.1. Reference TTDs and atmospheric tracer concentrations

The approach used in this article requires the use of a synthetic aquifer taken as a reference and providing flow weighted consistent transit time distributions (TTDs), apparent ages and predictions on renewal times. We derive the TTDs f_{ref} everywhere in the watershed, so f_{ref} is a distribution function of the transit time u conditioned by the position $\mathbf{x}$. The TTDs obtained are the references to which will be compared the approximations obtained with LPMs.

From the TTDs, we derive the reference tracer concentrations $C_{\text{Tr}}^{\text{ref}}$. For a given time and position $(t, \mathbf{x})$ these concentrations can be readily expressed from the TTD f_{ref} determined previously, the atmospheric concentration chronicle of the tracer $\mathcal{C}_{\text{Tr}}$ and its possible decay constant λ :

$$C_{\text{Tr}}(t, \mathbf{x}) = \int_0^t \mathcal{C}_{\text{Tr}}(t-u) e^{-\lambda u} f_{\text{ref}}(u, \mathbf{x}) du \quad (1)$$

where $t-u$ is the date when the tracer enters the aquifer. $C_{\text{Tr}}^{\text{ref}}$ corresponds to the concentration $C_{\text{Tr}}(t, \mathbf{x})$ at a given sampling date t and at the position $\mathbf{x}$. These concentrations computed for different environmental tracers such as CFC-11, SF_6 and ^{85}Kr (see Fig. 1) are taken as observables. They closely match sampled concentrations in field studies.

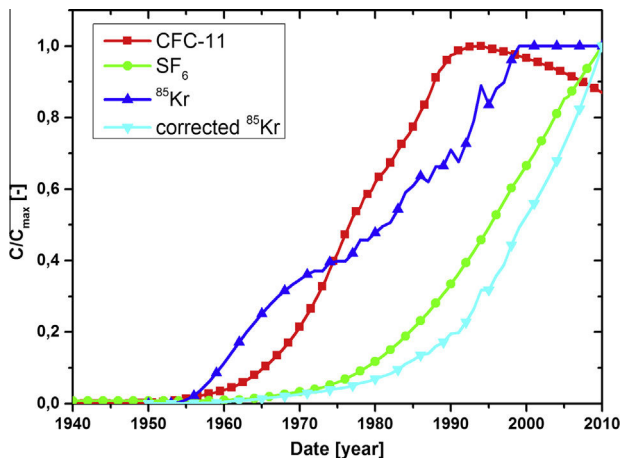


Fig. 1. Atmospheric concentrations of CFC-11, SF_6 and ^{85}Kr from 1940 to 2010. Being a radioactive tracer, ^{85}Kr concentration is corrected by its radioactive decay. Concentrations are normalized by their maximum to compare their relative evolution.

The concentrations can readily be converted to apparent ages $\hat{A}_{\text{Tr}}$:

$$C_{\text{Tr}}(t, \mathbf{x}) = \mathcal{C}_{\text{Tr}}(\hat{A}_{\text{Tr}}(t, \mathbf{x})) e^{-\lambda \hat{A}_{\text{Tr}}(t, \mathbf{x})} \quad (2)$$

Tracers are considered ideal, i.e. they do not have any interaction with the aquifer matrix (Maloszewski and Zuber, 1996). We also assume that tracers are at their atmospheric concentration at the aquifer recharge $\mathcal{C}_{\text{Tr}}$ (Eqs. 1 and 2).

2.1.2. Reference predictions

From the reference TTDs f_{ref} we also derive renewal times in the aquifer. For a given sampling zone, the renewal period t_y of a fraction y of the water to be renewed in aquifer is defined as

$$y = F_{\text{ref}}(t_y) = \int_0^{t_y} f_{\text{ref}}(u) du \quad (3)$$

where F_{ref} is the cumulative density function. The quartiles Q_1^{ref} (resp. Q_2^{ref} and Q_3^{ref}) of the reference TTD represent the renewal period of time for a given sampling zone in the aquifer so that 25%, 50% or 75% of the water is renewed. They are determined by: $F_{\text{ref}}^{-1}(25\%)$ (resp. $F_{\text{ref}}^{-1}(50\%)$ and $F_{\text{ref}}^{-1}(75\%)$). In the following, they will be expressed in years. The renewal times at 25%, 50% and 75% will be determined everywhere in the aquifer and reference maps will be drawn for the in silico model.

2.2. Inferring LPMs from environmental tracer concentrations

In the next step, we define candidate LPMs and calibrate them on the reference tracer concentrations determined in the in silico modeling phase. We underline that, at this stage, the tracer concentrations are the only data made available. LPMs are estimated without any knowledge of the TTDs.

2.2.1. Defining candidate LPMs

As we aim at determining the influence of the data amount on the prediction accuracy, we choose LPMs with evolving number of parameters to be calibrated on an increasing quantity of tracer concentrations. Basically, the number of parameters will be made equal to the number of tracers. As opposed to the approach of Corcho Alvarado et al. (2007), the number of degrees of freedom is always equal to 0 as the number of free parameters is made equal to the number of observations.

We choose seven LPMs that either correspond to prior information on the flow pattern or that are often used in hydrogeological studies. We sort them according to the number of parameters required to define them (see Table 1) and detail in the following their physical basis. They are all defined only for $t \geq 0$.

We have chosen the Dirac and exponential distributions as 1-parameter models. Physically, the Dirac distribution corresponds to the piston flow model (PFM), where tracers are advected along a single flowpath without any mixing within the flow line nor with the other flow lines. At the other extreme, the exponential model (EM) characterizes a well-mixed flow and is relevant to TTDs at convergent and outflow zones (pumping site, discharge). Both distributions are defined by a single parameter T equal in both cases to their mean.

A straightforward extension to 2-parameter models is the Shifted Exponential distribution corresponding to the exponential piston flow model (EPM) and representing a combination of exponential and piston flow models. Such a distribution can represent a system where recharge occurs in an unconfined zone (EM) and tracers are then advected in a confined part of the aquifer (PFM). It is defined by the same exponential constant T and by the time lag t_0 . The other classical 2-parameter model is the Inverse

Table 1
LPMs used in this study with their number of parameters N and their expression. The name referring to this LPM according to Maloszewski and Zuber (1996) is recalled in brackets.

N	LPM's name	Expression
1	Dirac (Piston Flow) Exponential (Exponential)	$f_T(t) = \delta(t - T)$ $f_T(t) = \frac{1}{T} \exp\left(-\frac{t}{T}\right)$
2	Inverse Gaussian (Dispersion) Shifted Exponential (Exponential Piston Flow) Uniform (Linear Piston Flow)	$f_{(T,Pe)}(t) = \left(\frac{TPe}{2\pi t^3}\right)^{0.5} \exp\left(-\frac{Pe(t-T)^2}{2Tt}\right)$ $f_{(T,t_0)}(t) = \begin{cases} \frac{1}{t_0} \exp\left(-\frac{t-(T-t_0)}{t_0}\right) & \text{for } t \geq T - t_0, \\ 0 & \text{otherwise.} \end{cases}$ $f_{(T,\epsilon)}(t) = \begin{cases} \frac{1}{\epsilon} & \text{for } T - \frac{\epsilon}{2} \leq t < T + \frac{\epsilon}{2}, \\ 0 & \text{otherwise.} \end{cases}$
3	Weighted sum of Diracs Shifted Inverse Gaussian	$f_{(t_0,t_1,\omega)}(t) = \omega \delta(t - t_0) + (1 - \omega) \delta(t - t_1)$ $f_{(T,Pe,t_0)}(t) = \begin{cases} \left(\frac{Pe(T-t_0)}{2\pi(t-t_0)^3}\right)^{0.5} \exp\left(-\frac{Pe(t-T)^2}{2(T-t_0)(t-t_0)}\right) & \text{for } t \geq t_0, \\ 0 & \text{otherwise.} \end{cases}$

Gaussian distribution. It is a solution to the classical advection dispersion equation (ADE) and is characterized by the distribution mean T and by the Peclet number Pe (Maloszewski and Zuber, 1996). Pe is related to macrodispersive watershed processes with potentially much smaller values than classical microscale hydrodynamic dispersion. The lower Pe is, the broader and the more asymmetrical the TTD will be. The last 2-parameter model considered is the uniform distribution corresponding to the linear piston flow model, which can represent the TTD in a partly confined aquifer (Cook and Bohlke, 1999). It is characterized by the distribution mean T and by the range of explored times ϵ .

As 3-parameter models, we have taken the weighted sum of two Diracs typically used in karstic systems (Long and Putnam, 2006) or when considering two independent poles or reservoirs characterized by the two times t_0 and t_1 and by the relative weight of the poles ω . Alternatively, we also consider the Shifted Inverse Gaussian distribution corresponding to an Inverse Gaussian model with a shifted origin t_0 . Fig. 2 shows the diversity of shapes of the 7 LPMs. All these LPMs have the same mean. LPMs with two and more parameters have the same variance. LPMs with three parameters have additionally the same skewness. Given to illustrate the diversity of shapes, these LPMs have not been calibrated with any tracer data.

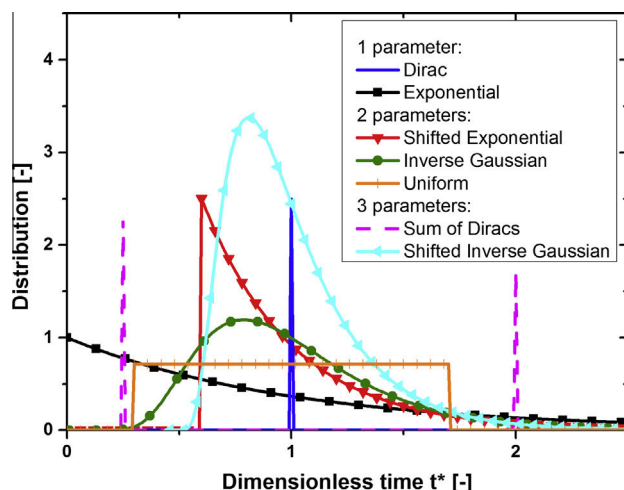


Fig. 2. Comparison of the seven candidate LPM models as functions of the time t normalized by the mean time T (t/T). All distributions have the same mean and all distributions with more than one parameter have the same variance, but display quite different shapes.

2.2.2. Calibrating LPMs on reference tracer concentrations

The 7 LPMs are calibrated to fit the reference concentrations C_{Tr}^{ref} derived from the in silico model. As previously underlined, the number of tracer concentrations in a sampling zone is made equal to the number of parameters of the model and is considered as a measure of the quantity of available information. For this analysis, we have taken the three most different atmospheric tracers available on the last 50 years period introducing them in this order (CFC-11, ^{85}Kr , SF_6) to get the best possible amount of potential information. In fact the more different the atmospheric concentration chronicles, the more complementary information can be extracted. 1-parameter LPMs are calibrated on the reference CFC-11 tracer concentration (C_{CFC}^{ref}). 2-parameter LPMs are calibrated on the reference CFC-11 and ^{85}Kr tracer concentrations (C_{CFC}^{ref} and C_{Kr}^{ref}). 3-parameter LPMs are calibrated on the reference CFC-11, ^{85}Kr and SF_6 tracer concentrations (C_{CFC}^{ref} , C_{Kr}^{ref} and $C_{SF_6}^{ref}$).

For each N -parameter LPM (where N equals either 1, 2 or 3) we seek for the parameters $(\pi_1, \dots, \pi_N)$ that solve the system of N equations:

$$\text{For } n = 1 \dots N, \quad C_{Tr_n}^{ref} = \int_0^t \mathcal{C}_{Tr_n}(t-u) f_{(\pi_1, \dots, \pi_N)}(u) du \quad (4)$$

where N is the number of parameters and Tr_n is the n th tracer (if $n = 1$, Tr_1 is CFC-11, if $n = 2$, Tr_2 is ^{85}Kr and if $n = 3$, Tr_3 is SF_6).

We use the Levenberg–Marquadt method of Matlab to find the set of parameters $(\pi_1, \dots, \pi_N)$ that minimize the objective function χ :

$$\chi = \sum_{n=1}^N \frac{|v_n(\pi_1, \dots, \pi_N)|^2}{C_{Tr_n}^{ref}} \quad (5)$$

where

$$v_n = C_{Tr_n}^{ref}(t) - \int_0^t \mathcal{C}_{Tr_n}(t-u) f_{(\pi_1, \dots, \pi_N)}(u) du. \quad (6)$$

We also choose the starting parameters for the Levenberg–Marquadt algorithm not far from the global minimum of the objective function χ by pre-calibrating the parameters of the LPM. This ensures faster and more systematic convergence to the global minimum of χ .

To evaluate the goodness of fit, we use the maximum of the relative residuals over the N reference tracer concentrations ρ :

$$\rho = \max_{n \in [1:N]} \frac{|v_n|}{C_{Tr_n}^{ref}}. \quad (7)$$

ρ , expressed in %, gives the relative error made on the tracer concentrations C_{Tr}^{ref} . If it is lower than 10%, we consider the fit acceptable as experimental uncertainties on field measurements are of the same order of magnitude (Cook and Solomon, 1997). We choose to express the residual with the maximum of the residuals obtained to calibrate one tracer so that the values taken by ρ do not depend on the number of parameters of the LPM. The maximum defining ρ highlights more the possible deviations of the model than the quadratic norm of the errors.

2.3. Predictive performances of LPMs

We derive the quartiles of the calibrated LPMs. As for the reference TTD, the quartiles of the LPMs $Q_1^{(\pi_1, \dots, \pi_N)}$, $Q_2^{(\pi_1, \dots, \pi_N)}$ and $Q_3^{(\pi_1, \dots, \pi_N)}$ correspond to the prediction of the renewal time at which 25% (resp. 50% and 75%) of the water in the aquifer is renewed. To evaluate the predictive performance of the LPMs we compare the reference renewal times given by TTDs to the prediction given by LPMs. We introduce the comparison criterion θ (given in years):

$$\theta = \frac{1}{3} \sum_{i=1}^3 |Q_i^{ref} - Q_i^{(\pi_1, \dots, \pi_N)}| \quad (8)$$

θ assesses the quality of the predictions given by a LPM on the quartiles. Small θ values indicate a good agreement. The analysis of the performance criterion θ will be made over all the aquifer with the different LPMs model.

This methodology is generic and can be applied to any aquifer model on which transport simulations can be performed. The most important limitation comes from the characteristic time ranges of the available atmospheric tracers. In the following, the analysis is relevant for recent circulations (less than 60 years in practice). Extension to longer times with different sets of tracers is discussed in Section 5.

3. The 3D numerical model of Plœmeur pumping site

The site of Plœmeur has several advantages for this study. It is a 3D crystalline aquifer with circulations of the order of some tens of years. Although developing in complex fractured geological structures, the flow pattern is fully 3D but remains mostly convergent to the actual pumping site. Moreover, it has been studied for almost 20 years and calibrated flow models have been developed (Carn, 1990; Borgne et al., 2006; Touchard, 1999).

3.1. Description of the 3D crystalline aquifer model

This study is based on one of the models of the Plœmeur aquifer developed by Leray et al. (2012). The Plœmeur aquifer is located in the south of Brittany (France) within a crystalline basement. It is produced from a single well since 1991 at 110 m³/h for the drinking water supply of the nearby city.

The site is composed of four major structures (Fig. 3). Two granitic plutons outcrop North and South of the site acting as no-flow boundaries. The recharge of 200 mm/year in average leaks into semi impervious overlying micaschists. A gently dipping fractured zone further drains recharge to the pumping well. This transmissive structure at the contact between the southern granite and the micaschists, named the contact zone, constitutes the aquifer. Another transmissive structure, a subvertical fault oriented North 20°, while clearly marked on the geological map, only slightly impacts the flow pattern (Leray et al., 2012). The pumping well is located at the intersection between the subhorizontal contact zone and the subvertical North 20° fault. Table 2 sums up the properties of the hydrogeological model used. The flow and transport model used in this study refers to the “deep” model of Leray et al., 2012. It has been calibrated with data at the pumping well of the mean piezometric level (−5.5 m above sea level) and of the CFC-12 atmospheric concentration measured in 2009 (30 years) (Leray et al., 2012). Transport simulations are performed by forward-tracking particles along the steady-state velocity field (advective transport only), mixing occurring by convergence of the flow lines within the sampling zones. Numerical methods were performed using the H2OLAB platform (Erhel et al., 2009) and are thoroughly described in Leray et al. (2012).

Table 2

Parameters of the model of Plœmeur used in this study with the associated references. H_{TOT} represents the mean thickness of the aquifer system composed of the micaschists and of the contact zone (see Fig. 3).

Parameters	Values	References
Potential recharge rate R (mm/year)	200	Carn (1990) and Touchard (1999)
Granites conductivity (m/s)	10^{-11}	
Mean thickness H_{TOT} (m)	280	Ruelleu et al. (2010)
Micaschists permeability K_{MS} (m/s)	5×10^{-6}	Leray et al. (2012)
Contact zone transmissivity T_{CZ} (m ² /s)	2.2×10^{-3}	Borgne et al. (2004, 2006)
North 20° fault transmissivity (m ² /s)	1.1×10^{-3}	Borgne et al. (2004, 2006)
Porosity ϕ (%)	2.7	Leray et al. (2012)

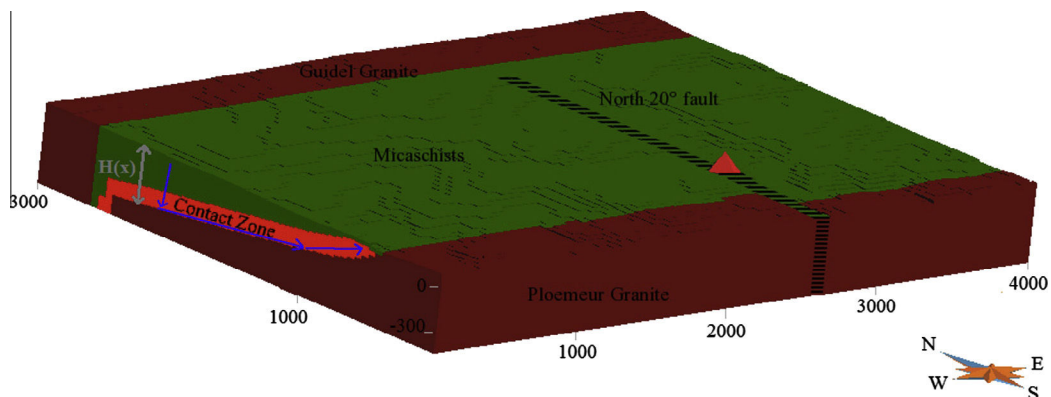


Fig. 3. Conceptual hydrogeological scheme of the Plœmeur aquifer with the different geological units. Granites in the North and in the South are shown in brown. The micaschists (green) overly the contact zone (red) and all units are crosscut by the N20 fault (block dashed line). The pumping site is identified by the red triangle. Blue arrows sketch the characteristic flow direction. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. In-silico reference results for the Plœmeur aquifer

3.2.1. Derivation reference TTDs per the in silico model

Following the methodology of Section 2.1, reference TTDs are obtained using the previously described hydrogeological model. Sampling zones have been designed in such a way as to stay close to field measurements conditions (Fig. 4). They are parallelepiped that cross the contact zone over all its thickness to sample the aquifer. 73 sampling zones of characteristic width of 250 m map the full extent of the aquifer contributing to the pumping zone. TTDs are built on all the flow lines crossing the sampling zones and are located at the center of the box. The issued TTDs fundamentally represent the residence time of the solutes flowing through the sampling zones around their center analogously with field sampling where abstracted water comes from a limited zone around the piezometer or well. Their size and number have been set in order to meet computational capacities with enough flow lines crossing the sampling zones and not too many sampling zones for fitting the seven LPMs.

TTDs display a wide variety of shapes (Fig. 5) closer to the exponential distribution at the well ($dW=0$) and more Inverse Gaussian like at intermediary distance ($dW=600$ m) or shifted exponential further away ($dW=1700$ m). Whatever the sampling zone, we have checked that TTDs converged to a steady shape with the number of particles used. In practice, at least 400 particles should intersect the sampling zone to reach convergence. This target is attained with an overall injection of 10^6 flow-weighted particles on the free surface. Most of the time, the number of particles crossing the sampling zones is well above the 400 particle threshold, and of the order of 10^4 – 10^5 .

3.2.2. Derivation of the apparent ages per the in silico model

Reference tracer concentrations are computed for CFC-11, ^{222}Rn and ^{85}Kr in all the sampling zones at year 2010. Maps of the different apparent ages are built by interpolating these 73 reference tracer concentration values (Fig. 6). Following the differences in the slopes of $\mathcal{C}_{\text{Tr}}$, we recover that $\hat{A}_{\text{Kr}} < \hat{A}_{\text{SF}_6} < \hat{A}_{\text{CFC}}$ as already indicated by (Waugh et al., 2003). For the ^{85}Kr however, we had to consider the slope of the input tracer concentration corrected from its radioactive decay: $\mathcal{C}_{\text{Tr}} e^{-\lambda}$. In this case, the slope of the corrected atmospheric tracer concentrations

$$\frac{d}{dt} \mathcal{C}_{\text{CFC}} < \frac{d}{dt} \mathcal{C}_{\text{SF}_6} < \frac{d}{dt} \mathcal{C}_{\text{Kr}} e^{-\lambda} \quad (9)$$

match the inverse of the order of the different ages.

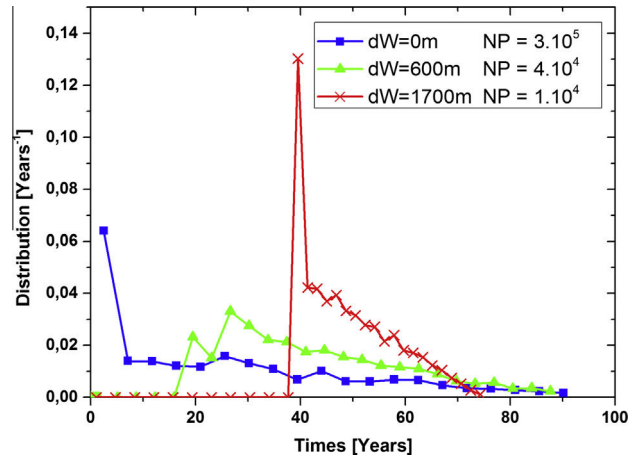


Fig. 5. Transit time distributions obtained with the in silico model of the Plœmeur site. dW is the distance between the sampling zone and the pumping well. NP is the number of particles intersecting the sampling zone used to build the transit times distributions.

3.2.3. Derivation of actual renewal times per the in silico model

Finally, maps of the different renewal times (so that 25%, 50% and 75% of the water is renewed) across the whole watershed are derived from the in silico modeling (Fig. 7). Q_1 , Q_2 and Q_3 all display the same overall South–North gradient of times corresponding to the deepening of the aquifer. Secondary tendencies come from the topography of the site. These are the ripples in Q_1 around 20 years where the relatively smaller renewal times around 20 years (cyan color) can be correlated with the topographic heights, which have also been shown to be correlated with higher gradients and faster circulations (Leray et al., 2012). It is also the systematic deviation towards the west of the smaller renewal times following the delineation of the watershed identified by the purple line on Fig. 4. The eastern limit of the watershed is well marked on Q_1 by the sharp east–west time gradient 500 m and 1000 m north of the well. It is also marked on Q_3 by the renewal time increase to over 60 years beyond the watershed limit.

4. Results

We present the results according to the number of atmospheric tracers used for specifying the TTD. As said in the methodological Section 2, our primary objective is to determine how prediction

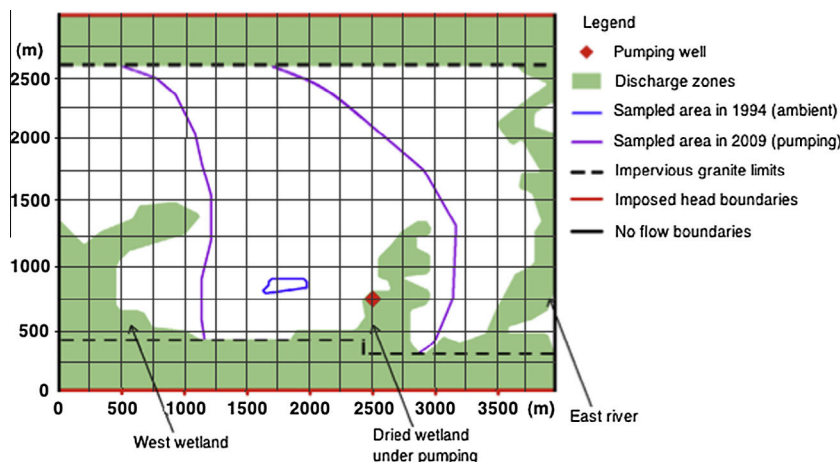


Fig. 4. Map of numeric sampling strategy used to get observables and TTDs values overall the aquifer. Boxes are 250×250 m. Their heights are determined to span the contact zone.

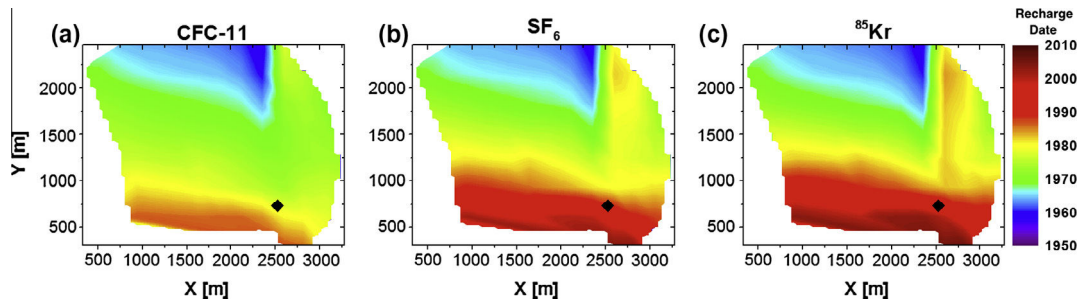


Fig. 6. Map of the “apparent” recharge dates obtained with the in silico model in the contact zone of the Plœmeur site. Contour of the map is determined by taking the supplying limit of the pumping well. From left to right: CFC-11, SF₆ and ⁸⁵Kr apparent ages. The pumping well is identified by the black square.

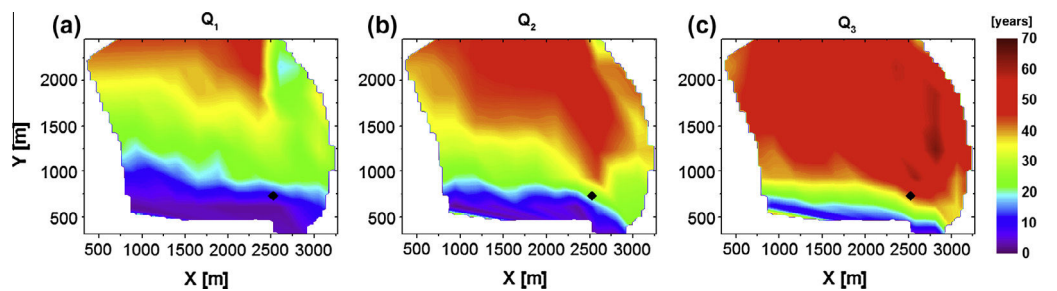


Fig. 7. Map of the different renewal times (from left to right, times at which 25%, 50% and 75% of the water is renewed) obtained with the in silico model. The pumping well is identified by the black square.

Table 3

Statistics on the residual ρ (Eq. 7) and on the predictive accuracy θ (Eq. 8) obtained with the calibrations carried on 73 sampling zones for the LPMs. N is the number of the parameters of the LPM considered, $P(\rho > 10\%)$ represents the percentage of sampling zones where ρ is superior to 10%.

N	LPM considered	Statistics on ρ (%)				Statistics on θ (years)			
		$\bar{\rho}$	$\sigma(\rho)$	$P(\rho > 10\%)$	$\max(\rho)$	$\bar{\theta}$	$\sigma(\theta)$	$\min(\theta)$	$\max(\theta)$
1	Dirac	0.0	0.0	0.0	0.0	8.9	4.9	0.6	21.5
	Exponential	99	198	45	1140	8.6	4.5	1.0	19.6
2	Inverse Gaussian	1.1	3.3	4.1	18	3.2	1.8	0.2	10.7
	Shifted Exponential	3.8	3.6	5.5	16	3.3	1.7	0.6	8.4
	Uniform	3.7	6.4	12	38	3.7	1.8	0.0	8.9
3	Shifted Inverse Gaussian	2.0	3.6	5.5	20	2.4	1.6	0.1	6.6
	Sum of Diracs	0.01	0.03	0.0	0.04	4.9	3.1	0.0	16.4

capacities taken as aquifer renewal times depend on the quantity of available information in the atmospheric tracer data. The analysis is performed independently on the 73 TTDs obtained in the contact zone of the Plœmeur aquifer described in Section 3 with the 7 LPMs models of Section 2.2. Depending on the LPM shape, on the number of parameters, we determine the goodness of fit ρ in percentage (Eq. 7) and the prediction accuracy θ in years (Eq. 8). We present systematically the mean and standard deviations of ρ and θ over the 73 sampling zones denoted as $\bar{\rho}$, $\bar{\theta}$, $\sigma(\rho)$, $\sigma(\theta)$, as well as the percentage of the zones for which the discrepancy of the observed versus modeled groundwater ages exceeds 10% ($P(\rho > 10\%)$) (Table 3).

4.1. 1-parameter LPMs calibrated on CFC-11

Statistics on ρ and θ are summarized in the upper part of Table 3. The residual for the Dirac distribution ρ is always equal to 0. This is expected because by centering the Dirac on the apparent age given by the CFC-11, the residual is equal to 0, i.e. the Dirac distribution perfectly fits the CFC-11 tracer observable. At the opposite, for the exponential distribution, the mean and standard deviation of the residual ($\bar{\rho}$ and $\sigma(\rho)$) are very high. They are above the 10% acceptable limit for 45% of the sampling zones. The spatial distribution of

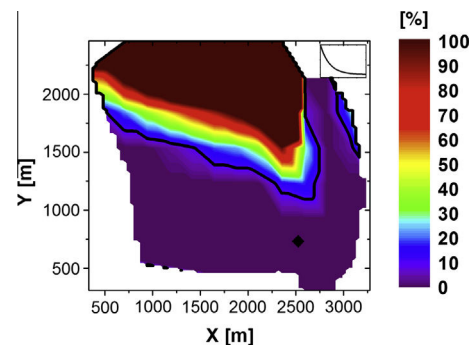


Fig. 8. Map of the residual ρ expressed in % obtained by fitting CFC-11 concentrations C_{CFC}^{ref} with concentrations obtained from an exponential TTD. The black line identifies the limit for which the residual ρ is equal to 10%. The Exponential model gives acceptable residual only on the lower southern part of the aquifer close to the pumping site identifiable by the black square.

ρ (Fig. 8) shows that ρ is high away from the discharge zone but always under 10% close to the convergence zone of the aquifer where a broad range of transit times are collected. The limits of the exponential distribution come from the large weight given to

the more recent atmospheric tracer concentrations, which represent the largest values (Fig. 1). Considering that the CFC-11 atmospheric concentration is essentially increasing over the last 75 years, the minimum concentration that can be obtained with any exponential model is the one obtained when the exponential model tends to a uniform distribution over the last 75 years. This minimum concentration is thus equal to the mean atmospheric concentration of CFC-11 over the same period corresponding to an age given by Eq. (2) of about 40 years. Away from the discharge zone, apparent ages in the watershed larger than 40 years cannot be fitted by the exponential distribution. The same type of inadequacy occurs for all other atmospheric tracers like ^{85}Kr or SF_6 .

Predictions of the renewal time of 25% of the groundwater to the sampling zones (Q_1) show that neither the exponential nor the Dirac distribution model (Fig. 9) can give everywhere accurate predictions of the reference renewal times displayed by Fig. 7a. For the Dirac distribution, the quartiles Q_1 , Q_2 and Q_3 are taken as the characteristic time of the Dirac distribution. The Dirac is predictive only very close to the diverging recharge areas while the exponential model is accurate only in the discharge converging areas. Conversely the Dirac LPM overestimates the renewal times while the exponential LPM underestimates them in most of the aquifer. None of the model can give even close predictions away from the pumping and recharge zones. Results for the Q_2 and Q_3 are very similar and are thus not displayed.

While highly attractive because characterized by only one parameter, the Dirac and exponential models are relevant only in very limited zones of the aquifer. For the Dirac distribution, these zones are very far away from the pumping zone. For the exponential model, the relevant zones are only those very close to the pumping well. In between these two cases, other LPMs should be applied with more than one parameter.

4.2. 2-parameter LPMs calibrated on CFC-11 and ^{85}Kr

Fitting the 2-parameter models to CFC-11 and ^{85}Kr concentrations gives both much better fits and predictions (middle part of

Table 3). For both models, the fit of the concentrations is excellent with only 3–4 zones out of the 73 sampling zones for which ρ is larger than 10%. It means that both models are good for fitting concentrations almost everywhere in the aquifer.

Statistics on the prediction accuracy θ gives surprisingly very similar results for the Inverse Gaussian, Shifted Exponential and Uniform models despite the broadly differing shapes of the distributions (Fig. 2). Average prediction accuracy $\bar{\theta}$ is of 3.5 years for groundwater ages of the order of decades (Table 3). Standard deviations of the accuracy $\sigma(\theta)$ are small and less than 2 years. Models do not perform well in only some restricted areas in the north of the aquifer far away from the pumping well where velocities are substantially smaller and travel times larger (Fig. 10). Outside of these areas, predictions are two to three times more accurate than for the 1-parameter Exponential and Dirac models and lead to only small errors in absolute values. A few years of differences can be deemed acceptable compared to the broad time ranges of the TTD, which can be evaluated at 37 years by the span of the uniform distribution $[t_0; t_1]$. So the accuracy in terms of predictions is of the order of a few years on some decades.

The agreement with the reference tracer concentrations measured by ρ displays relatively more differences between the Inverse Gaussian, Shifted Exponential and Uniform models. The inverse Gaussian gives on average much better agreements than the two other distributions. The uniform model leads to larger deviations than the 2 other models. 12% of the zones have more than 10% deviations to the reference concentrations ($P(\rho > 10\%)$ in Table 3). Maximum deviation is about 38%, more than twice larger than for the 2 other models. This is consistent with the characteristic shape of the TTDs that looks more inverse Gaussian than uniform, and in a less extent than the shifted exponential (Fig. 5). While the inverse Gaussian model is more representative of the TTD, it does not yield higher predictive capability, as if predictions depend more on some basic characteristics of the distribution like its two first moments than on its precise shape. It is confirmed by the spatial distribution of the 25% renewal times (Fig. 10). All three LPMs lead to very similar patterns.

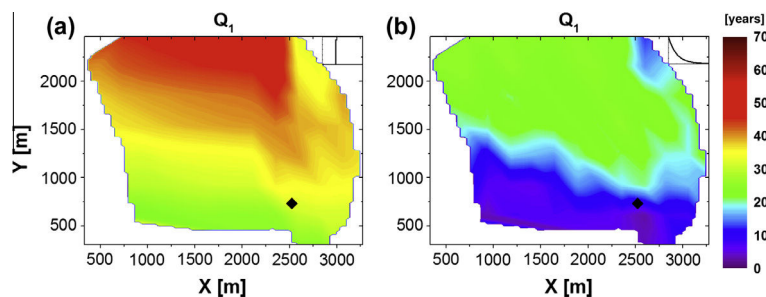


Fig. 9. Characteristic renewal time of 25% of the water to the sampling zone (Q_1) for the 1-parameter (a) Dirac LPM and (b) exponential LPM. The insert in the topright corner of the figure shows a sketch of the corresponding LPM.

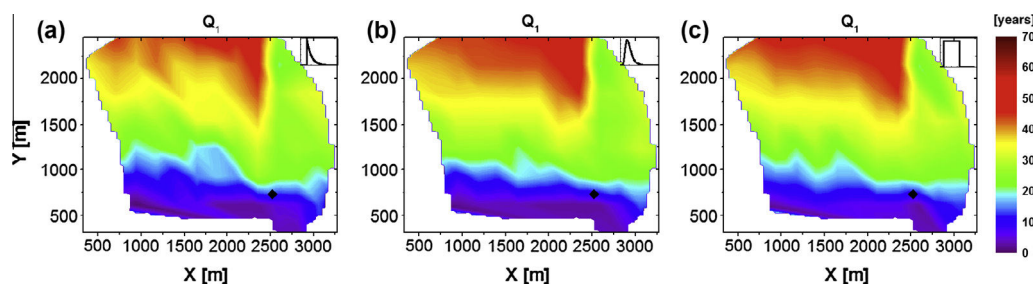


Fig. 10. Characteristic renewal time of 25% of the water to the sampling zone (Q_1) for the 2-parameter LPMs. From left to right, times derived by the shifted exponential model, by the inverse gaussian model and by the uniform model. The insert of each of the figure show on sketch of the LPM.

There are only somewhat steeper gradients for the exponential shape likely coming from the initial irregularity of its shape.

4.3. 3-parameter LPMs calibrated on CFC-11, ^{85}Kr and SF_6

The 3-parameter Shifted Inverse Gaussian leads to slightly less accurate calibration than the 2-parameter Inverse Gaussian (Table 3). It is relatively more difficult to find a 3-parameter distribution calibrated on the CFC-11, ^{85}Kr and SF_6 than a 2-parameter distribution calibrated on just the CFC-11 and ^{85}Kr . This confirms that there is an additional information contained in the SF_6 concentration compared to the sole CFC-11 and ^{85}Kr concentrations despite the apparent similarities of the SF_6 and ^{85}Kr atmospheric concentration chronicles. The additional information obtained using SF_6 improves the mean accuracy of the renewal time predictions $\bar{\theta}$ by only 0.8 years while keeping its standard deviation $\sigma(\theta)$ unchanged (Table 3). The gain in terms of predictions is marginal. It does not necessarily mean that the additional information is itself marginal, as the accuracy with the 2-parameter models is already very good and any improvement can only be marginal.

The other 3-parameter Dirac combination can closely fit the atmospheric tracer concentrations. The fitting criterion ρ around 0.01% is lower than the temporal resolution of the atmospheric tracer concentration and can thus be considered negligible. Predictions are however not as good as with the 2-parameter inverse Gaussian or 3-parameter shifted inverse Gaussian. Spatial renewal time predictions especially show irregular variations of the predictions likely related to the inability of the Dirac distributions to match the smoother variations of the TTD (Fig. 11). This shows that the Lumped Parameter Model should have a shape related to the real shape of the TTD. As shown with the comparison of the 2-parameter models, the LPM does not have to follow all the variations of the TTD. It should not be however completely off as shown here. The shape of the distribution taken as the prior in the Bayesian framework remains a key factor of the prediction accuracy and should be carefully chosen depending on the hypothesized flow pattern likely to happen.

5. Discussion

The previous results show that the quality of the calibration does not grant the accuracy of the predictions. The lowest ρ values are obtained for the Dirac distribution (residual always equal to 0) and for the sum of two Dirac distributions. However, they give the worst predictions of renewal times. It is not a matter of the number of parameters as the sum of two Dirac has three parameters. It is rather the lack of relevance of the Dirac distribution away from the recharge zones, where it is in fact expected to be relevant. In the discharge zone, it still perfectly fits the observed CFC-11 concentration but it is no longer relevant. More generally, the concentration residual ρ obtained with the seven candidate LPMs cannot

be linked to the accuracy of the predictions. While ρ is interesting because it is the sole quantitative criterion that can be obtained in the field, it is neither a necessary nor a sufficient condition for the accuracy of the predictions.

We use the quartiles of the renewal time distribution to assess the quality of the predictions rather than the full distribution. The quartiles correspond to the renewal time of 25%, 50% or 75% of the water within the sampling zones. This choice is motivated by the two following reasons. First, quartiles give numerical indicators of practical interest while comparing shapes of LPMs as in Eberts et al. (2012) is more qualitative and remote. Quartiles can be straightforwardly used to build statistics on prediction errors as in Table 3. Quantitative indicators could still be derived from the comparison of the LPMs and TTDs shapes like the Root Mean Square Error (RMSE). However they can be artificially large because of the irregularities of the TTDs (see Fig. 2) that cannot be accurately reproduced by any reduced model (Green et al., 2014). Besides, these irregularities are of little influence to integrated predictions like renewal times. The second motivation for using quartiles is indeed their integrative nature. Management decisions depend on global indicators like renewal times, flushing and dilution capacities rather than on detailed but approximate distribution shapes. Quartiles correspond to the time after which 25%, 50% or 75% of the water reaching a piezometer or well have been flushed. On top of the median (second quartile Q_2) Green et al., 2014, we also use the first and third quartiles to enhance sensitivity of the predictions to the variance and skewness of the TTDs.

It is not the concentration fit nor the number of parameters of the model but rather the likelihood of the distribution shape that conditions the accuracy of the predictions (Table 3) as also concluded by Green et al. (2014). Thus “likely” distributions imply considering analytic distributions with at least two parameters. Indeed, LPMs with only one parameter (Dirac, exponential) give accurate predictions only in very narrow sections of the aquifer. 2-parameter LPMs on the contrary give already very accurate predictions that cannot be made much better using an additional third parameter. The 2-parameter LPMs capture in various ways the mean and standard deviation of the distribution, predictions becoming almost insensitive to higher order moments. Because they are flexible and can evolve continuously from Dirac to broad distributions, the 2-parameter LPMs are appropriate almost everywhere in the aquifer as shown by the similarity of Figs. 7c and 12b. There are only some spurious variations of Q_3 that are corrected by the 3-parameter shifted inverse Gaussian model. In fact the residence time distributions display some initial shift outside of the pumping area linked to the transit time of the water through the micaschist aquitard zone to get to the aquifer sampling zones (Fig. 5). But even this striking distribution feature is not essential for establishing good predictions.

The distribution of Q_1 prediction errors represented on Fig. 13 for the tested distributions confirm these conclusions. 1-parameter

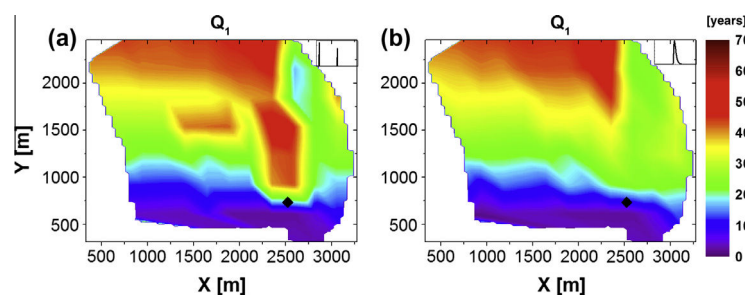


Fig. 11. Characteristic renewal time of 25% of the water to the sampling zone (Q_1) for the 3-parameter LPMs. From left to right, times derived by the sums of Dirac model and by the shifted inverse gaussian model. The insert of each of the figure show on sketch of the LPM.

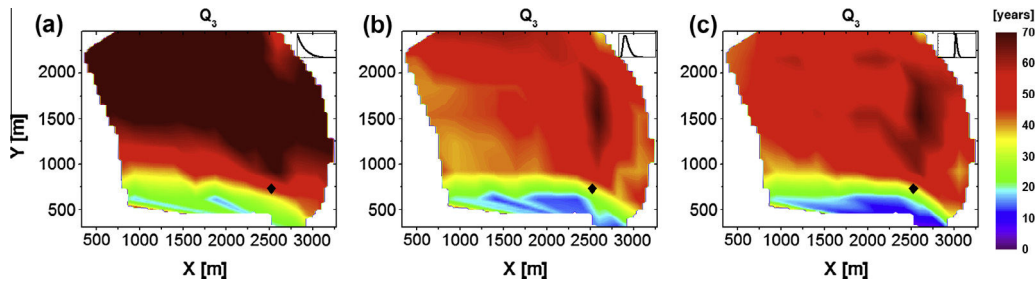


Fig. 12. Characteristic renewal time of 75% of the water to the sampling zone (Q_3). From left to right, times derived by a 1-parameter LPM (exponential model), by a 2-parameter LPM (inverse gaussian) and by a 3-parameter LPM (shifted inverse gaussian). The insert of each of the figure show on sketch of the LPM.

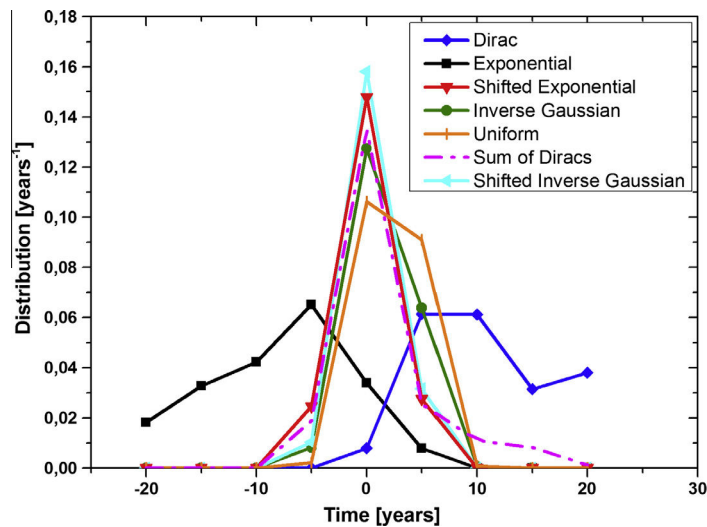


Fig. 13. Histogram of the differences in predictions between reference Q_1 (25% renewal time) and Q_1 predictions given by the LPMs.

LPM errors are much larger than those of the 2 and 3-parameter LPMs. Errors are considerably reduced from 1-parameter LPMs to 2-parameter LPMs. 3-parameter LPMs do not significantly improve the predictions. When the shape of the LPM deviates more from the reference TTD, errors become somewhat larger like for the Dirac composition and uniform distributions. The error distribution of Fig. 13 additionally reveals that 1-parameter LPMs prediction errors are not symmetric (centered on 0). The Dirac LPM tends to underestimate renewal times while the exponential LPM tends to overestimate them. This comes from the specific shape of these LPMs. The exponential distribution overestimates the large transfer times to fit the right mean. On the opposite, the Dirac distribution underestimates the variability, underestimates Q_1 predictions and overestimates Q_3 predictions. In comparison to that, prediction errors of 2-parameter LPMs and of the 3-parameter shifted inverse Gaussian appear to have error in predictions centered on 0, which means that in average, predictions are not biased by a tendency to over- or under-estimate renewal times.

Appropriate distributions should be continuous and relatively broad covering a wide range of transit times. Beyond these general characteristics, the details of the distributions have little importance. The Inverse Gaussian and the Shifted Exponential distributions give the same prediction quality. We can show that it is a general result. We consider an Inverse Gaussian distribution with parameters T and Pe respectively equal to 20 and 3/2. From Eq. 1 we compute the tracer concentrations and ages obtained with such a TTD and find $\hat{A}_{CFC}^{IG} = 1986$ and $\hat{A}_{Kr}^{IG} = 1997$. With the method developed in Section 2.2.2, we determine the parameters T and t_0 of the shifted exponential distribution that fits best these

concentrations (Eq. 5). The residual ρ is equal to 3%. The two distributions (Fig. 14) are very close and their cumulative density function lead to extremely close predictions. Similar conclusions have been drawn by [Vaugh et al. \(2003\)](#) with an inverse Gaussian and a combination of two inverse Gaussian distributions.

As the number of parameters has been taken equal to the number of available concentrations, the practical consequence of the previous results is to seek for two tracers in the same age range to reach satisfying predictions. Indeed, one tracer concentration is not enough to determine two parameters. Two tracer concentrations are necessary to give the complementary information needed to inform the mean and standard deviation of the TTD in this given age range, consistent with the theoretical result of [Massoudieh and Ginn \(2011\)](#). Redundant tracers remain of key interest for checking potential contamination, excess air and geogenic production, and for reducing the uncertainties inherently linked to measurement errors ([Green et al., 2014](#); [Massoudieh et al., 2012](#)). To ensure complementarity, the atmospheric tracer chronicles should cover comparable date range and be as different as possible as shown by the convolution product (see Eq. 1) of $C_T^n \exp^{-\lambda}$ by the TTD f . [Leray et al. \(2013\)](#) show that knowing apparent ages of two CFCs did not bring much to calibrate an hydrological model since their atmospheric chronicles were too similar. Tracer couples with more different atmospheric chronicles should be preferred. For recent waters ([0;60] years) preferential couples are: [CFC, ^{85}Kr], [CFC, SF_6], [CFC, $^3\text{H}/^3\text{He}$], [SF_6 , $^3\text{H}/^3\text{He}$] or [^{85}Kr , $^3\text{H}/^3\text{He}$].

For an aquifer with longer characteristic transit times, other couples of tracers should be considered despite the technological challenges. [^{39}Ar , ^{14}C] could be used in a range of time of

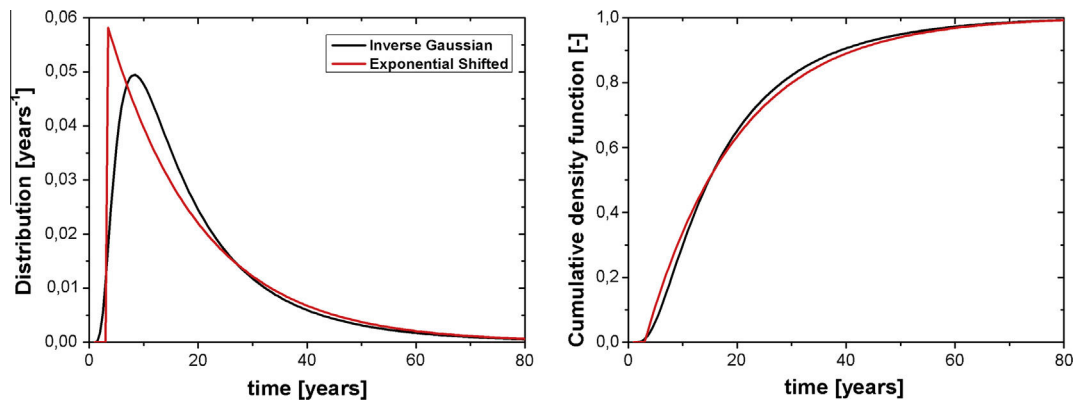


Fig. 14. Distribution and cumulative density function associated of an Inverse Gaussian distribution with $(T, Pe) = (20, 3/2)$ and of the Shifted Exponential distribution that fits the observables C_{CFC}^{IG} and C_{Kr}^{IG} obtained with the Inverse Gaussian distribution.

[500; 2000] years. In oceanography, Broecker and Peng (2000) first calibrated LPMs with both of these tracers. Waugh et al. (2003) studied the dependence of the $[\hat{A}_R, \hat{A}_C]$ to the mean and standard deviation of an Inverse Gaussian TTD. For much older water, $[^{81}\text{Kr}, ^{36}\text{Cl}]$ (for transit times bigger than 10,000 years) should be tested.

Illustrated here on the site of Plœmeur, the methodology developed in this article can be applied to a broad variety of aquifer models. We may expect different outcomes when mixing different characteristic transit times on a broader range (e.g. [0; 1000] years) either from different aquifers or from an aquitard and an aquifer. In such cases the combination of Dirac distributions might be more appropriate. Two tracers on different age ranges (for example CFC-11 and ^{39}Ar) might be tested to characterize different parts of the TTD. This is a valuable method to identify potential mixing of younger and older waters in the aquifer but cannot be applied directly to determine the shape of the TTD. Indeed, the younger tracer characterizes the local flow (with transit times under 100 years) whereas the older tracer characterizes more regional flow with longer transit times. Other multitracer approaches could also be tested by considering the ratio of the same date ranging tracer concentrations. Indeed, such ratios have the advantage to be independent of the mixing affecting the groundwater. With two ratios, in the same way as what have been done previously, one can characterize the piecewise TTD on the support of the date ranging of these tracers. Building two ratios however requires to provide at least three independent tracer concentrations and not two. Moreover, the choice of predictive indicators gains in importance as soon as the TTD gets broader (i.e. with an increasing coefficient of variation, ratio of standard deviation upon average). In this case, more precise metrics (deciles or even centiles) instead of quartiles might be considered to get indicators with useful predictive power.

6. Conclusion

We develop a methodology to assess Lumped Parameter Model prediction capacities in realistic 3D aquifer cases. Lumped Parameter Models (LPMs) are simple analytical distributions designed to approximate natural transit time distributions (TTDs). LPMs are appealing for establishing predictions directly from groundwater age data. Predictions are generally framed in some kind of aquifer renewal times and do not require involved hydrogeological models. Our methodology assesses the prediction capacities of LPMs on realistic 3D aquifer synthetic models. Aquifer modeling cannot be avoided as reference TTDs as well as reference

renewal time predictions cannot be directly measured on the field. Beyond LPMs assessment, we aim at finding the right balance between the information available in groundwater age data and the knowledge required to establish accurate predictions. We simply rate the amount of available information as the number of parameters that can be calibrated on a set of groundwater age data. When considering gas molecules like CFCs, SF_6 and ^{85}Kr with sufficiently different atmospheric concentration chronicles, the amount of available information is the number of parameter of the LPM chosen equal to the number of tracers.

We apply this methodology on the kilometric-scale crystalline aquifer of Plœmeur (France). The aquifer is located in a sloping contact zone between granites and micaschists overlain by a semi-pervious aquitard. Flow pattern is globally convergent to a well steadily produced for the nearby city. A previous model calibrated on head and age data shows that local topographical as well as geological features yield to complex 3D flow structures. It results in a variety of Transit Time Distributions ranging from Dirac-like close to recharge zones to exponential-like at the well. Outside of these zones, distributions cannot be evidently modeled as one of the classically used LPM like the composition of Diracs, the shifted exponential or the inverse Gaussian distributions. Extensive analysis on 73 sampling zones located everywhere in the aquifer however shows that LPMs can be highly effective for establishing accurate predictions. The 2-parameter inverse Gaussian or shifted exponential LPMs calibrated on CFC-11 and ^{85}Kr concentrations both yield almost everywhere accurate renewal times at less than 10% precision. By comparison, the 1-parameter exponential and Dirac LPMs calibrated on CFC-11 could not give any relevant predictions in most of the aquifer. The 3-parameter models calibrated with the additional knowledge of SF_6 do not lead to any better prediction.

For the type of studied crystalline aquifer system, we conclude that two tracers with sufficiently different atmospheric concentration chronicles give highly accurate renewal time predictions, provided that hydrogeologically relevant LPMs be used. Relevant LPM shapes are also necessary to yield to unbiased estimations. In this case, the relevant LPMs should be broad and relatively smooth like the shifted exponential or inverse Gaussian distributions. More details on the distribution provided by additional tracers are not necessary for the type of renewal time predictions targeted. On the contrary, distributions made up of some Dirac combinations do not give any close predictions despite good agreements with the reference tracer concentrations. More extensive analysis should be undertaken in a wider variety of realistic aquifer cases to assess the representativeness and relevance of these conclusions.

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1.3 Bilan

Cet article évalue donc l'apport des traceurs atmosphériques (CFCs et ^{85}Kr) pour caractériser la distribution des temps de résidence sur la période 0 – 70 ans. Nous avons montré que l'apport de deux traceurs atmosphériques avec des chroniques atmosphériques suffisamment distinctes peuvent conduire à faire des prédictions sur les temps de renouvellement avec une erreur acceptable (moins de 5 ans) si la distribution choisie initialement est à deux paramètres, permettant ainsi de renseigner moyenne et variance. En particulier, nous avons montré que le choix de la distribution importait peu pourvu qu'elle respecte des critères classiques de distributions typiques des milieux souterrains (présence d'un « *bulk* » et d'une queue de distribution, impliquant le choix d'une distribution avec asymétrie – « *skewness* » - positive). Cette bonne capacité de prédiction est dû au fait que la seule présence de CFCs dans les eaux de cet aquifère cristallin de Ploemeur nous renseigne déjà sur le fait que la majorité du support de cette distribution se situe sur l'échelle 0 – 70 ans. En effet, quelques pourcents d'eaux plus âgées dilueraient de manière très importante la concentration en CFCs et ne permettraient pas d'expliquer des concentrations si fortes. La présence vs l'absence de CFCs donne donc une information capitale sur la distribution des temps de résidence. Deuxièmement le type de prédiction qui intéresse les gestionnaires (savoir en combien de temps un certain pourcentage de l'aquifère sera renouvelé) est en fait une prédiction intrinsèquement robuste puisqu'elle s'intéresse à la cumulée de la distribution des temps de résidence. Faire des prédictions directement sur des caractéristiques de la distribution de temps de résidence et non sur sa cumulée (comme prédire le temps moyen de la distribution des temps de résidence ou ses autres moments), c'est s'exposer à de plus grands risques de fausses prédictions puisque les moments de la distribution sont plus sensibles à la forme de la distribution que sa cumulée.

Chapitre 2 Développer des traceurs géochimiques pour déterminer les temps de résidence en aquifère cristallin

2.1 Introduction

Dans la partie précédente, nous avons étudié l'apport des données en traceurs atmosphériques (CFCs) pour renseigner la distribution des temps de résidence en aquifère. Cependant, ces traceurs atmosphériques, très largement utilisés dans la communauté, ont deux points négatifs. Premièrement, la chronique atmosphérique qui conditionne leur utilisation a, depuis la fin des années 90, atteint un plateau du fait de leur interdiction depuis le protocole de Montréal (Figure 21). Les CFCs sont en effet responsables de la destruction de la couche d'ozone. Cette chronique atmosphérique n'augmente donc plus mais au contraire stagne et amorce maintenant une décroissance qui laisse présager qu'ils ne pourront plus être utilisés dans le futur (puisque la chronique atmosphérique n'offrira plus une fonction d'entrée univoque, capable de discriminer le temps de résidence en fonction de la concentration mesurée). Deuxièmement, leur utilisation nécessite une instrumentation de pointe puisque les concentrations sont extrêmement faibles (de l'ordre de la centaine de pptv). Ils ne sont donc pas accessibles pour tous techniquement et financièrement, et leur déploiement est difficile à envisager à large échelle. Ces deux limitations poussent la communauté scientifique à s'intéresser à des alternatives, plus pérennes et moins coûteuses, pour quantifier le temps de résidence dans les aquifères [Beyer *et al.*, 2016].

Utiliser la géochimie des eaux pour avoir une information sur son origine n'est pas nouveau [Appelo and Willemsen, 1987; Genereux *et al.*, 2009; Kenoyer and Bowser, 1992; Plummer *et al.*, 2001; Solomon *et al.*, 2010]. La géochimie a souvent été utilisée pour déterminer les origines de l'eau souterraine ainsi que leur mélange. Un outil de choix pour les géochimistes est l'utilisation de mélanges binaires voire ternaires pour qualifier les différentes origines des eaux souterraines, en fonction d'une structure d'écoulement représentative du mélange d'eaux de provenances différentes, inférée par l'expertise [Genereux *et al.*, 1993; Solomon *et al.*, 2010]. Cependant, la nécessité de quantifier précisément les temps de résidence des eaux dans les aquifères demande de développer des outils dédiés, où la distribution des temps de résidence est la fonction qui caractérise le mélange.

Dans ce contexte, nous évaluons le potentiel de données géochimiques des ions majeurs et mineurs pour quantifier les temps de résidence alors que la découverte de nouveaux traceurs d'âge de l'eau se fait rare et d'utilisation toujours plus complexe [Du *et al.*, 2003]. Cet article vise à déterminer et à quantifier si la silice dissoute (DSi) peut être un traceur des temps de résidence en aquifère et si ce proxy peut être utilisé localement, i.e. en nécessitant une calibration spécifique à chaque site, ou régionalement. Dans ce dernier cas, il convient de déterminer à quelle échelle ce traceur peut être utilisé.

Nous développons donc un cadre de modélisation semi-explicite reposant sur l'hypothèse que l'eau se concentre en silice dissoute au cours du temps de manière linéaire et que cette loi est particulière à chacun des sites considérés. Nous faisons l'hypothèse que la distribution des temps de résidence en chaque puits peut être modélisée par une loi inverse gaussienne caractéristique du transport advectif dispersif en milieu souterrain. Le choix de la distribution est ici motivé par des critères physiques mais comme l'a montré le chapitre 1, ce choix de distribution n'est pas critique tant qu'il est composé d'une distribution à deux paramètres avec une asymétrie positive (queue de distribution sur les temps longs). Nous testons cette approche sur 4 sites agricoles bretons dont l'un d'eux est pompé par la ville de Lorient Agglomération pour l'approvisionnement en eau potable (Plœmeur). Nous testons aussi cette approche

sur un site situé dans les montagnes des Vosges (Strengbach). Nous comparons ensuite nos résultats à des mesures trouvées dans la littérature et évaluons le potentiel de ce proxy pour la datation.

2.2 Article: Dating groundwater with dissolved silica and CFC concentrations in crystalline aquifers



Dating groundwater with dissolved silica and CFC concentrations in crystalline aquifers

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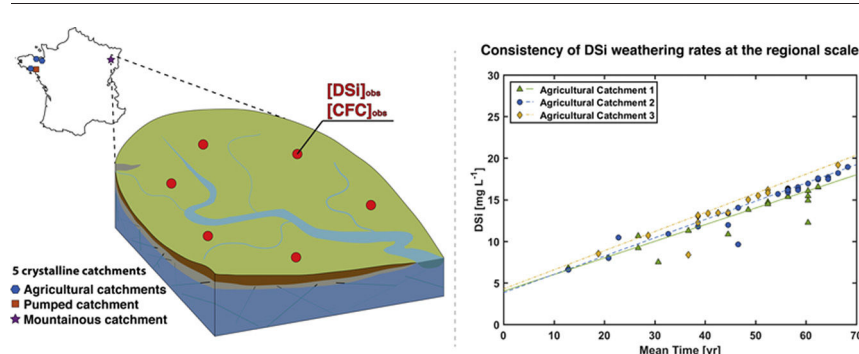
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HIGHLIGHTS

- Silicate concentration is a robust proxy of residence time in crystalline aquifer
- Extensive groundwater dating revealed near constant silica weathering rates.
- Silicate weathering rates are sensitive to climate and anthropogenic activities.

GRAPHICAL ABSTRACT



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ABSTRACT

Estimating intermediate water residence times (a few years to a century) in shallow aquifers is critical to quantifying groundwater vulnerability to nutrient loading and estimating realistic recovery timelines. While intermediate groundwater residence times are currently determined with atmospheric tracers such as chlorofluorocarbons (CFCs), these analyses are costly and would benefit from other tracer approaches to compensate for the decreasing resolution of CFC methods in the 5–20 years range. In this context, we developed a framework to assess the capacity of dissolved silica (DSi) to inform residence times in shallow aquifers. We calibrated silicate weathering rates with CFCs from multiple wells in five crystalline aquifers in Brittany and in the Vosges Mountains (France). DSi and CFCs were complementary in determining apparent weathering reactions and residence time distributions (RTDs) in shallow aquifers. Silicate weathering rates were surprisingly similar among Brittany aquifers, varying from 0.20 to 0.23 mg L⁻¹ yr⁻¹ with a coefficient of variation of 7%, except for the aquifer where significant groundwater abstraction occurred, where we observed a weathering rate of 0.31 mg L⁻¹ yr⁻¹. The silicate weathering rate was lower for the aquifer in the Vosges Mountains (0.12 mg L⁻¹ yr⁻¹), potentially due to differences in climate and anthropogenic solute loading. Overall, these optimized silicate weathering rates are consistent with previously published studies with similar apparent ages range. The consistency in silicate weathering rates suggests that DSi could be a robust and cheap proxy of mean residence times for recent groundwater (5–100 years) at the regional scale. This methodology could allow quantification of seasonal groundwater contributions to streams, estimation of residence times in the unsaturated zone and improve assessment of aquifer vulnerability to anthropogenic pollution.

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1. Introduction

Human activity has fundamentally altered global nutrient cycles (Galloway et al., 2008), polluting aquatic ecosystems and threatening human health and water security (Spalding and Exner, 1993). It is widely held that anthropogenic loading of nitrogen has exceeded planetary capacities, representing one of the most pressing environmental issues (Rockstrom et al., 2009; Steffen et al., 2015). International, national, and regional initiatives have been undertaken in the past several decades to reduce nitrogen loading, though assessment of efficacy is difficult in complex natural systems with unknown and overlapping memory effects (Jarvie et al., 2013; Jenny et al., 2016; Meter and Basu, 2017; Wilcock et al., 2013). Estimating the recovery time of surface and groundwater ecosystems following nitrogen pollution is key to quantifying effectiveness of changes in agricultural practices, mitigation methods, and developing realistic timelines for meeting regulatory goals (Abbott et al., 2018; Bouraoui and Grizzetti, 2011; Jasechko et al., 2017). Recovery time depends largely on water and solute residence time in the surface and subsurface components of the catchment. The majority of catchment transit time occurs in the subsurface, where water can spend months to years in the soil or unsaturated zone (Meter et al., 2016; Sebilo et al., 2013), and decades to centuries in near-surface aquifers (Böhlke and Denver, 1995; Kolbe et al., 2016; Singleton et al., 2007; Visser et al., 2013). Because no single tracer can determine the distribution of groundwater ages across these timescales, multi tracer approaches are necessary for reliable groundwater dating (Abbott et al., 2016).

Several tracers are well suited to determine residence times for timescales relevant to nutrient pollution, including $^3\text{H}/^3\text{He}$ and chlorofluorocarbons (CFCs), because the atmospheric concentration of these gases were altered by human activity coincident with the great acceleration of nutrient loading in the mid-1900s (Aquilina et al., 2012b; Cook and Herczeg, 2000; Labasque et al., 2014; Steffen et al., 2015; Visser et al., 2014). However, CFC methods now lack resolution in the 5–20 years range because their atmospheric concentrations peaked around 1998 following their prohibition by the Kyoto Protocol (Fig. 1). This reversal of atmospheric trends means any measured concentration between 1995 and 2018 corresponds to two dates. Additionally, $^3\text{H}/^3\text{He}$ and CFC samples are relatively difficult to collect and costly to analyze, limiting their use to infer residence times of groundwater in remote environments and much of the developing world. Therefore, there is great interest in developing new tracers for inferring mean residence time of young groundwater (Morgenstern et al., 2010; Peters et al., 2014; Tesoriero et al., 2005).

One promising family of potential groundwater tracers is natural weathering products such as Ca^{2+} , Na^+ , and dissolved silica (DSi) (Abbott et al., 2016). DSi has been found to be correlated with apparent

age in several site-specific studies (Böhlke and Denver, 1995; Burns et al., 2003; Clune and Denver, 2012; Denver et al., 2010; Edmunds and Smedley, 2000; Kenoyer and Bowser, 1992; Kim, 2002; Lindsey et al., 2003; Morgenstern et al., 2015; Morgenstern et al., 2010; Peters et al., 2014; Rademacher et al., 2001; Stewart et al., 2007; Tesoriero et al., 2005). However, variability of weathering rates has not been precisely investigated and DSi has rarely been considered a robust tracer of groundwater age, though it has been used as a relative indicator of residence time (Beyer et al., 2016; Edmunds and Smedley, 2000). Two specific challenges to using DSi as a widespread proxy of mean residence times are: 1. DSi lacks a time-based modeling framework and 2. it is unknown if silicate weathering rates are stable enough at geologic formation to regional scales to practically exploit DSi concentration.

In this context, we developed a new approach using groundwater DSi to determine residence time distributions (RTDs) by calibrating apparent silicate weathering rates with atmospheric groundwater age tracers (CFCs). We were motivated by the following questions: 1. Over what timescales can DSi be used as a tracer of groundwater age? 2. How variable is the rate of silicate weathering among shallow aquifers, i.e. a few tens of meters deep, with different lithology? We hypothesized that a simple zero-order kinetic reaction could simulate weathering rate in shallow aquifers, because hydrolysis would remain transport-limited to thermodynamically-limited on decadal timescales (detailed in Section 2.1). Conversely, a time-variant weathering rate (i.e. a first order kinetic reaction) would be necessary to account for mineral equilibrium limitation in aquifers with longer residence times and a broader range of residence times (Appelo and Postma, 1994; Maher, 2010). We tested these hypotheses by modeling residence time distributions (RTDs) and weathering dynamics in 5 shallow crystalline aquifers with contrasting lithology in Brittany and the Vosges Mountains, France. We used conventional groundwater chemistry and dissolved CFCs from agricultural and domestic wells to calibrate chemodynamic models for each catchment, using an inverse Gaussian lumped parameter model to simulate RTDs. We compared our approach with previous methods and explored potential applications for regional issues of groundwater quality.

2. Approach, catchment description, and geochemical data

2.1. Silicate weathering and DSi concentration

Natural weathering products like DSi are cheap to measure and potentially contain additional information on residence time distribution compared to atmospheric tracers. Indeed they are sensitive to the overall residence time in both the unsaturated and saturated zones (Fig. 2), whereas atmospheric tracers are only sensitive to the residence time in the saturated zone (Cook and Herczeg, 2000).

Weathering is a rate-limited, non-equilibrium reaction consisting of physical, chemical, and biological processes that occur when mineral surfaces (e.g. bedrock) are exposed to water flow (Anderson et al., 2002). Weathering occurs in virtually all terrestrial environments including soils, sediments, and subsurface aquifers, and depends partly on the time that groundwater has spent in contact with the rock (Maher, 2011). Silicate weathering is the predominant weathering process because silicate minerals constitute >90% of the Earth's crust (White, 2008).

As water moves through porous or fractured silicate substrate, it dissolves some silica by hydrolysis (Maher, 2010). When surface water enters the subsurface, the initial rate of silica hydrolysis is determined solely by the contact area between water and rock (*surface-limited weathering*). As water percolates deeper, DSi concentration increases at the rock-water interface, slowing hydrolysis unless diffusive and advective mixing remove weathering products from the interface (*transport-limited weathering*). Finally, as DSi concentration in the whole water mass approaches saturation, second-order equilibrium

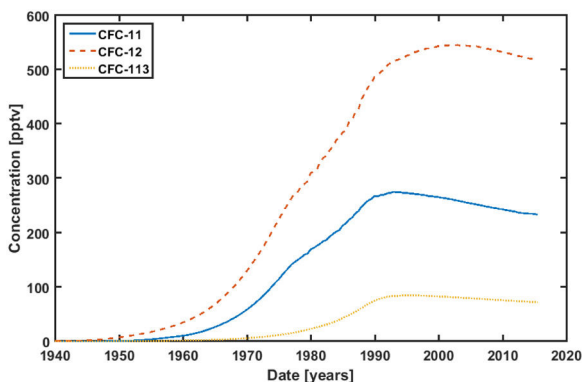


Fig. 1. Atmospheric time series of CFC concentrations [pptv] since 1940. The lack of variations since the 2000s limits their resolution in the last 20 years. Adapted from (Cook and Herczeg, 2000).

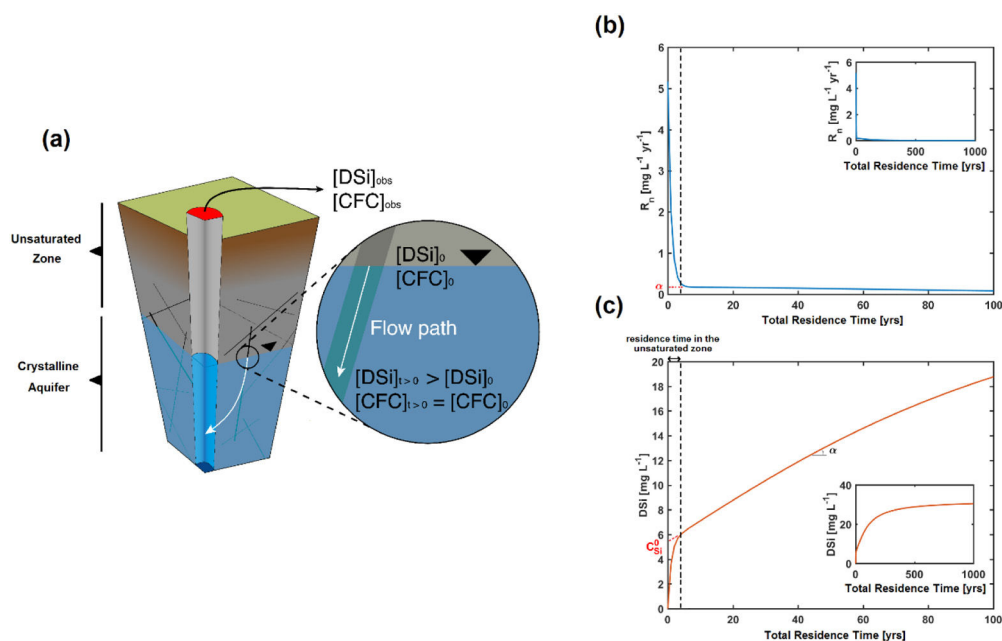


Fig. 2. Weathering dynamics justifying our hypothesis of a zero-order kinetic reaction for the weathering of silicate minerals in shallow crystalline aquifers. On the time scales considered (5–50 years), the weathering rate α can be considered constant due to transport-limited and thermodynamically-limited conditions (Maher, 2010). (a) Conceptual scheme illustrating the evolution of a groundwater flow path from the unsaturated zone into the shallow aquifer. (b) Corresponding weathering rate evolution on two different timescales. (c) Resulting DSi groundwater concentration evolution along a groundwater flow path.

reactions control hydrolysis through precipitation of secondary phases (*thermodynamically-limited weathering*) (Ackerer et al., 2018; Lucas et al., 2017; Maher, 2010). Consequently, hydrologic processes directly mediate weathering rate, because the speed and routing of water flow control the transport of solute and the cumulative mineral surface encountered by a volume of water.

Differences in weathering rates along and among flow lines can create spatial variations in DSi concentrations, depending on multiscale dispersive and mixing transport processes (Gelhar and Axness, 1983). While the signature of detailed water-rock interactions is progressively erased by mixing processes, the homogenized concentration is more representative of mean weathering rate. Bulk transport models, including lumped parameter models, have been developed to analyze the distribution of residence times making up a mean value on the basis of realistic transport conditions (Green et al., 2014; Haggerty and Gorelick, 1995; Maloszewski and Zuber, 1996). Because these models simulate recharge conditions and transfer processes through time, they can integrate both atmospheric and lithologic tracers, providing a flexible framework for inferring transport and weathering information from multiple proxies of fundamental physical and chemical processes (Abbott et al., 2016; Marçais et al., 2015). Specifically, lumped parameter models overcome practical limitations in inferring weathering rates and determining residence times (e.g. determining the mixing that led to observed CFC concentrations), by explicitly accounting for vertical sample integration in wells and the diversity of flow paths contributing to that point (Maher and Druhan, 2014; Marçais et al., 2015).

2.2. Catchment description

We assessed the suitability of DSi as a groundwater age tracer with data from five catchments. Four of the five study catchments (Fig. 3) are located in Brittany, France, where the climate is oceanic and average precipitation ranges from 900 mm yr⁻¹ in Plœmeur and Guidel catchments to 960 mm yr⁻¹ in Pleine Fougères and Saint Brice catchments (Jiménez-Martínez et al., 2013; Thomas et al., 2016; Touchard, 1999). Land use in all these catchments is dominated by agriculture (i.e.

70–90% of arable land used for row crops) and in one of them, the aquifer is intensively pumped for municipal water supply (Plœmeur, hereafter the *pumped catchment*; pumping rate = 110 m³ hr⁻¹). The Pleine Fougères, Saint Brice and Guidel catchments are designated hereafter as *agricultural catchments* 1, 2, and 3, respectively. The fifth catchment is located in the Vosges Mountain (Strengbach, hereafter the *mountainous catchment*), in a forested region with elevation ranging from 880 to 1150 m, an oceanic mountainous climate, and average annual precipitation of 1400 mm yr⁻¹ (Pierret et al., 2014; Viville et al., 2012). Though all 5 catchments are underlain by crystalline bedrock (Fig. 3), they differ in underlying lithology (granite or schist) and catchment size (from 0.8 to 35 km²; Table 1). They all have slightly acidic groundwater with pH between 5 and 7 (Table 1). Groundwater temperature is more variable among the catchments, ranging from 8 °C in the high-elevation mountainous catchment to ~13 °C in the lowland Brittany catchments. The pumped catchment displays the strongest spatial variability of groundwater temperature, varying between 12 and 17 °C due to the pumping activity (Table 1). References detailing the different characteristics of the sites are listed in Table 1.

2.3. Geochemical data

For each catchment, we analyzed CFC-12, CFC-11, CFC-113, and DSi concentrations determined during field campaigns between 2001 and 2015. We only used sampling dates where DSi and at least one CFC were simultaneously measured. Because the sampling of DSi and CFCs is relatively straightforward (a filtered and acidified water sample for DSi and water collected in a stainless-steel vial for CFCs), there were multiple, spatially-distributed replicates for each catchment corresponding to different sampling wells or sampling campaigns (i.e. 32 replicates on average for each catchment, see Table 1). DSi was quantified as H₄SiO₄ (mg L⁻¹), from 0.2 µm filtered and acidified samples by inductively coupled plasma mass spectrometry (ICP-MS) at the Geosciences Rennes laboratory, with an uncertainty of ±2% (Bouhnik-Le Coz et al., 2001; Roques et al., 2014b). CFC concentrations were measured by purge and trap gas chromatography at the CONDITE EAU laboratory, at the OSUR in the University of Rennes 1 (France), with a precision

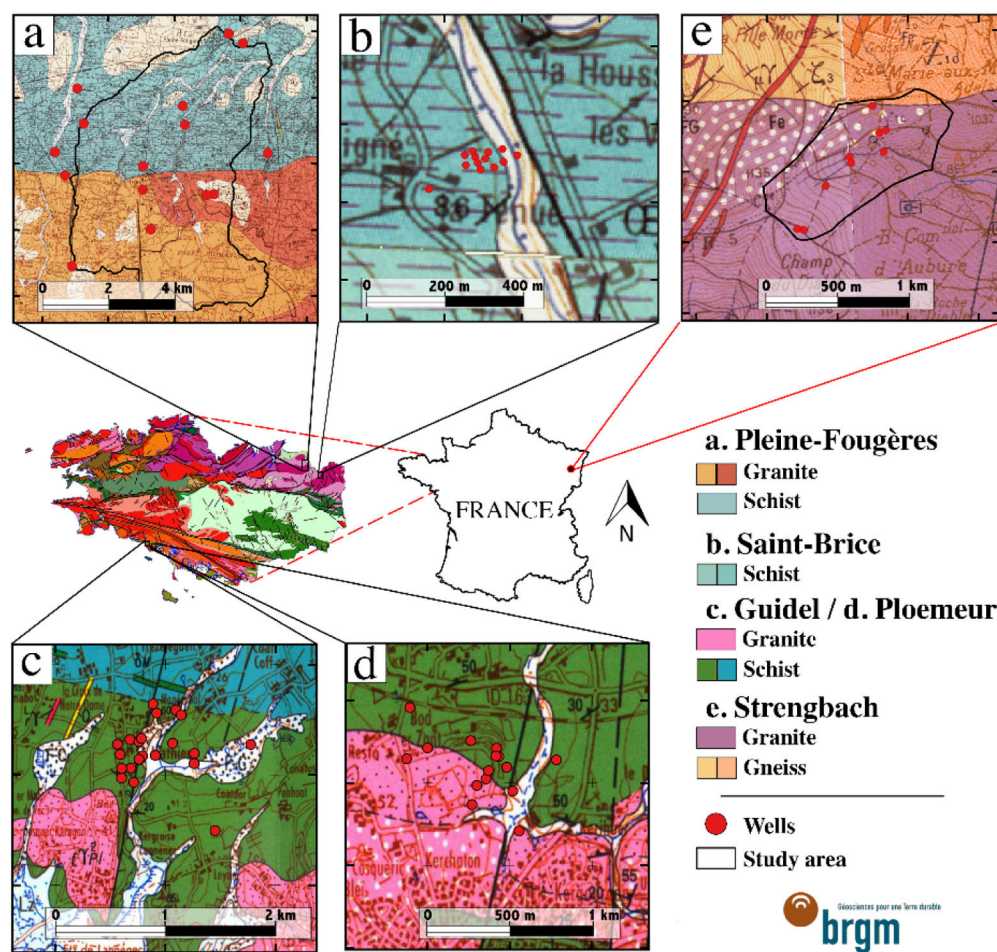


Fig. 3. Site locations on the geological map of Brittany (center-left) with detailed site maps of lithology and well location for (a) Pleine Fougères, (b) Saint Brice (c) Guidel, and (e) Plœmeur, which is a pumping site for drinking water supply. (d) Strengbach is a headwater located in the Vosges Mountains (east part of France). Adapted from the Bureau de Recherches Géologiques et Minières (BRGM) data.

of $\pm 4\%$ for high concentrations and $\pm 20\%$ for samples near the quantification limit (0.1 pmol L^{-1} ; Labasque et al. (2014); Labasque et al. (2006)). Dissolved concentrations were converted to atmospheric partial pressures (pptv) with Henry's law, considering gas solubility and excess air effects (Busenberg and Plummer, 1992). Samples showing obvious

contamination with CFCs were excluded from the analysis (7% of samples were above the maximum atmospheric concentration of CFC). Contamination, which occurred primarily at the pumped catchment, was likely due to manufacturing or maintenance activities in the nearby military airport.

Table 1

Characteristics of the study sites. The sites display contrast in size, lithology, and geochemical conditions especially regarding water temperature. For the unsaturated zone thickness, the minimum, average and maximum thickness of the unsaturated zone (m) are reported.

Catchment ID	Catchment Name	Area (km ²)	Lithology	Number of Wells	Number of data (number of data used)	Percentage of polluted data	pH	Water temperature (°C)	Unsaturated zone thickness (m)	Supplementary information	References
Agricultural catchment 1	Pleine Fougères	35	Granite (50%) and Schist (50%)	18	21(20)	0%	5.2–7.2	11–14	–	Moderate agricultural inputs	(Kolbe et al., 2016)
Agricultural catchment 2	Saint Brice	1	Mainly Schist	11	48(45)	6%	5.3–7.1	12–14.6	2.2–5.1–9.4	Moderate agricultural inputs	(Roques et al., 2014b)
Agricultural catchment 3	Guidel	2.9	Schist	10	18(18)	0%	–	14–14.7	0.5–5.3–18	1 km from the sea - Moderate agricultural inputs	(Bochet, 2017; Bochet et al., under revision)
Pumped catchment	Plœmeur	2.5	Granite and Schist	16	65(58)	11%	5.4–6.5	12–17.3	7–12–30	Pumping site	(Le Borgne et al., 2006; Leray et al., 2012)
Mountainous catchment	Strengbach	0.8	Granite	11	17(17)	0%	5.6–7	7.6–9.3	0–2.5–6	Mountainous headwater (Vosges)	(Chabaux et al., 2017; Viville et al., 2012)

3. Modeling residence times and silicate weathering rates

To test our regional uniformity hypothesis, we simultaneously inferred residence times and silicate weathering rates for all five catchments, using data from the spatially distributed replicates within each catchment to derive representative weathering rates. We developed a standardized methodology requiring minimal a priori information to calibrate the lumped parameter models for the determination of RTDs. CFCs and DSI concentrations were jointly used to calibrate the lumped parameter models for each replicate (i.e. well), while weathering rates were optimized for each catchment to minimize the overall mismatch between modeled and measured concentrations. Following this procedure, silicate weathering rates were derived from DSI concentrations calibrated with CFC concentrations, which showed broad variability in mean residence time among sites.

Because CFC concentrations depend primarily on the date of groundwater recharge, while DSI concentration depends on water-rock interactions, these two tracers potentially contain complementary information about RTDs. In the following sections, we present the assumptions about weathering and types of RTDs, and then detail the calibration strategy aiming at determining weathering at the scale of the catchment and RTD properties for each well.

3.1. Weathering assumptions

Chemical weathering of silicate minerals is the net result of the dissolution of primary silicate minerals minus the precipitation of secondary mineral formation (Anderson and Anderson, 2010). To model the effect of residence times on overall observed DSI concentrations, we considered that precipitation and dissolution rate constants lead to a net weathering rate α [$\text{mg L}^{-1} \text{yr}^{-1}$], which corresponds to the enrichment rate of groundwater in DSI.

At the intermediate scale (10s to 100s of meters), this net weathering rate encounters a rapid transition from surface-limited to transport-limited weathering. During this transition, weathering rates may differ in the unsaturated zone as minerals differ from the deeper unaltered zone and water contains lower DSI concentrations, which together favor surface reaction-limited processes. While we did not estimate unsaturated zones weathering rates, we did account for differences in DSI concentration at the water table (see next paragraph). Time-based observations in crystalline formations show that weathering rates do not depend on residence times for groundwater older than few months to decades, due to transport and thermodynamic controls, which sustain the weathering (Ackerer et al., 2018; Maher, 2010; White and Brantley, 2003). Given that the shallow crystalline aquifers investigated in this study have CFC apparent ages >25 years (Ayraud, 2005; Ayraud et al., 2008; Kolbe et al., 2016; Leray et al., 2012; Roques et al., 2014a), we assumed that α stays constant i.e. that the net weathering follows a zero-order kinetic reaction.

The DSI concentration from the dissolution of silicates in the unsaturated zone is assumed to lead to an initial DSI concentration C_{Si}^0 , which does not depend on the groundwater residence time t (i.e. the amount of time water spends in the unsaturated zone may be unrelated to the subsequent residence time in the aquifer). t only represents the residence time in the aquifer because it is inferred from CFC concentrations, which equilibrate at the water table (Fig. 2a). Therefore, assuming a constant weathering rate α and an initial DSI concentration C_{Si}^0 reached at the water table results in a linear expression of the DSI concentration as a function of the residence time t [yr]:

$$C_{Si}^{prod}(t) = \begin{cases} \alpha t + C_{Si}^0 & \text{if } t < t_{\max} \\ C_{Si}^{\max} = \alpha t_{\max} + C_{Si}^0 & \text{if } t \geq t_{\max} \end{cases}, \quad (1)$$

where $t_{\max}$ is the time at which groundwater becomes saturated in DSI (i.e. precipitation or removal equals dissolution). Indeed, at larger scale, mineral equilibrium can be reached. However, recent hydrogeochemical modeling of weathering in the mountainous catchment showed that silica equilibrium is not reached until kilometers of transport, much farther than typical flow distance between recharge areas and sampling wells or surface water features (Ackerer et al., 2018; Kolbe et al., 2016; Lucas et al., 2017). Additionally, for many catchments there is a negligible contribution of groundwater with residence times longer than 100 years (age at which the groundwater is likely to encounter DSI saturation) as shown by the presence of CFCs in the groundwater of these catchments. Therefore, C_{Si}^{prod} only depends on residence time t , weathering rate α and initial DSI concentration C_{Si}^0 at the water table.

3.2. Modeling groundwater mixing

Multiple geological, topographical, and hydraulic factors influence RTDs. Distributed groundwater flow and transport models were previously developed for the agricultural catchment 1 and the pumped catchment, showing that the general shape of the RTDs can be well approximated by an inverse Gaussian function in most cases (Kolbe et al., 2016; Marçais et al., 2015). Inverse Gaussian distributions have proved especially efficient for providing accurate predictions of distribution quantiles and integrated renewal times within the time range where information can theoretically be extracted from CFC tracers (i.e. 0–70 years, Fig. 1). Previous studied sites have also shown that the choice of the lumped parameter model is not critical as long as it has two parameters and is unimodal (Eberts et al., 2012; Kolbe et al., 2016; Marçais et al., 2015). Inverse Gaussian distributions have the additional advantage of being physically grounded as they are the solution of the 1D advection dispersion equation:

$$f_{\mu,\sigma}(t) = \frac{1}{\sigma} \sqrt{\frac{\mu^3}{2\pi t^3}} \exp\left(-\frac{\mu(t-\mu)^2}{2\sigma^2 t}\right), \quad (2)$$

where t is the residence time, μ is mean time and σ is the standard deviation. The two degrees of freedom of an inverse Gaussian distribution are sufficient to adapt to most observed hydraulic conditions found in upland sites, which show narrow distributions similar to Dirac distributions, and in lowland sites near the surface flow outlet, which express more exponential shapes (Haitjema, 1995). We therefore used inverse Gaussian distributions for all catchments, though a different lumped parameter model's choice could be easily implemented if hydraulic conditions required it (Leray et al., 2016).

Inferring RTDs with an inverse Gaussian LPM requires determining two parameters: the mean residence time μ and the standard deviation σ of the distribution. For a given Inverse Gaussian RTD $f_{(\mu,\sigma)}$, the concentrations in CFCs can be modeled as:

$$\begin{aligned} C_{CFC-12}^{mod}(t_s, \mu, \sigma) &= \int_0^{+\infty} C_{CFC-12}(t_s - u) \cdot f_{(\mu,\sigma)}(u) du \\ C_{CFC-11}^{mod}(t_s, \mu, \sigma) &= \int_0^{+\infty} C_{CFC-11}(t_s - u) \cdot f_{(\mu,\sigma)}(u) du, \\ C_{CFC-113}^{mod}(t_s, \mu, \sigma) &= \int_0^{+\infty} C_{CFC-113}(t_s - u) \cdot f_{(\mu,\sigma)}(u) du \end{aligned} \quad (3)$$

where u is the residence time, t_s is the sampling date, $t_s - u$ is the recharge date (when the water reaches the water table) and C_{CFC} is the corresponding CFC atmospheric time series (Fig. 1). Integrating over all the potential residence times, the product of the RTD $f_{(\mu,\sigma)}$ with the CFC concentration present at the water table at $t_s - u$ gives the modeled

CFC concentration. Similarly, the modeled concentration in DSi can be expressed as:

$$C_{Si}^{mod}(\alpha, C_{Si}^0, \mu, \sigma) = \int_0^{+\infty} C_{Si}^{prod}(\alpha, C_{Si}^0, u) \cdot f_{(\mu, \sigma)}(u) du, \quad (4)$$

where C_{Si}^{prod} is the DSi concentration produced during the residence time u via weathering (Eq. (1)). Eqs. (3) and (4) give the modeled concentrations of CFCs and DSi, which depend on the LPM parameters (μ, σ), and on the catchment-based weathering parameters (α, C_{Si}^0), related to site characteristics.

3.3. Calibration strategy: inferring conjointly RTDs and silicate weathering rates

With N wells on a given catchment and N concentrations of CFCs and DSi ($C_{CFC-12k}^{mes}, C_{CFC-11k}^{mes}, C_{CFC-113k}^{mes}, C_{Si}^{mes}$) $_{1 \leq k \leq N}$, the calibration strategy consisted in optimizing together (i.e. for the N datasets) the weathering rate α , the initial concentration of DSi C_{Si}^0 , and the best inverse Gaussian LPMs (μ_k, σ_k) $_{1 \leq k \leq N}$ for each of the N wells. We defined the following objective function to optimize the calibration:

$$\Phi(\alpha, C_{Si}^0, \mu_1, \sigma_1, \dots, \mu_N, \sigma_N) = \frac{1}{3N} \sum_{k=1}^N \left[\left| \tilde{C}_{Si}^{mes} - \tilde{C}_{Si}^{mod}(\alpha, C_{Si}^0, \mu_k, \sigma_k) \right| + \min \left(\left| \tilde{C}_{CFC-12k}^{mes} - \tilde{C}_{CFC-12k}^{mod}(t_{s_k}, \mu_k, \sigma_k) \right|, \left| \tilde{C}_{CFC-11k}^{mes} - \tilde{C}_{CFC-11k}^{mod}(t_{s_k}, \mu_k, \sigma_k) \right|, \left| \tilde{C}_{CFC-113k}^{mes} - \tilde{C}_{CFC-113k}^{mod}(t_{s_k}, \mu_k, \sigma_k) \right| \right) \right] \quad (5)$$

where $\tilde{C}$ are the standardized and centered values of C . In Eq. (5), the minimum conveys that we only retain the two most coherent CFC concentrations with their respective modeled counterparts out of the three CFC concentrations available (Jurgens et al., 2012).

Because of some non-convexity of the objective function Φ , we use a two-step optimization method with an initial calibration of α, C_{Si}^0 with the simulated annealing Monte-Carlo method in MATLAB (Ingber, 2000), and a second gradient-based Levenberg-Marquardt optimization to complete the reduction of the set of parameters. Using this methodology, weathering rates were compared among the catchments to test for regional differences in weathering rate.

4. Results

We first report observed CFC and DSi concentrations for the different catchments and then use the methodology presented in Section 4 to derive the catchment-level weathering rates and individual well RTDs.

4.1. Observed CFC and DSi concentrations

The relationship between CFCs and DSi was generally negative, though the strength of the relationship and range of values varied by catchment (see Fig. 4). Given the theoretical relationship between CFCs and DSi, Fig. 5 shows the concentrations of CFC-12 and DSi that can be reached with Inverse Gaussian RTDs, whatever their mean and standard deviations in the range of 0–100 years for the two silicate weathering rates, i.e. ($\alpha = 0.25 \text{ mg L}^{-1} \text{ yr}^{-1}, C_{Si}^0 = 4 \text{ mg L}^{-1}$) and ($\alpha = 0.5 \text{ mg L}^{-1} \text{ yr}^{-1}, C_{Si}^0 = 8 \text{ mg L}^{-1}$). Each point represents an Inverse Gaussian RTD with specific parameters. Sampling well data of the agricultural catchment 1 are shown as green triangles on the same plot for illustrative purposes and the best RTD associated for each well sampled is represented among the different Inverse Gaussian RTD by orange circles. The lower weathering scenario ($\alpha = 0.25 \text{ mg L}^{-1} \text{ yr}^{-1}, C_{Si}^0 = 4 \text{ mg L}^{-1}$) explained much of the variability observed in the CFC-12 and DSi

concentrations, suggesting that it is closer to the in situ rate. The difference between the two envelopes underlines the high sensitivity of the weathering model and gives some preliminary illustration of the capacity of extracting meaningful weathering properties.

4.2. Catchment-based optimal weathering rates

We applied the same optimization method for each of the 5 catchments. ρ (the average model error) varied significantly among catchments, with relatively small values (below 0.25) for most of the catchments, but higher values for the pumped catchment ($\rho = 1.64$; Table 2). Optimal weathering rates were relatively similar among catchments, especially for the agricultural catchments, which ranged from 0.20 to 0.23 $\text{mg L}^{-1} \text{ yr}^{-1}$ ($\text{CV} = 7\%$), demonstrating regional consistency among different rock types. The weathering rate was significantly slower ($0.12 \text{ mg L}^{-1} \text{ yr}^{-1}$) in the mountainous catchment and significantly faster in the pumped catchment ($0.31 \text{ mg L}^{-1} \text{ yr}^{-1}$).

Optimal initial DSi concentrations (C_{Si}^0) displayed some variability with a coefficient of variation of 19% among catchments. On the extremes, the mountainous catchment showed an initial DSi of 2.9 mg L^{-1} while the pumped catchment had an initial concentration of 5.0 mg L^{-1} , likely due to differences in weathering in the unsaturated zone.

4.3. Models of RTDs

The largest differences between well-level RTDs occurred in the agricultural catchment 2 (Fig. 6). The wells intersecting deep productive fractures had high DSi concentration and low CFC concentrations (Fig. 4) and displayed broad RTDs between 40 and 100 years (Table 2 and yellow and purple curves in Fig. 6). The low CFC concentrations corresponded with the modeled RTDs, which indicated limited modern water (<15 to 20 years' old). High DSi concentration requires much longer timescales and can be modeled as well by the contribution of residence times above 40 years. The water residence time distributions of the shallow wells (blue and red curves of Fig. 6) showed significantly younger water due to the lack of the old water contributions coming from deeper fractures (Fig. 6).

To get an idea of the type of RTDs obtained for the other catchments, we also compared some statistics of the RTDs between sites, obtained with the optimization reported in Table 2. All catchments have RTDs with mean residence times, which range on average between 30 years for the mountainous catchment and 60 years for the agricultural catchment 2.

4.4. Relations between DSi and mean residence times

A byproduct of the calibration of the inverse Gaussian lumped parameter model for the DSi and CFC concentrations was the relation between the modeled mean residence times and the observed DSi concentrations here shown for the three agricultural catchments located in Brittany (Fig. 7). For each catchment, the relation appeared to be linear, reinforcing the consistency between the observed and modeled concentrations, and providing support for the assumptions of the modeling approach. More specifically, the direct proportionality of the DSi concentration to the mean residence time validated weathering assumptions modeled by a zero-order kinetic reaction (Eq. (1)). The linear relations were also similar among catchments with coefficients of variation of respectively 7% and 6%, for the different weathering rates and the initial DSi concentration of the agricultural catchments.

We compared these modeled mean residence times obtained with the CFC and DSi concentrations with the mean residence times calibrated only with the CFC concentrations (Fig. 8). These CFC-only mean residence times were obtained using Eq. (1) without considering DSi concentrations. For each of the wells in the different catchments, the

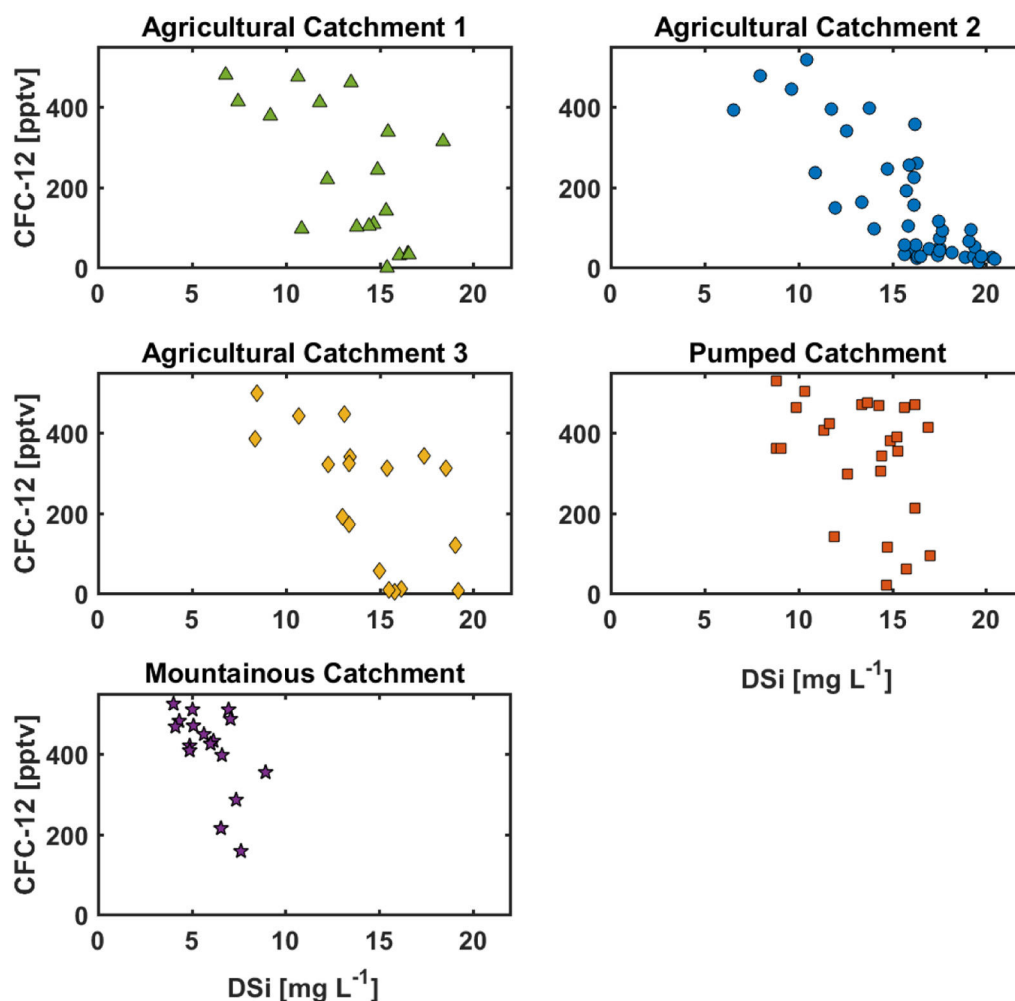


Fig. 4. CFC-12 vs DSi concentrations obtained for each of the field sites.

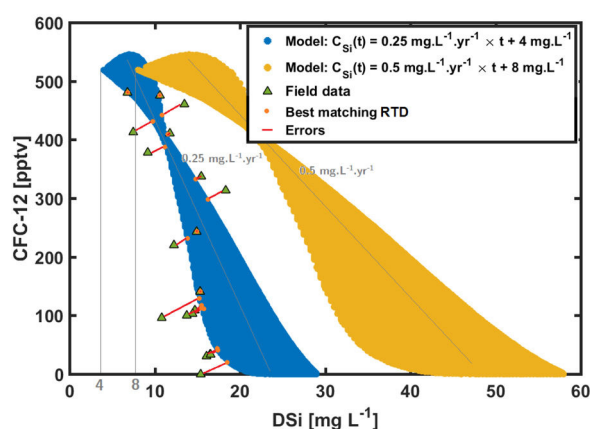


Fig. 5. Calibration methodology. For each dataset representative of one site (Field data), the equation of weathering (1) is optimized by minimizing the sum of the square errors between the well data and their best matching Inverse Gaussian RTD in the RTD model ensemble. Two models ensemble are represented: the blue one with $(\alpha, C_{Si}^0) = (0.25 \text{ mg L}^{-1} \text{ yr}^{-1}, 4 \text{ mg L}^{-1})$ and the yellow one with $(\alpha, C_{Si}^0) = (0.5 \text{ mg L}^{-1} \text{ yr}^{-1}, 8 \text{ mg L}^{-1})$. Notice how C_{Si}^0 controls the horizontal position of the RTDs models in the (CFC, DSi) plot, especially for the young fraction of the RTDs (high CFC-12, low DSi) while α controls the overall DSi spreading of the models ensemble, especially for the old fraction of the RTDs (low CFC-12, high DSi). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mean residence times obtained were quite consistent, especially for mean residence times ranging between 0 and 50 years. For such a time range, a linear regression gives $\mu_{DSi-CFCs} = 1.03 \mu_{CFCs}$ with a R^2 of 0.36.

5. Discussion

While DSi has been used as a site-specific indicator of groundwater residence time (Burns et al., 2003; Kenoyer and Bowser, 1992; Morgenstern et al., 2010; Peters et al., 2014), it was unknown how consistent silica weathering rates were, and consequently if DSi could be a useful tracer at regional scales. In this study, we evaluated the use of DSi for groundwater dating at four catchments in Brittany and one catchment in the Vosges Mountains. The data and our simulations supported the hypothesis that silica weathering can be described by a zero-order kinetic reaction at the catchment scale, and we calibrated silicate weathering laws using CFC atmospheric tracers. We found that DSi provided complementary information to CFC atmospheric tracers on RTDs. The relative stability of weathering rates among the Brittany agricultural catchments validates the use of DSi as a regional groundwater age proxy. We discuss below how these weathering rates may be modified by climatic context (from the oceanic conditions of Brittany to the mountainous climate of the Vosges) and by external factors, e.g. groundwater abstraction. Finally, we discuss the use of DSi for evaluating residence times in unsaturated zones and compare these optimized silicate weathering rates to weathering rates estimated in previous studies.

Table 2

Results obtained from the calibration. ρ is the residual (see Eq. (5)). α is the weathering rate in $\text{mg L}^{-1} \text{yr}^{-1}$. C_{Si}^0 , the initial DSi concentration in mg L^{-1} . The two last columns present some statistics about the parameters of the inverse Gaussian distributions optimized for each well: the average of the mean residence time μ in years and the average of the standard deviation σ in years of the residence time distributions for each catchment.

Catchment	ρ [–]	α [$\text{mg L}^{-1} \text{yr}^{-1}$]	C_{Si}^0 [mg L^{-1}]	mean (μ) [yr]	mean (σ) [yr]
Agricultural catchment 1	0.12	0.20	4.0	52	39
Agricultural catchment 2	0.26	0.22	3.8	60	32
Agricultural catchment 3	0.23	0.23	4.3	52	49
Pumped catchment	1.64	0.31	5.0	40	53
Mountainous catchment	0.19	0.12	2.9	30	59

5.1. Practical use of DSi as a proxy of groundwater residence time

DSi concentration appears to be a highly complementary tracer to atmospheric tracers such as CFCs. For example, at the agricultural catchment 2 (Fig. 6), the comparison of wells of different depths (shallow wells for P3 and T7, and deeper wells for MFT20 and MFT80) revealed that DSi concentration can infer the RTD even when CFCs are not discriminating because they are below their detection limit for older ages (>70 years) or during the flat portion of their atmospheric trend (i.e. the last 0–20 years). These time ranges where CFCs are less informative are further exacerbated by the widening of the concentration area reachable by the inverse Gaussian function towards lower and higher CFC-12 concentration (Fig. 5). For such CFC range (for example, for CFC-12 between 450 and 550 pptv and between 0 and 50 pptv), DSi is particularly useful to better characterize RTD. The comparison between the modeled mean residence times and those calibrated only with CFCs (Fig. 8) also displayed an increased consistency for the time range between 0 and 50 years. For mean residence times above 50 years, DSi appears to give complementary information to mean residence times from CFCs as depicted by the increased variability of mean residence times around the identity line $y = x$.

The bulk linear relation for weathering rate (Eq. (1)) is also of interest for dating purposes as DSi concentrations can be seen as a direct proxy of the mean residence time (Fig. 7), which is not the case for other tracers such as CFCs (Fig. 1) (Leray et al., 2012; Marçais et al., 2015; Suckow, 2014). While this result has been obtained with a specific Lumped Parameter Model (inverse Gaussian), it is generally applicable for a broad range of distributions as it relies on the zero-order weathering assumption that leads to a linear dependence of the DSi concentration on residence times (Eq. (1)).

Even if the small residuals obtained in Table 2 indicate that the inverse Gaussian model may be appropriate for RTDs, other types of

distributions, like the Gamma distribution, can be tested to assess the sensitivity of the LPM choice to the RTD-related prediction. For the agricultural catchment 1 and the pumped catchment, shapes of the Inverse Gaussian LPM as well as the statistics obtained regarding the optimized RTDs (Table 2) are consistent with results obtained synthetically from calibrated 3D flow and transport models developed for these aquifers (Kolbe et al., 2016; Leray et al., 2012).

The 5 to 100 years' time range of the RTDs observed here is the most favorable case for using DSi for groundwater dating since it leads to thermodynamic-limitation conditions which sustains chemical weathering (Maher, 2010). Even though weathering rates α might be quite variable between different crystalline rock types, the fluid-rock contact time controls the evolution of DSi concentrations for residence times ranging from years to decades (5–100 years) where dissolution is the dominant process. On the contrary, attainment of the mineral equilibrium restricts the use of DSi for estimating longer residence times (>300 years) when dissolution is balanced by re-precipitation (Edmunds and Smedley, 2000).

5.2. Stability of silica weathering rates at the regional scale

5.2.1. DSi as a robust regional groundwater age proxy

Our results indicate that DSi can be used as groundwater age tracing tool in relatively diverse geologic contexts, as indicated by the consistency of the weathering rates for the different Brittany catchments (Fig. 7). This homogeneity suggests that only a few mineral phases are responsible for silica production in the studied residence-time range; typically phyllosilicates, plagioclase, and accessory minerals such as apatite are the major sources of silica (Aubert et al., 2001). Applying a uniform weathering rate ($0.22 \text{ mg L}^{-1} \text{yr}^{-1}$) and initial DSi concentration (4.0 mg L^{-1}) can provide a first order estimate of mean residence

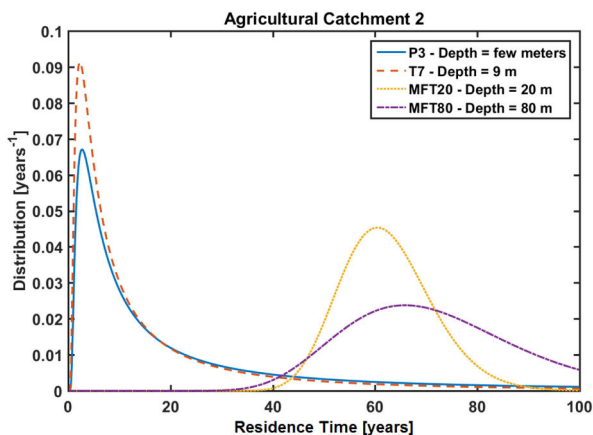


Fig. 6. Illustration of the calibrated Inverse Gaussian RTD obtained on the agricultural catchment 2 (Saint Brice). The wells lying in the shallowest part of the aquifers have small residence times and exponential shapes. The wells lying in the deepest part of the aquifer display some skewed distributions.

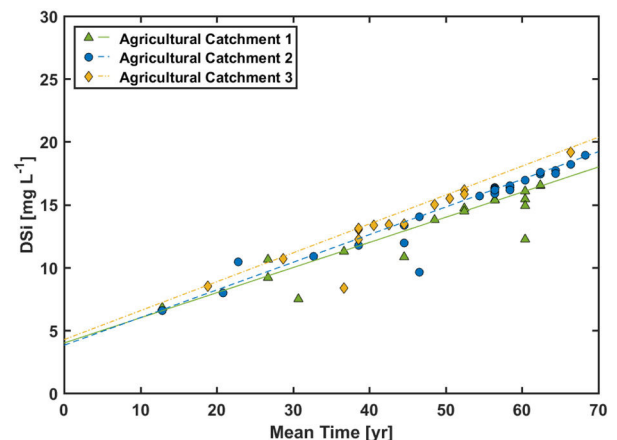


Fig. 7. Measured DSi concentration versus the optimized mean residence time of the inverse Gaussian lumped distribution for three of the Brittany sites. Straight lines represent the optimized weathering law for each of the sites. Note that it fits the measurements. Considering a constant weathering rate allows direct interpretation of DSi apparent ages into mean residence times.

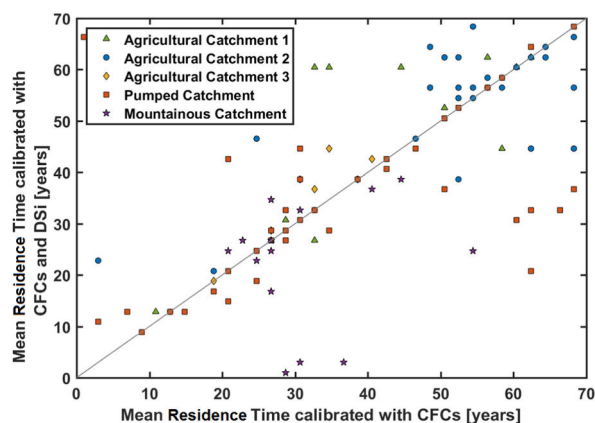


Fig. 8. Comparison between the mean residence time obtained with CFCs and DSI concentrations with those obtained only with the CFC concentrations.

time, as displayed by the blue curve presented in Fig. 9 compared to the weathering rates of each of the Brittany catchments displayed in Fig. 7. The relatively small error associated with catchment specific differences justifies the possible use of DSI as a regional groundwater dating tracer, as long as a weathering law can be applied based on similar catchments or land lithologies. If more complete modeling is available, the choice between weathering laws can be bypassed by directly solving the mass balance of the geochemical water content (Burns et al., 2003).

Silicates are ubiquitous in most geological matrices, including crystalline and sedimentary rocks (Iler, 1979). There is some evidence for using DSI as a groundwater age proxy in other rock types (e.g. sedimentary rocks coming from glacial deposits, see Section 5.4) (Becker, 2013; Kenoyer and Bowser, 1992). DSI concentration is widely measured and accessible through public observatories and databases (Abbott et al., 2018; De Dreuzey et al., 2006; Thomas et al., 2016b). While previous studies have shown dependency of weathering rates on lithology and climate (White and Blum, 1995; White et al., 1999; White et al., 2001), DSI might be considered a “contextual tracer”, allowing at least local and potentially regional groundwater dating (Beyer et al., 2016).

A major advantage of DSI is that it persists in open surface waters (e.g. lakes and streams), whereas other tracers of intermediate transit times such as $^3\text{H}/\text{He}$ and CFCs quickly equilibrate with the atmosphere. Additionally, because artificial sources are few and background concentration is usually high, DSI is robust to contamination, unlike CFCs,

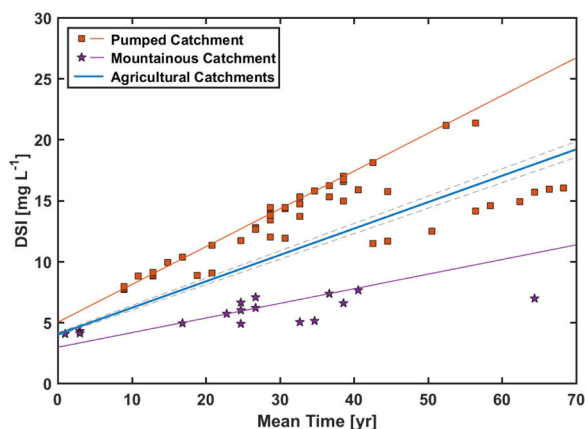


Fig. 9. DSI concentrations versus the optimized mean residence time of the inverse Gaussian displayed for each wells for the mountainous and the pumped catchment. Straight lines represent the optimized weathering law for each of the sites. Note that it fits the measurements. Considering a constant weathering rate enables to indistinctly consider Si apparent ages and mean residence times.

which cannot be in contact with the atmosphere during sampling nor with any plastic surfaces (Labasque et al., 2014). However, uptake of DSI by some vegetation and diatoms could potentially limit the use of DSI in some environments especially during the growing season (beginning of summer) (Delvaux et al., 2013; Pfister et al., 2017). This uptake is more likely in large rivers systems where DSI spend enough time to be effectively captured by diatoms whereas it is less prone to occur in headwaters systems with much smaller stream residence times (Hughes et al., 2013). To track this potential additional process into account, diatom uptake could be modeled (Thamtrakoln and Hildebrand, 2008) and/or isotopic DSI ratios could be investigated to link in stream DSI concentration to mean transit time (Delvaux et al., 2013).

5.2.2. Comparison between the agricultural catchments and the mountainous catchment

Weathering rates were relatively constant within a given regional geological and climatic context (e.g. for the three catchments in Brittany), but they were significantly different from the mountainous catchment (Vosges Mountains). Differences in lithology could control overall weathering rates, but this was not supported by the observed homogeneity of the weathering rate across different lithologies (Section 5.2.1). Acidity could not either explain this variability, as pH was comparable for all the catchments (Table 1). The lower rates in the mountainous catchment may be due to a difference in climatic conditions (i.e. temperature and rainfall) between Brittany and the Vosges Mountain (Table 1). The ~3 factor difference between DSI in the Vosges and Brittany could be explained by the combined effect of the groundwater temperature difference (~6 °C) and precipitation difference (~1.5-fold). Indeed, temperature affects weathering rates by one order of magnitude from 0 to 25 °C (White and Blum, 1995; White et al., 1999). This increase is further emphasized by increasing recharge fluxes, which is related to rainfall conditions. Another effect which could explain the difference for the mountainous catchment is lack of anthropogenic pressure related to agriculture. Brittany is a region of intensive agriculture characterized by high nitrogen loads, which induce soil acidification. High weathering rates have been observed related to fertilized additions (Aquilina et al., 2012a) which may also partially explain the Vosges-Brittany difference. Anyway, climatic and anthropogenic influences are not exclusive and may be combined to explain the high weathering rate difference.

5.2.3. Effect of groundwater abstraction on the weathering rate

The weathering law for heavily-pumped catchment in Plœmeur (orange line, Fig. 9) displayed a substantially higher weathering rate ($0.31 \text{ mg L}^{-1} \text{ yr}^{-1}$) compared to the average Brittany weathering rate ($0.22 \text{ mg L}^{-1} \text{ yr}^{-1}$). This might be due to the presence of CFC contamination leading to artificially enriched CFC concentrations compared to their actual residence times. The pumped catchment is indeed especially vulnerable to CFC contaminations (Table 1). However, long-term monitoring of CFC and SF_6 and $^3\text{H}/^3\text{He}$ measurements in this site makes the contamination hypothesis unlikely (Tarits et al., 2006). The difference is more likely explained by the facts that: i) high and long-term pumping has mobilized older waters (>100 years), which increase DSI concentrations without substantially altering CFC concentrations (only dilution effect) (Fig. 4); ii) pumping leads to a renewal of groundwater flow paths with more reactive surfaces, leading to an increase of the reactive surface/groundwater ratio.

5.3. Use of DSI for inferring residence times in the unsaturated zone

We hypothesized that the differences in initial DSI concentration are due to residence time in the unsaturated zone, suggesting that DSI concentration at the groundwater table surface (or modeled intercepts) could be used to infer residence times in the unsaturated zone. Indeed the variability in C_0^{DSI} observed in Table 2 is correlated with the average unsaturated zone thickness (Table 1), a major, though not exclusive,

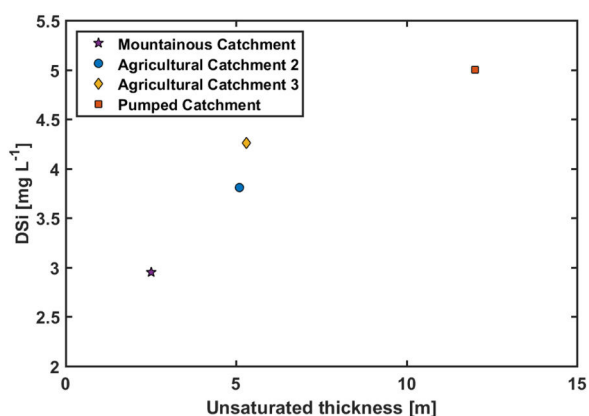


Fig. 10. Initial DSI concentrations versus the average unsaturated zone thickness. The average unsaturated zone thickness of the agricultural catchment 1 was not available.

control on the time spent in the unsaturated zone (Fig. 10). The high C_{Si}^0 for the pumped catchment (5.0 mg L^{-1}) could be due to pumping-induced drawdown of the water table, which significantly increases the unsaturated zone thickness. Likewise, the mountainous catchment has a much shallower water table depth, which might be related to the low initial DSI concentration (2.9 mg L^{-1}). DSI could therefore be a tracer of the full residence time in both unsaturated and saturated zones. Yet, unless weathering rates in the unsaturated zone can be

constrained, DSI estimates would remain qualitative. Through tracing experiments, Legout et al. (2007) estimated the residence time in the mobile-compartment of the unsaturated zone of the Kerrien catchment (South Brittany) as $2\text{--}3 \text{ m y}^{-1}$, which induces weathering rates about 4 times higher than in the saturated zone. However, the ratio mobile/immobile water is unknown but may represent a large fraction of groundwater with long residence-time that may contribute to high DSI. Because the unsaturated zone, including the base of the soil profile, is often the site of elevated rates of biogeochemical activity (e.g. nitrogen retention and removal) (Legout et al., 2005) or storage, constraining the residence time of water and solutes in this zone would allow better estimation of catchment and regional-scale resilience to nutrient loading and overall ecological functioning (Abbott et al., 2016; Meter et al., 2016; Pinay et al., 2015).

5.4. Comparison of weathering rates to previously estimated weathering rates

We compared the weathering rates obtained in this study with previously published studies (Table 3). The catchments considered in these studies have crystalline or sedimentary bedrocks derived from the erosion of crystalline formations. Apparent weathering rates have been estimated by different methods, either by implementing the geochemical evolution of groundwater through advanced reactive transport modeling (Burns et al., 2003; Rademacher et al., 2001) or by directly comparing DSI concentrations with apparent ages derived from atmospheric tracer data (Böhlke and Denver, 1995; Clune and Denver, 2012;

Table 3

Published weathering rates in different catchments obtained either directly or by fitting DSI concentrations against apparent ages. The typical age range gives the spread of the water age data obtained from the different sampled wells. Note that for the Sagehen Springs catchment, ranges of weathering rates are derived for specific minerals (plagioclase or hornblende) as explained in the complementary information.

Catchment	$\alpha \text{ [mg L}^{-1} \text{ yr}^{-1}]$	Geological context	Apparent age range	Complementary information	References
Chesterville Branch	0.34	Permeable sand and gravel units of the fluvial Pensauken Formation and the marine glauconitic Aquia Formation.	5–40 yrs	Part of Locust Grove Catchment	(Böhlke and Denver, 1995)
Morgan Creek Drainage	0.37	Permeable sand and gravel units of the fluvial Pensauken Formation and the marine glauconitic Aquia Formation.	4–50 yrs	Part of Locust Grove Catchment	(Böhlke and Denver, 1995)
Panola Mountain Research Watershed	0.62	Panola Granite (granodiorite composition), a biotite–oligoclase–quartz–microcline granite of Mississippian to Pennsylvanian age.	0–25 yrs	Mainly Riparian Saprolite Aquifer	(Burns et al., 2003)
Bucks Branch Watershed	0.91	Sediments of the Beaverdam Formation.	15–30 yrs	mainly fluvial and estuarine deposits of sand, gravel, silt, and clays	(Clune and Denver, 2012)
Fairmount catchment	0.26	Permeable quartz sand and gravel of the Beaverdam Formation and underlying sandy strata of the Bethany Formation.	5–35 yrs	well-drained settings with relatively deep water tables and thick sandy aquifers	(Denver et al., 2010)
Locust Grove catchment	0.16	Permeable quartz sand and gravel of the Pensauken Formation underlain by highly weathered glauconitic sands of the Aquia Formation.	5–50 yrs	well-drained settings with relatively deep water tables and thick sandy aquifers	(Denver et al., 2010)
Lizzie Catchment	0.36	Several Pleistocene-age terrace deposits that are underlain by a confining unit on the top of the Yorktown Formation.	5–50 yrs	predominantly poorly drained settings with shallow water tables	(Denver et al., 2010)
Willards Catchment	0.83	The lowermost unit of the system is the Beaverdam Sand, which is overlain by a 3 to 8 m thick layer of clay, silt, peat, and sand of the Omar Formation.	0–18 yrs	predominantly poorly drained settings with shallow water tables	(Denver et al., 2010)
Polecat Creek Watershed	1.0	Piedmont crystalline coastal plain sediments and alluvium. Presence of Saprolite.	0–30 yrs	Bedrock garnet-biotite gneiss	(Lindsey et al., 2003)
Crystal Lake, Vilas County (Wisconsin)	3.94	50 m of glacial sediment which overlies Precambrian bedrock.	0–4 yrs	Glacial sediments were eroded from Precambrian bedrock lithologies	(Kenoyer and Bowser, 1992)
Sagehen Springs (CA).	0.17–1.11	Extensive glacial till deposits derived from a combination of andesite and granodiorite basement rocks. The granodiorite consists primarily of plagioclase (40%), quartz (30%), hornblende (20%), and biotite (10%), and the andesite consists primarily of plagioclase (45%) with varying amounts of hornblende (5–25%) and augite (1–25%) and a small amount of glassy groundmass.	0–40 yrs	Range of weathering rate determined for each spring, only for plagioclase mineral.	(Rademacher et al., 2001)
Sagehen Springs (CA).	0.06–0.35	Several Pleistocene-age terrace deposits that are underlain by a confining unit on the top of the Yorktown Formation.	0–40 yrs	Range of weathering rate determined for each spring, only for hornblende mineral.	(Rademacher et al., 2001)
Lizzie Catchment	0.34		5–50 yrs	Unconfined aquifer.	(Tesoriero et al., 2005)

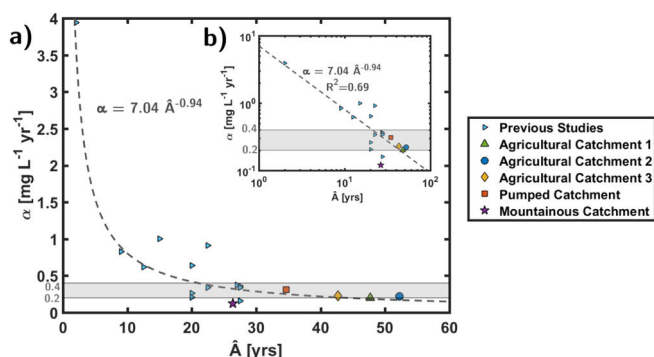


Fig. 11. Silicate weathering rates α against the typical apparent age range $\hat{A}$ from which they have been obtained, in this study and in previous studies (insert: log-log representation, p-value of $2 \cdot 10^{-5}$ obtained for the fit).

Denver et al., 2010). Our methodology is intermediary as it combines lumped residence time distributions with apparent weathering rates and inlet concentrations (atmospheric chronicles for CFCs and initial concentration C_{Si}^0 for DSI).

Except for the data reported in Kenoyer and Bowser (1992), which consists of young groundwater (0–4 yrs), all DSI weathering rates referred in Table 3 are within one order of magnitude (0.1 to $1 \text{ mg L}^{-1} \text{ yr}^{-1}$). For catchments with apparent ages between 10 and 50 years, weathering rates are clustered between 0.2 and $0.4 \text{ mg L}^{-1} \text{ yr}^{-1}$ (Fig. 11), which is consistent with weathering rates estimated in this study.

The initial decrease of weathering rates with the typical apparent ages might suggest a power law dependence of weathering rates on groundwater age (Fig. 11). However, for older apparent ages, the weathering rates might also stabilize around 20 years (Fig. 11, insert) suggesting a transition from transport-limited to thermodynamically-limited conditions consistent with what has been observed for feldspar minerals (Maher, 2010) with a slightly older transition time (20 years here instead of 10 years). It will require more studies on this residence time range (0–100 yrs) to decide between these two competing hypotheses (power law dependence versus stabilization) and precisely locate the transition time (Ackerer et al., 2018). This could be investigated by systematically combining weathering studies with groundwater age tracer analysis in a diversity of environmental observatories. If predictable rates are not found, the use of a constant weathering rate (Eq. (1)) could be refined by considering a first order kinetic reaction, although it would require the inference of an additional parameter to describe weathering.

6. Conclusion

We investigated the relationship between DSI and groundwater age tracers (CFCs) in five different crystalline catchments, including lowland, mountainous, and actively pumped catchments. For each catchment, we quantified the weathering rate and the RTDs at multiple wells using inverse Gaussian lumped parameter models calibrated with geochemical data. Overall, the DSI was strongly related to the exposure time between rocks and recently recharged groundwater (i.e. between 5 and 100 years). We found that DSI was highly complementary to CFCs, allowing better quantification of RTDs, including in the unsaturated zone and for water masses younger and older than the now rapidly closing CFC use's window. The consistency of DSI weathering rates in three Brittany catchments suggests that DSI may be a robust and cheap groundwater age proxy at regional scales for catchments with comparable geology and climate. We interpreted DSI accumulation differences in the Brittany pumped site and the mountainous region, as a consequence of temperature differences and alterations of flow from groundwater abstraction respectively. If the temperature sensitivity of weathering can be constrained, this tracer

could allow widespread determination of water transit time at the catchment scale for the unsaturated zone, aquifer, and surface waters.

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2.3 Bilan

Cet article montre donc que la silice peut être utilisée, une fois calibrée avec un traceur des temps de résidence comme les CFCs, comme un proxy du temps moyen de résidence dans les aquifères cristallins bretons. La relative uniformité du taux d'altération des roches silicatées (0.2 mg/L/yr) à l'échelle de plusieurs sites bretons montre que son utilisation peut être envisagée comme un traceur régional des temps de résidence.

La robustesse et la facilité de sa mesure laisse envisager de nombreuses perspectives. Premièrement, la silice pourrait être utilisée en rivière pour caractériser directement les temps de transit des eaux dans un bassin versant donné. Utiliser les CFCs en rivière requiert une méthodologie complexe qui est sensible aux erreurs [Sanford *et al.*, 2015]. En effet, les CFCs sont des gaz dissous qui s'équilibrent rapidement avec l'atmosphère. Par ailleurs, nous n'avons jusqu'à maintenant qu'accès à des méthodes indirectes pour mesurer en rivière les temps de transit dans le bassin versant (comparaison de chroniques de données isotopiques ou de données de chlore) [Harman, 2015; Heidbüchel *et al.*, 2012; McGuire and McDonnell, 2006]. Or Kirchner [2016] a montré qu'on ne pouvait pas caractériser le temps moyen de transit avec ces données mais uniquement la fraction d'eaux jeunes. En particulier, ces données ne permettent pas de renseigner de manière intégrée la quantité et la répartition des volumes d'eaux « anciennes » stockées dans le bassin versant (voir Partie I1.3 et Partie I2.1) [Botter, 2017]. Une autre possibilité que laisse entrevoir cette étude, c'est l'utilisation de la silice pour inférer le temps de résidence des eaux dans la zone non saturée. En effet, les gaz dissous ne sont pas sensibles à ce temps de résidence là puisque par définition, cette zone n'est pas isolée de l'atmosphère.

Si ces méthodes semi-explicites permettent d'arriver directement à une des caractéristiques centrales pour comprendre l'héritage des pratiques agricoles passées, i.e. la détermination des temps de résidence dans les aquifères, elles ne permettent pas de relier cette quantité à des facteurs de contrôles qu'ils soient climatiques, topographiques, géologiques ou anthropiques. Comprendre l'origine de la variabilité des temps de résidence dans les aquifères demande de progresser dans la connaissance de la structure et du fonctionnement de la zone critique pour 1. identifier quels sont les avantages comparatifs de certains bassins versants par rapport à d'autres pour stocker les nitrates et *in fine* les dégrader, 2. savoir comment on envisage l'évolution de ces capacités de rétention dans un futur soumis à des changements climatiques avec une variation de la saisonnalité en recharge [Jasechko *et al.*, 2014] ou 3. prédire les impacts de changements de pratiques agricoles sur la qualité de l'eau. Pour tester comment ces effets agissent et s'entremêlent pour former la distribution des temps de résidence en aquifère et, leur corollaire en rivière, la distribution des temps de transit des eaux dans le bassin versant, une méthode de choix est de calibrer un modèle explicite, mécaniste, spatialement distribué avec des données de traceurs atmosphériques via la méthode du problème inverse, paradigme classique de l'hydrogéologie. C'est le sujet du prochain chapitre.

Chapitre 3 Intégrer des traceurs atmosphériques dans des modèles hydrogéologiques

3.1 Introduction

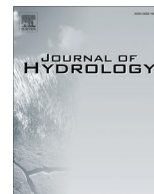
Nous avons vu dans le chapitre précédent quel pouvait être l'apport de la géochimie pour informer la distribution des temps de résidence en aquifère à partir de modélisation semi-explicite avec un *a priori* physique (les « *Lumped Parameter Models* »). Dans cette partie, nous nous intéresserons à la manière dont ces données géochimiques peuvent être utilisées pour contraindre des modèles de flux et de transport. Ces modèles, une fois calibrés, permettent de tirer une information spatialisée sur la distribution des temps de résidence et donc de relier cette information à des données de contrôle spatialisées (topographie, géologie). Par ailleurs, le modèle permet de faire des expériences numériques pour évaluer la sensibilité de différents facteurs de contrôles (e.g. climat, topographie, géologie) sur la distribution des temps de résidence.

Dans cette partie, nous montrons, sur un observatoire breton situé dans la baie du Mont Saint Michel, le bassin versant de Pleine Fougères (Long Term Ecological Research - LTER), comment la majorité des écoulements cristallins s'effectue dans la zone altérée proche de la subsurface (quelques dizaines de mètres) et paradoxalement, comment ces écoulements ont des temps de circulation très lents (de l'ordre de 50 ans).

Ceci a plusieurs implications pour la gestion des eaux souterraines. D'une part, la qualité de l'eau en aquifère hérite des pratiques agricoles passées avec une large gamme de temps (0-50 ans). D'autre part, le fait que la majorité des circulations soit située dans la proche subsurface (i.e. quelques dizaines de mètres) implique que les circulations sont locales, pilotées par la topographie et donc que la qualité de l'eau dans les aquifères cristallins superficiels intègre une étendue spatiale limitée, de l'ordre du versant.

3.2 Article: Coupling 3D groundwater modeling with CFC-based age dating to classify local groundwater circulation in an unconfined crystalline aquifer

Ma contribution : En plus des discussions générales relatives à l'écriture de cet article, j'ai particulièrement participé à la recherche de facteurs de contrôles des écoulements souterrains. J'ai été spécifiquement impliqué dans la comparaison quantitative des écoulements de subsurface (aquifère) aux écoulements de surface (topographique) grâce à l'élaboration du ratio $r_{GW-LOCAL}$ comparant la distance caractéristique des écoulements souterrains à la distance caractéristique des écoulements de surface. J'ai aussi participé à l'analyse de sensibilité pour quantifier l'impact de la recharge sur les distances de parcours de l'eau en milieu souterrain. Ceci a conduit à l'identification du paramètre contrôlant le stock d'eau, i.e. le pourcentage de remplissage de l'aquifère, comme étant un contrôle majeur sur la structure des écoulements car il détermine les interactions potentielles entre la topographie et le toit de la nappe.



Coupling 3D groundwater modeling with CFC-based age dating to classify local groundwater circulation in an unconfined crystalline aquifer



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SUMMARY

Nitrogen pollution of freshwater and estuarine environments is one of the most urgent environmental crises. Shallow aquifers with predominantly local flow circulation are particularly vulnerable to agricultural contaminants. Water transit time and flow path are key controls on catchment nitrogen retention and removal capacity, but the relative importance of hydrogeological and topographical factors in determining these parameters is still uncertain. We used groundwater dating and numerical modeling techniques to assess transit time and flow path in an unconfined aquifer in Brittany, France. The 35.5 km² study catchment has a crystalline basement underneath a ~60 m thick weathered and fractured layer, and is separated into a distinct upland and lowland area by an 80 m-high butte. We used groundwater discharge and groundwater ages derived from chlorofluorocarbon (CFC) concentration to calibrate a free-surface flow model simulating groundwater flow circulation. We found that groundwater flow was highly local (mean travel distance = 350 m), substantially smaller than the typical distance between neighboring streams (~1 km), while CFC-based ages were quite old (mean = 40 years). Sensitivity analysis revealed that groundwater travel distances were not sensitive to geological parameters (i.e. arrangement of geological layers and permeability profile) within the constraints of the CFC age data. However, circulation was sensitive to topography in the lowland area where the water table was near the land surface, and to recharge rate in the upland area where water input modulated the free surface of the aquifer. We quantified these differences with a local groundwater ratio ($r_{\text{GW-LOCAL}}$), defined as the mean groundwater travel distance divided by the mean of the reference surface distances (the distance water would have to travel across the surface of the digital elevation model). Lowland, $r_{\text{GW-LOCAL}}$ was near 1, indicating primarily topographical controls. Upland, $r_{\text{GW-LOCAL}}$ was 1.6, meaning the groundwater recharge area is almost twice as large as the topographically-defined catchment for any given point. The ratio $r_{\text{GW-LOCAL}}$ is sensitive to recharge conditions as well as topography and it could be used to compare controls on groundwater circulation within or between catchments.

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1. Introduction

Groundwater flow is a key factor in determining the fate of non-point source agricultural pollution such as nitrate (Böhlke, 2002; Dunn et al., 2012; Weyer et al., 2014). In contrast with surface flow paths, which can rapidly transport contaminants to streams and

rivers, contaminant transport in aquifers is thought to be much slower and to span larger distances, depending on geological structure and hydraulic conductivity (Forster and Smith, 1988; Grathwohl et al., 2013; McDonnell et al., 2007). These long transit times can enhance biogeochemical alteration of solutes if reactants encounter each other (McClain et al., 2003; Pinay et al., 2015; Vogel et al., 2015). Moreover, the high surface area to volume ratio of the geological substratum in aquifers enhances interactions between water and rock, leading to weathering and chemotrophic

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metabolism such as autotrophic denitrification of nitrate by pyrite oxidation (Appelo and Postma, 2005; Engesgaard and Kipp, 1992). Along with stimulating removal of pollutants, the mixing of multiple water sources can reduce contaminant concentrations by dilution (Chapelle et al., 2009; Green et al., 2010). The overall impact of groundwater on the fate of nonpoint source contaminants depends on transit time, location and timing of recharge inputs, and internal flow structure either promoting or limiting lateral and vertical exchange in the aquifer. While internal flow structures in the saturated zone are difficult to measure, they can be approximated by mechanistic numerical models, a robust tool to follow water molecules and pollutants through the aquifer, even if they simplify prevailing flow dynamics (Anderson et al., 2015; Bear and Verruijt, 2012).

Groundwater circulation in aquifers has typically been conceptualized in terms of local, intermediate, and regional flow paths (Tóth, 1963, 2009). These flow paths contribute differentially to the overall groundwater flow, resulting in a multi-modal distribution of transit times (Cardenas, 2007; Goderniaux et al., 2013). For hard-rock aquifers the majority of groundwater flow occurs in the weathered zone, typically varying from a depth of a few meters to tens of meters, and is characterized by a highly heterogeneous physical structure and variable hydraulic conductivity (Jaunat et al., 2012; Lebedeva et al., 2007; Rempe and Dietrich, 2014). The fact that the weathered zone overlays the fractured bedrock (Wyns et al., 2004), means that the most active groundwater compartment (and the most vulnerable to pollution) may be conceptualized with only local or local and intermediate flow paths. Topography also has a strong influence on shallow aquifers because the water table is close to the land surface. Consequently, groundwater circulation is controlled by a combination of geologic structure, topographical gradients, and recharge conditions (Freer et al., 1997; Gleeson and Manning, 2008; Haitjema and Mitchell-Bruker, 2005; McGuire et al., 2005; Tetzlaff et al., 2009). Haitjema and Mitchell-Bruker (2005) developed a criterion for large aquifers to quantify the relative importance of topography and recharge rate in determining water table height (Eq. (1)):

$$\frac{RL^2}{mkHd} > 1 \rightarrow \text{water table is topography controlled} \quad (1)$$

$$\frac{RL^2}{mkHd} < 1 \rightarrow \text{water table is recharge controlled}$$

where R is the effective recharge (m d^{-1}), L is the distance between hydrological boundaries (m), m is a coefficient equal to 8 for rectangular areas or 16 for circular shapes, k is the hydraulic conductivity (m d^{-1}), H is the saturated thickness (m) and d is the maximum terrain raise (m). For a topography controlled groundwater table, local circulation dominates total flow, whereas intermediate and regional circulation is predominant in aquifers with a recharge controlled groundwater table (Gleeson and Manning, 2008).

Despite the limited depth of shallow aquifers, groundwater age stratification has been observed based on atmospheric tracers such as chlorofluorocarbons (CFCs) and SF_6 , providing some important constraints on the flow structure (Ayraud et al., 2008; Busenberg and Plummer, 1992; Cook and Herczeg, 2000). Groundwater age information can be integrated into groundwater models to generate new understanding about the relationship between flow structure and transit time distribution (Cook and Herczeg, 2000; Eberts et al., 2012; Leray et al., 2012; Molénat and Gascuel-Oudoux, 2002; Molson and Frind, 2012).

To determine the extent of groundwater flow circulations and to quantify topographical and hydrogeological controls on groundwater flow, we modeled groundwater flow dynamics of a shallow hard-rock aquifer in Brittany France. Given the relatively old observed groundwater ages (~ 40 years based on CFC

concentrations), we hypothesized that groundwater would have traveled long distances from the recharge location to the sampling zone, integrating water recharge from a large area and increasing the likelihood of agricultural contamination. Furthermore, we hypothesized that these travel distances would increase moving from uplands towards lowlands due to the increasing contributing area (catchment size) and the relatively large topographical relief in this catchment. To test these hypotheses, we constructed and calibrated groundwater flow models using geological, topographical, hydrological, and groundwater age data to constrain groundwater transit time distributions, flow line organization, and the distance that groundwater traveled from recharge locations to sampling zones. To test the influence of topography on groundwater circulation, we compared modeled groundwater travel distances with corresponding flow lengths across the digital elevation model (DEM), further called reference distances. Similar reference and groundwater travel distances would suggest strong topographical control on the groundwater table, while relatively longer groundwater travel distances would indicate less connection with the land surface and more of a recharge control on the groundwater table with hydrogeological properties dominating the flow circulation.

2. Material and methods

We performed our study in a 35 km^2 agricultural catchment near the town of Pleine-Fougères in Brittany, France (Fig. 1 and $48^\circ 36' \text{N}$, $1^\circ 32' \text{W}$), which is part of the European Long-Term Ecosystem Research network LTER (www.lter-europe.net). Extensive background data from previous studies (Jaunat et al., 2012; Lachassagne et al., 2011; Thomas et al., 2016a) provided physical and chemical constraints allowing the construction of realistic groundwater flow models to test our hypotheses about flow dynamics and transit time distributions. The transit time was defined as the time a water molecule spends between the recharge location and the sampling zone. All transit times of water molecules arriving at the sampling zone were used to calculate the mean transit time of the sample.

2.1. Pleine-Fougères aquifer

The Pleine-Fougères aquifer is located in the northern part of the east–west shear zone of the North Armorican Massif (Fig. 1a). This zone is underlain by a crystalline basement (Bernard-Griffiths et al., 1985). The aquifer straddles a geologic transition between granite in the south and schist in the north (Fig. 1b). The unconfined groundwater flow mainly occurs in the weathered zone which overlies a less pervious fractured zone (Jaunat et al., 2012; Lachassagne et al., 2011; Wyns et al., 2004). The mean thickness of the weathered and fractured zone is respectively 9 m and 48 m, though the thickness of both layers is variable (Fig. 2a and b). Elevation ranges from 9 to 118 m, with most of the relief occurring at a steep slope at the boundary between schist and granite with a mean gradient of 7.5%, creating three distinct landscape components: upland, lowland and the transition area (Fig. 3). Most rivers in the catchment flow from the south to the north. Secondary topographical gradients from the differential incision of rivers are oriented in an east–west direction. Mean groundwater recharge R is estimated at 167 mm y^{-1} using meteorological data and the one dimensional Interaction Soil–Biosphere–Atmosphere-Model (Boone et al., 1999; Noilhan and Mahfouf, 1996; Noilhan and Planton, 1989). We estimated mean annual groundwater discharge, constituting the baseflow at the outlet of the catchment (Fig. 4), at $4.5 \times 10^6 \text{ m}^3 \text{ y}^{-1}$, based on hydrograph separation of predicted long term stream discharge (mean of

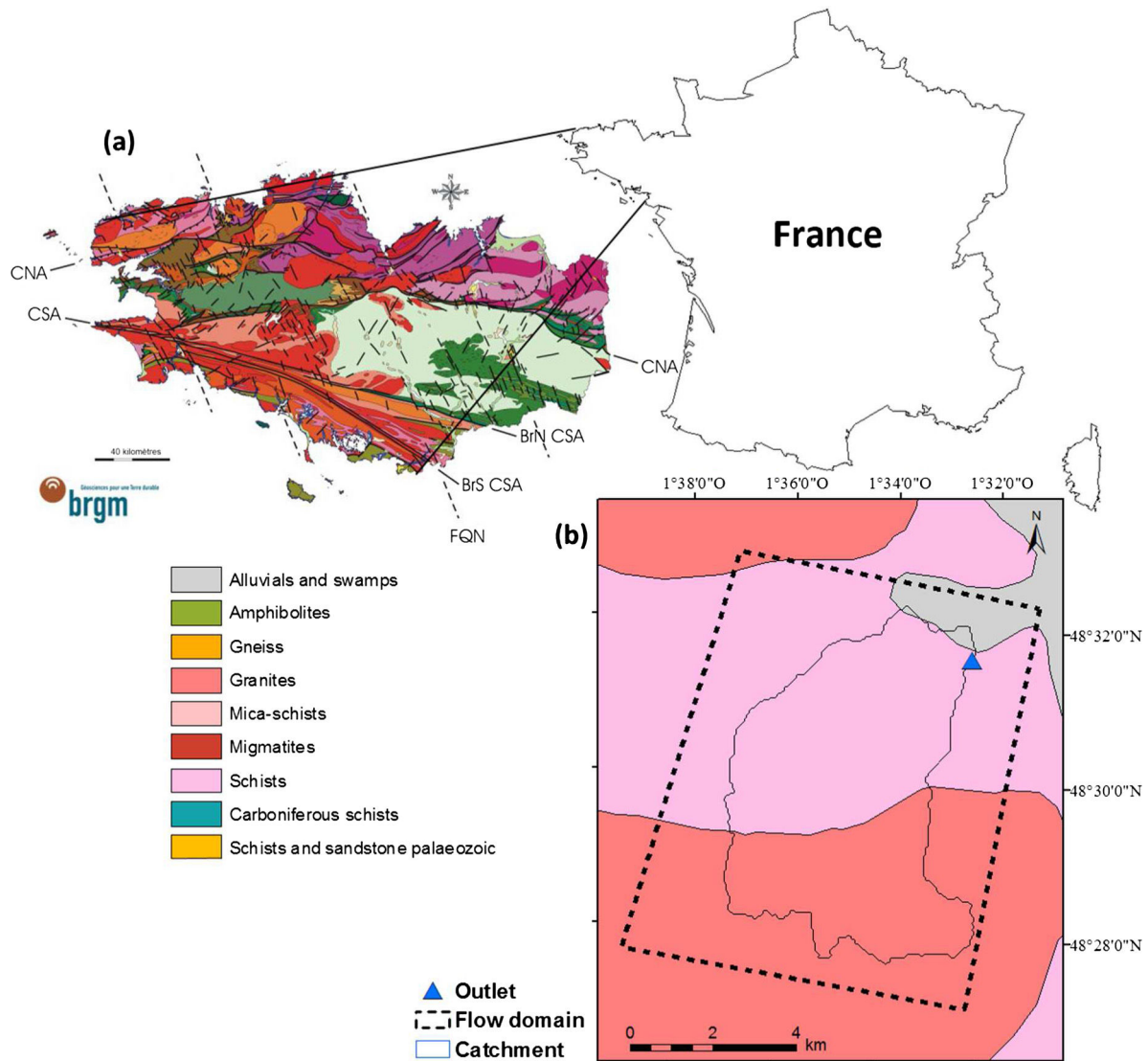


Fig. 1. Location of the Pleine-Fougères site, (a) on the geological map of the Armorican Massif (west of France), (b) geological map of the studied zone. The black dashed rectangle indicates the flow domain. The black polygon and blue triangle delineate the monitored catchment boundary and its outlet, respectively. Map layers were provided by the French Geological Survey (BRGM). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$9.1 \text{ m}^3 \text{ y}^{-1}$) using a power equation. The hydrograph separation was performed with a one-parameter algorithm described in Chapman (1999, Eq. 8), where the baseflow was determined as a simple weighted average of the direct runoff and the baseflow at the previous time interval. In the absence of direct runoff, the baseflow was constant.

2.2. Groundwater models

The effective modeled zone (76 km^2) was substantially larger than the drainage basin (35 km^2) to limit boundary effects. The modeled zone extended beyond the watershed divide in the south (upland) and downslope from the outlet in the north, and was delimited by two rivers in the east and west (Fig. 4). We selected hydraulic conductivities based on average values in the literature (Ayraud et al., 2008; Batu, 1998; Grimaldi et al., 2009; Kovács, 2011), assigning a single conductivity value to each of the four compartments, i.e. weathered schist (K_{WS}), fractured schist (K_{FS}), weathered granite (K_{WG}), and fractured granite (K_{FG}). In the reference groundwater model (REF), the hydraulic conductivity of granite was double that of schist ($K_{WG} = 2K_{WS}$ and $K_{FG} = 2K_{FS}$) and the

thickness of the weathered and fractured zones was derived from near-surface geologic maps of the area (Fig. 2). We assigned a greater hydraulic conductivity to the weathered granite compared to the hydraulic conductivity in the weathered schist, because of its higher susceptibility to weathering (Bala et al., 2011; Dewandel et al., 2006; Edet and Okereke, 2004). In the calibration procedure, hydraulic conductivities were optimized within a range of 8.64×10^{-2} – 1.7 m d^{-1} predetermined by previous studies performed in similar weathered zone aquifers in Brittany (Ayraud et al., 2008; Clement et al., 2003; Le Borgne et al., 2004; Martin et al., 2006; Roques et al., 2014). Due to weathering processes in the weathered zone, porosities up to 50% are reported in the literature (Kovács, 2011; Wright and Burgess, 1992). Below the weathered zone, bedrock metamorphic and igneous rocks like schist and granite have a very low primary porosity (0.1–1%; Singhal and Gupta, 2013). However, depending on the fracture and fissure density, the porosity in the fractured zone can be up to 10% (Earle, 2015; Hiscock, 2009). For our models, the effective porosity, i.e. the pore volume that contributes to fluid flow, was set higher in the weathered zone (θ_W) than in the fractured zone (θ_F) and was assumed to be uniform across both geologies. Values were derived

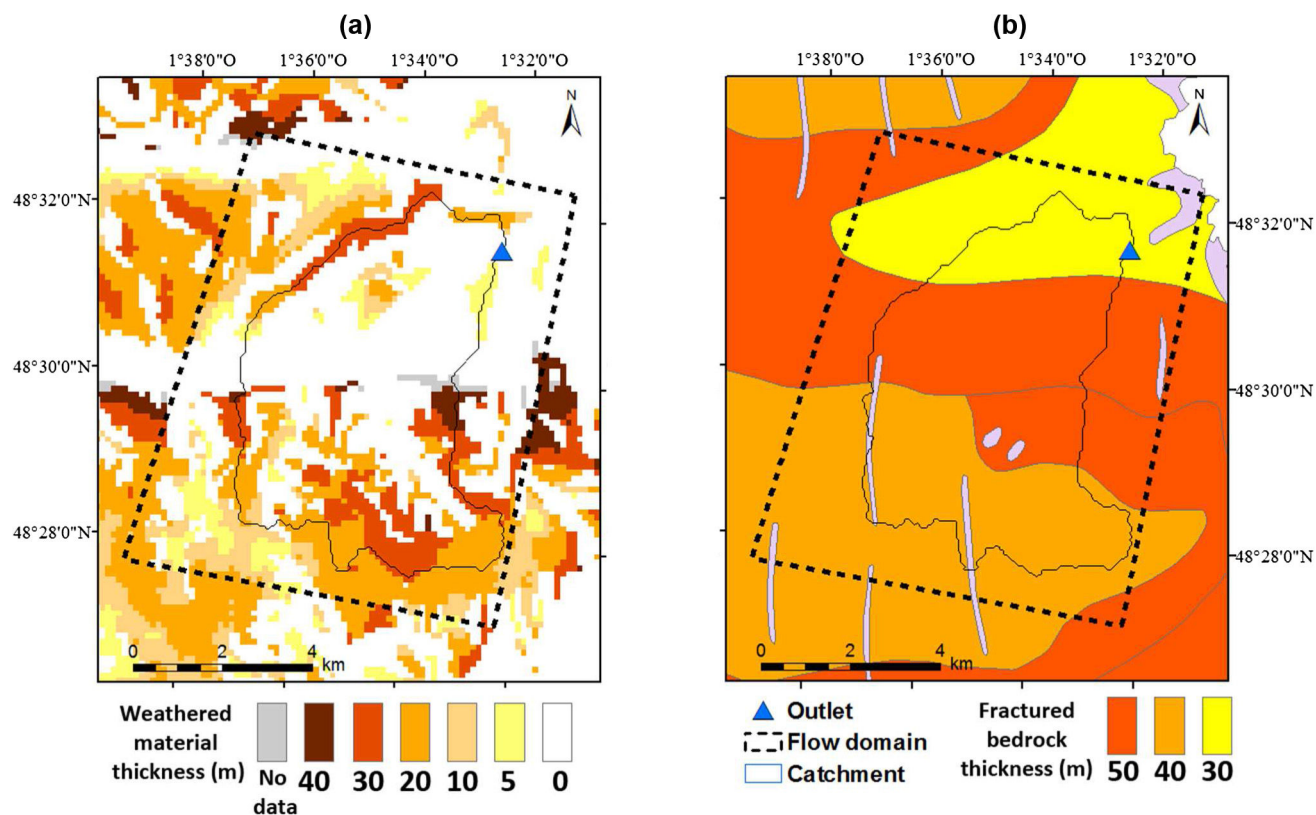


Fig. 2. Map of (a) weathered zone thickness and (b) fractured bedrock zone thickness. Permeable weathered zone lies over the less fractured bedrock zone. Map data were provided by the French Geological Survey (BRGM).

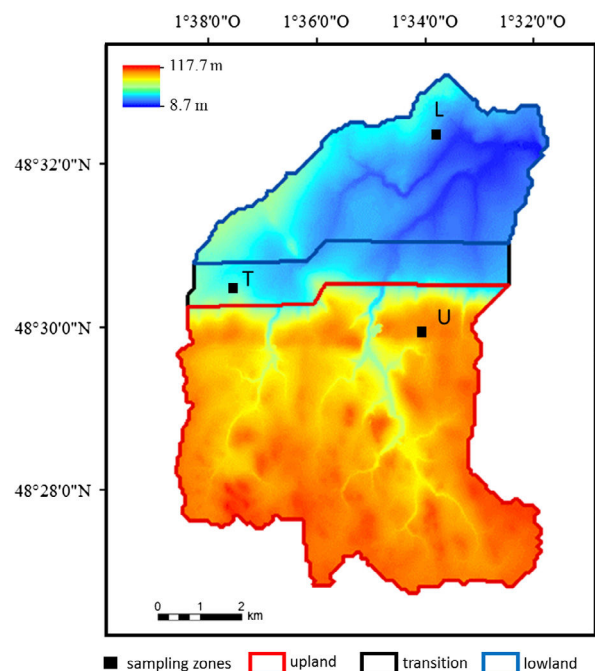


Fig. 3. Digital elevation model with a 5 m resolution. Colored polygons represent the three distinct areas of the Pleine-Fougères site, i.e. upland in red, transition in black and lowland in blue. Three representative sampling zones (black squares) identified by letters (U, T and L) are shown in each area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

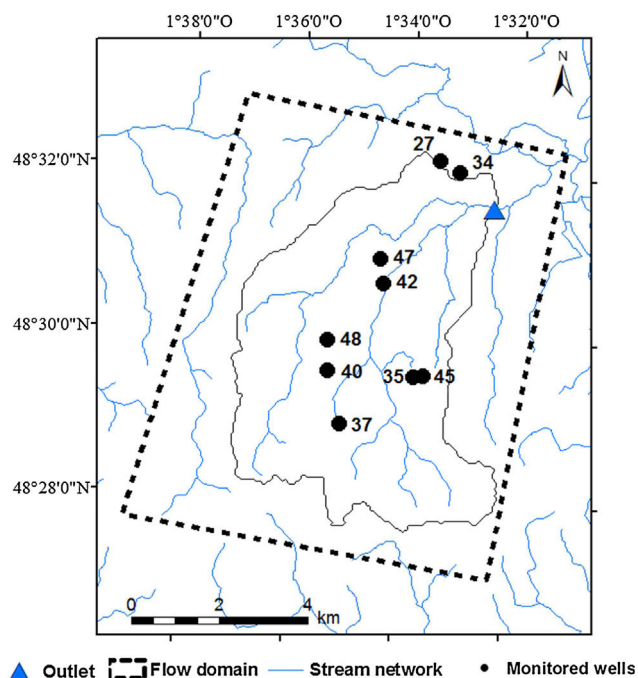


Fig. 4. Stream network (blue lines) of the Pleine-Fougères site (black polygon). Monitored well positions (black points) indicating mean CFC groundwater ages from sampling performed in December 2014 and March 2015. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

through the calibration against the measured groundwater ages (see Section 2.5.). Altogether, the groundwater model was parameterized by K_{WG} , K_{FG} , θ_W , and θ_F . All four parameters were calibrated against baseflow at the catchment outlet, and groundwater age data estimated using CFC measurements from 9 wells (Fig. 4; see Section 2.4 for detailed description of calibration).

In total, five groundwater flow models were developed (Table 1). To investigate the influence of weathered zone thickness on groundwater flow, we tested three models with different ratios of weathered to fractured zone thickness. We compared the model with a thin weathered zone, half the thickness of the reference model (THIN), to a model with twice the thickness of the reference model (THICK). For the reference groundwater model (REF), the ratio of the weathered to fractured zone thickness was 0.19, for the THICK model the ratio was 0.58, and for the THIN model it was 0.05. To test our assumptions about differences in hydraulic conductivity between the two geologies, we developed a fourth groundwater model (AHC) with an alternative hydraulic conductivity ratio ($K_{WG} = 10K_{WS}$), but the same thickness ratio as the reference model. To test the impact of these modifications, we developed a homogeneous model (HOM) that had a uniform hydraulic conductivity and effective porosity. All five models were calibrated using the same procedure, described in detail in Section 2.4. The comparison of the reference model with the alternative models is developed in Section 3.3.

2.3. Groundwater flow simulations

Groundwater flow of the unconfined aquifer was simulated in the 76 km² flow domain (black dashed rectangle in Fig. 4) under free surface conditions (Bear, 1973). Flow was simulated in steady state, because the groundwater ages measured at high and low groundwater conditions at the site did not show any significant variations (data not shown). Also seasonal recharge variations over 42 years derived from the ISBA model (Boone et al., 1999; Noilhan and Mahfouf, 1996; Noilhan and Planton, 1989) did not show any trend, indicating that transient flow simulations were unnecessary. We applied a uniform recharge of 167 mm y⁻¹ on the top layer of the model. The effective recharge of 5.8×10^6 m³ y⁻¹ over the 35.5 km² catchment is 25% larger than the discharge of 4.5×10^6 m³ y⁻¹. This is explained by seepage areas that are not integrated in the discharge computation, which cover 8% of the land surface. Lateral and bottom boundary conditions were set as no flow.

Groundwater flow equations with the previously described recharge and boundary conditions were solved with the finite

element modeling package FEFLOW (Diersch, 2013). The movable free surface was iteratively determined with the best-adaptation-to-stratigraphic-data technique (BASD), an algorithm that adapts the mesh structure to the free surface height, while respecting as far as possible the layering of the hydraulic conductivity. Because the underlying bedrock at our site had a uniform and very low hydraulic conductivity of 1×10^9 m d⁻¹, it acted effectively as an impervious layer. Its variable thickness gave an overall uniform aquifer domain thickness appropriate for FEFLOW modeling purposes. The mesh generated by FEFLOW contained 6188 triangle prisms per slice, with 2 slices per layer. The vertical discretization was adapted to the weathered zone thickness for each of the different models. The mesh contained 12,218 mesh elements per layer, with a total of 122,180 mesh elements over 10 layers. The mesh followed surface structures and was automatically refined close to surface waters, where convergence induces larger flows (Fig. 5). The DEM (Fig. 3) shows a marked difference in elevation near channel banks where mesh refinement was implemented.

2.4. Groundwater flow lines and sampling

Flow lines were determined using the particle tracking algorithm of FEFLOW (Diersch, 2013), with particles seeded at a density proportional to the imposed recharge at the water table. In order to provide a sufficient representation of the flow field, at least 4×10^5 flow lines were required. Groundwater flow lines in the modeled area are presented in Fig. 6. The red lines mark the seepage zones, which were defined as zones where the groundwater table (extracted from the groundwater flow model) reaches the land surface.

In a post-processing step, we used MATLAB to analyze the flow lines. We created a regular grid of 100 × 100 m sampling zones over the whole flow domain and sampled flow lines where they intersected the rectangular columns of the grid at any depth. The selected grid size ensured sufficient flow lines in each sampling zone while avoiding spurious mixing effects. Ultimately model results, e.g. mean transit times, were quite robust to sampling zone size with sensitivity tests revealing little difference between 50 × 50 m and 200 × 200 m sampling zones sizes (Fig. A.1). The 100 × 100 m grid over the whole catchment area resulted in sampling zones every 340 m, for a total of 278 sampling zones in the catchment area without considering sampling zones that were located in streams.

2.5. Calibration

We used groundwater flow simulations to determine the overall groundwater discharge at the catchment outlet. Hydraulic conductivities (K_{WG} and K_{FG}) were manually calibrated to fit the observed discharge value of 1.2×10^4 m³ day⁻¹ derived from hydrograph separation.

We estimated the mean groundwater age at the 9 sampling wells with CFC concentrations. CFCs are anthropogenic gases whose atmospheric concentrations increased linearly from 1960 to 1990 (when they were banned) and have been gradually decreasing, allowing the calculation of the average time since a groundwater parcel was in equilibrium with the atmosphere (Ayraud et al., 2008). Groundwater samples were collected in December 2014 and March 2015 and were analyzed at the Geoscience Laboratory (Rennes, France; for detailed methodology see Ayraud et al., 2008; Busenberg and Plummer, 1992; Cook and Herczeg, 2000). No systematic spatial trends were apparent in the measured groundwater age data from the sampled wells (Fig. 4), so we calibrated the model parameters K_{WG} , K_{FG} , θ_W and θ_F (Table 1) based on the mean and standard deviation of the groundwater age and the discharge (Table 2). The model

Table 1

Characteristic parameters (K : hydraulic conductivity, H_{mean} : mean thickness of the zone, θ : effective porosity; subscript W : weathered zone, subscript F : fractured zone) of the five models (REF: reference model, THICK: model with thicker weathered zone, THIN: model with thinner weathered zone, AHC: model with higher hydraulic conductivity in granite, HOM: homogeneous model).

		REF	THICK	THIN	AHC	HOM
K_W (m d ⁻¹)	G	0.68	0.3	0.68	2	0.15
	S	0.34	0.6	0.34	0.2	0.15
K_F (m d ⁻¹)	G	0.34	0.15	0.34	1	0.15
	S	0.17	0.3	0.17	0.1	0.15
$H_{W,\text{mean}}$ (m)	G	11.3	19.5	3.7	22.3	
	S	6.6	22	1.9	4.3	
$H_{F,\text{mean}}$ (m)	G	49.3	37.1	56.3	42.8	90
	S	47.4	34.8	51.7	43.4	
$H_{B,\text{mean}}$ (m)	G	30.6	35.4	31.3	23.8	
	S	34.5	30.4	34.9	41.5	
θ_W (-)	G, S	0.45	0.45	0.55	0.45	0.35
θ_F (-)	G, S	0.15	0.15	0.25	0.15	0.35

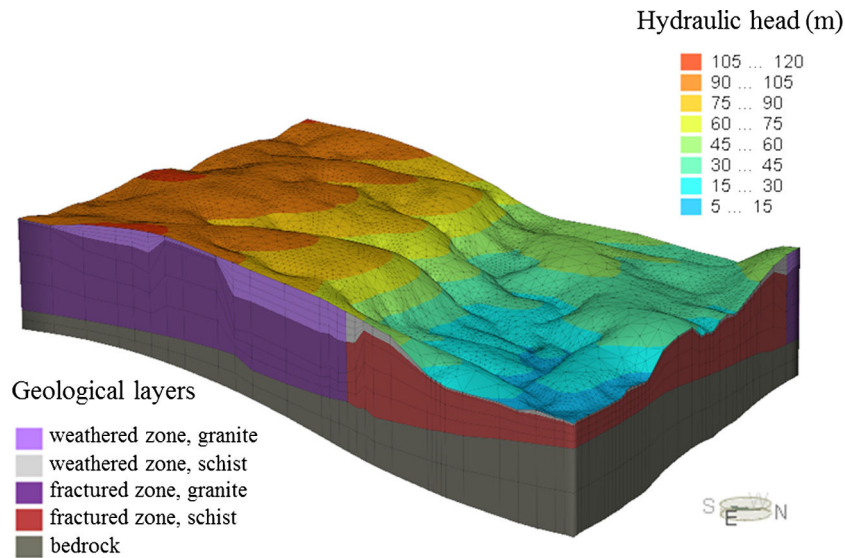


Fig. 5. Three-dimensional representation of the geological layers. Each color on the lateral boundaries correspond to a particular geological layer. Hydraulic heads are shown by colors projected on the free surface. The model is vertically exaggerated by a factor of 20. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

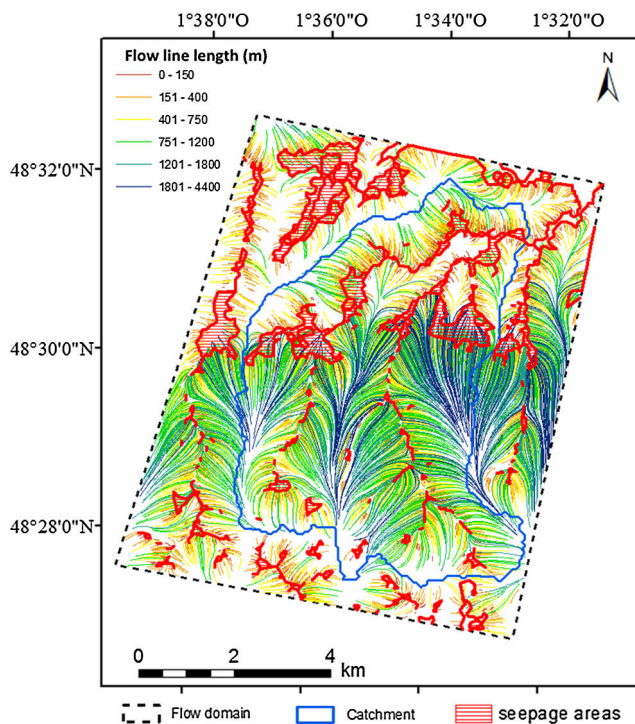


Fig. 6. Flow lines of the reference model projected in 2D. Colored lines identify the groundwater flow lines according to their overall length (from recharge point to discharge location). Seepage areas are identified by red lines. The catchment boundary is represented by the blue polygon. The model domain is delineated by the black dashed rectangle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

calibration against the measured mean groundwater age was also done manually. We used the same sampling zone size (100×100 m) for the 9 wells when calculating modeled groundwater ages. Modeled groundwater ages are the convolution product of the recorded tracer input chronicle and the transit time distribution (Maloszewski and Zuber, 1996; Marçais et al., 2015).

For model calibration this meant reducing hydraulic conductivity decreases the overall discharge and increases the groundwater age or vice versa. As expected, effective porosity did not have any influence on the catchment discharge at steady state conditions, but was positively correlated with the groundwater age. Ratios of effective porosities and hydraulic conductivities were constrained by the dispersion of the groundwater age. All five models were considered to be satisfactory calibrated (Table 2).

2.6. Transit time and groundwater travel distance distributions

For each of the 100×100 m sampling zones, we derived transit time distributions as well as groundwater travel distance distributions and computed spatial statistics for intersecting flow lines. We computed the transit time for each particle and the mean transit time of all particles reaching the sampling zone. We also calculated the lateral distance traveled by particles intersecting the water column defined by the sampling zone. The groundwater travel distance was defined as the distance from the flow line origin to the center of the sampling zone projected on the ground surface (Fig. 7). These groundwater travel distances were used to build groundwater travel distance distributions and mean groundwater travel distances for each of the 278 sampling zones. We calculated summary statistics for the three catchment areas: upland, transition, and lowland. Because the influence of the topographical transition on transit time and groundwater travel distance distributions extended beyond the steep section of the slope, we defined the transition area as the area extending from the head of the slope to 650 m to the north of the slope (Fig. 3). Upland and lowland areas were then defined to the south and north of the transition area.

We also compared the groundwater travel distance with the mean distance between two streams, which represented the average Euclidean distance between surface channels calculated with the ArcToolbox of ArcMap (ESRI® ArcMapTM, 2010).

2.7. Analysis of groundwater circulation

To determine the local nature of the groundwater circulation which is related to the groundwater table configuration, we compared groundwater travel distances with reference surface

Table 2

Groundwater discharge, mean and standard deviation of groundwater ages of the five models (REF: reference model, THICK: model with thicker weathered zone, THIN: model with thinner weathered zone, AHC: model with higher hydraulic conductivity in granite, HOM: homogeneous model). ε is the relative error between the modeled and measured values. Measured baseflow = $1.24 \times 10^4 \text{ m}^3 \text{ d}^{-1}$, mean of the sampled groundwater ages = 38.9 y, standard deviation of the sampled groundwater ages = 7.2 y.

	REF	THICK	THIN	AHC	HOM
Groundwater discharge ($\text{m}^3 \text{ d}^{-1}$)	1.25×10^4	1.27×10^4	1.23×10^4	1.23×10^4	1.28×10^4
ε (%)	1.8	3.2	0.2	0.2	3.8
Groundwater age, mean (y)	37.5	37.7	38.1	37.8	38.5
ε (%)	3.6	3.1	2.0	2.8	1.0
Groundwater age, SD (y)	6.2	6.8	7.6	6.6	5.8
ε (%)	13.9	5.5	5.5	8.3	19.4

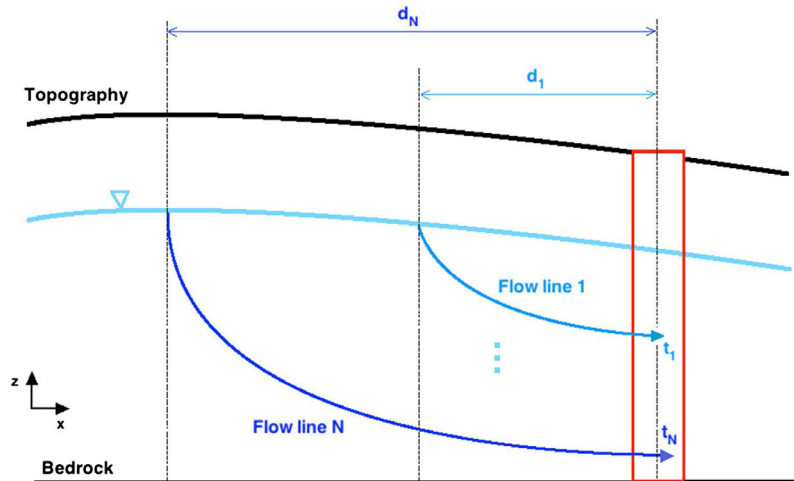


Fig. 7. Cross-section illustrating the sampling in a sampling zone (red) over the whole water column. For each flow line N , the groundwater distances (d_{1-N}) and times (t_{1-N}) are calculated. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

distances. We determined the length of those reference distances as the travel distance water would have traveled along the impermeable ground surface from a topographical height to the sampling zone. We used a 5 m LiDAR DEM with the D8 algorithm implemented in the TopoToolbox Matlab software (Schwanghart and Kuhn, 2010; Schwanghart and Scherler, 2014). Using a D8 algorithm, the flow passes from each cell to its lowest neighboring cell. Reference distances were generated for the whole model domain to calculate mean values for each of the 287 sampling zones ($100 \times 100 \text{ m}$) and summary statistics for the upland, transition and lowland area. The comparison of mean groundwater travel distances with mean reference distances was performed for sampling zones with mean distances greater than 100 m because the mesh size and flow processes that the numerical model accounted for were insufficient for an analysis at a smaller groundwater flow scale (less than 100 m).

We used the ratio of mean groundwater travel distance to mean reference distance ($r_{\text{GW-LOCAL}}$) as a metric of the relative influence of topography and recharge on the groundwater table (Fig. 8). Conceptually, when the mean groundwater travel distance is similar to the mean reference distance ($r_{\text{GW-LOCAL}}$ approaches 1), the saturated fraction of the subsurface volume (defined as the volume between the land surface and the impermeable bedrock) is higher than 95%. The groundwater table is therefore limited by the land surface and groundwater flow is strongly influenced by topographical gradients (Fig. 8a). When $r_{\text{GW-LOCAL}}$ is greater than 1, the saturated fraction fills less than 95% of the subsurface volume, meaning the groundwater table elevation depends mainly on the recharge rate and groundwater flow circulation is dominated by the hydrogeological conditions (Fig. 8c). Fig. 8b demonstrates that locally topography and recharge controls can occur at the same time in

an aquifer. We calculated $r_{\text{GW-LOCAL}}$ based on the average of the mean groundwater travel distances (see Section 2.4) and the mean of the reference distances in the upland and lowland area of the aquifer. We did not calculate this ratio for the transition area due to less well-constrained distances and compound uncertainties, meaning that flow lines crossed that zone could not be associated exclusively with the transition area. We also determined the subsurface fraction of subsurface volume for the upland and lowland areas separately. We used this metric at the small catchment scale to quantify groundwater travel distances of local circulation, but it would equally applicable at larger scales where it could be used to classify groundwater circulations in relation to the reference distances.

3. Results

In Sections 3.1 we present the results of the reference model. In Section 3.2 we compare the modeled groundwater travel distances with reference distances and explore their ratio $r_{\text{GW-LOCAL}}$ in relation to the saturated fraction of the subsurface volume. In Section 3.3 we present how modifications in the alternative models alter model behavior. Specifically we report the relationship between the groundwater travel distances, transit times, and their spatial arrangement in the catchment.

3.1. Transit times and groundwater travel distances

All of the metrics of groundwater travel distance and transit time followed the same pattern, with greatest mean transit times and distances in the transition area, followed by the upland, and

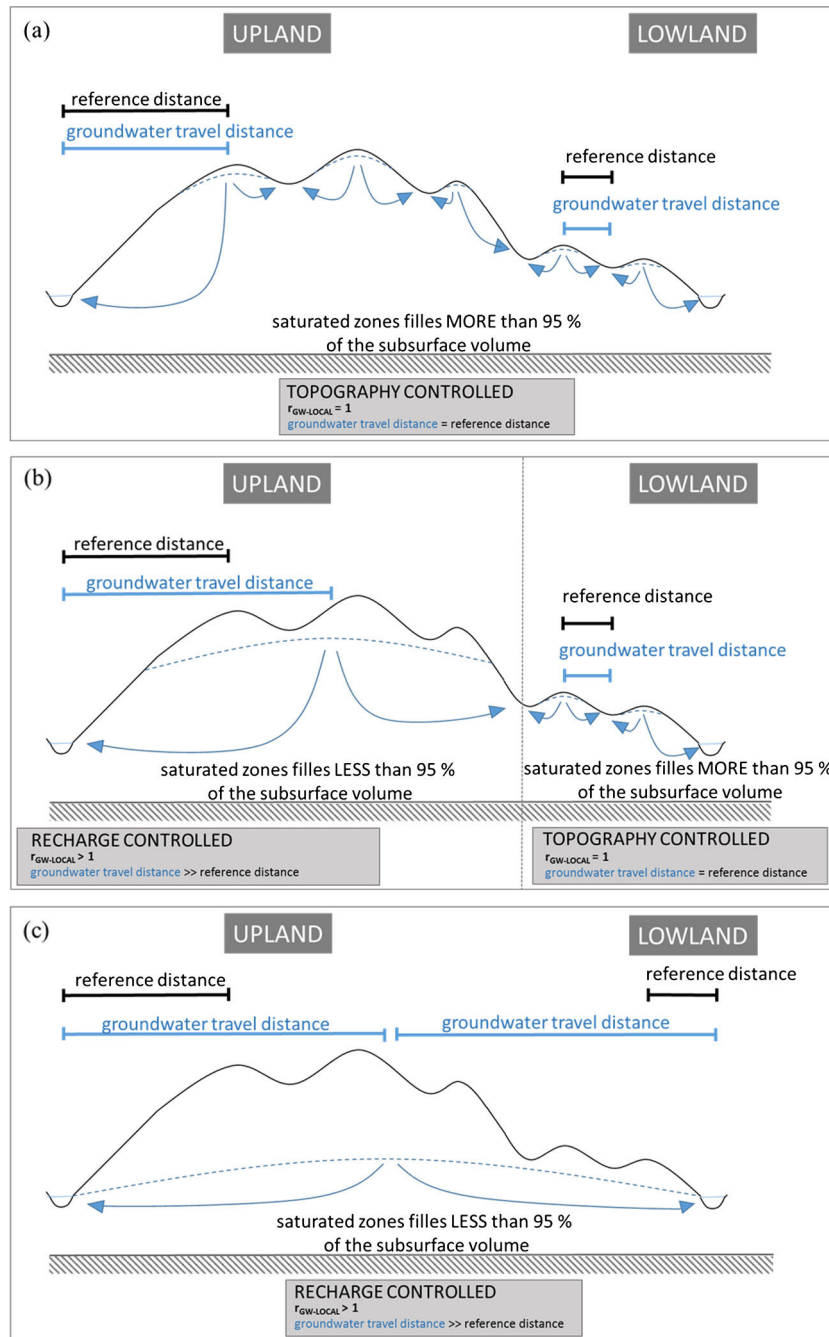


Fig. 8. Conceptual representation of recharge and topography controlled groundwater table conditions in a shallow aquifer. High groundwater table conditions result in topography controls in the upland and lowland area (a). For lower groundwater table conditions, a recharge controlled system in the upland and a topography control system in the lowland can occur (b). Very low groundwater table conditions (c) can result in recharge control in both areas. The authors were inspired by [Haitjema and Mitchell-Bruker \(2005, Fig. 4\)](#).

then lowland area (Table 3). Mean transit times were on the order of decades, while groundwater travel distances remained on the order of hundreds of meters.

Considering transit time and groundwater travel distance distributions for individual sampling zones of the reference model, Fig. 9 shows distributions for three representative sampling zones in the upland, transition, and lowland area (Fig. 3). The three sampling zones are representative for their area as they show a common shape with an appropriate mean value of all investigated distributions in the related area. In the upland and lowland area, the transit time distributions had an exponential-like shape while the transition zone had a more bimodal shape with maxima around zero and

65 years (Fig. 9a). The mean transit time was 42 years (SD = 43) in the upland sampling zone and 35 years (SD = 29) in the lowland sampling zone. These results were consistent with an exponential distribution, where the mean transit time is equal to the standard deviation, and also with the mean transit time τ_A given by [Haitjema \(1995\)](#):

$$\tau_A = \frac{\theta \cdot H}{R} \quad (2)$$

where τ_A is the mean transit time, H is the mean hydraulic thickness of the aquifer, θ is the effective porosity and R is the recharge. The mean transit time according to this equation averaged 30 years

Table 3

Groundwater mean distances and mean transit times and their coefficient of variation for each of the five groundwater flow models (REF: reference model, THICK: model with thicker weathered zone, THIN: model with thinner weathered zone, AHC: model with higher hydraulic conductivity in granite, HOM: homogeneous model).

		REF	HOM	THIN	THICK	AHC
Catchment	Mean distance (m)	334	358	323	307	438
	CV distance (%)	59	62	60	65	57
	Mean time (y)	51	148	65	55	53
	CV time (%)	29	26	31	26	30
Lowland	Mean distance (m)	219	285	214	300	202
	CV distance (%)	59	52	62	48	0.72
	Mean time (y)	47	141	62	52	53
	CV time (%)	34	26	35	23	48
Transition	Mean distance (m)	576	713	572	639	398
	CV distance (%)	49	35	49	34	44
	Mean time (y)	57	171	75	51	53
	CV time (%)	44	28	43	27	32
Upland	Mean distance (m)	326	296	313	223	566
	CV distance (%)	40	47	41	48	38
	Mean time (y)	51	146	64	58	53
	CV time (%)	18	24	21	26	14

for the upland area and 16 years for the lowland area when the aquifer thickness was constrained to the weathered zone (11.3 m and 6 m for the two areas respectively). The mean transit time increased to 74 years upland and 58 years lowland when the

aquifer thickness was allowed to include both, the weathered and fractured zones (60.3 m and 54 m, respectively). The groundwater travel distance distribution in Fig. 9b resembled an exponential distribution in the upland and transition sampling zone. The distance distribution in the lowland sampling zone peaked around 50 m and only included distances less than 750 m.

The differences of mean transit times and groundwater travel distances for the whole aquifer were visible on the map derived from interpolation of the pointwise values obtained in each sampling zone (Fig. 10a and b). Mean values and the coefficient of variation (CV) of all sampling zones in an area revealed mean transit times of 51 (CV = 18%), 57 (CV = 44%), and 47 (CV = 34%) years, and mean groundwater travel distances of 326 m (CV = 40%), 576 m (CV = 49%), and 219 m (CV = 59%) in the upland, transition, and lowland area, respectively. Variability was higher for distances than for times. The transition area had the highest mean groundwater travel distance, though even in this area circulation remained local according to Tóth's flow structure definitions (Tóth, 1963, 2009), because flow lines did not extend under any streams. Even the maximum of the mean groundwater travel distances in the three areas were small compared to the size of the catchment (9 km from south to north and 5 km from east to west) at 751, 1741, and 648 m in the upland, transition, and lowland area, respectively. The mean distance between two streams was ca. 1000 m upland and 600 m lowland indicating a denser stream network in the lowland area. Only 0.1% of the flow lines connected

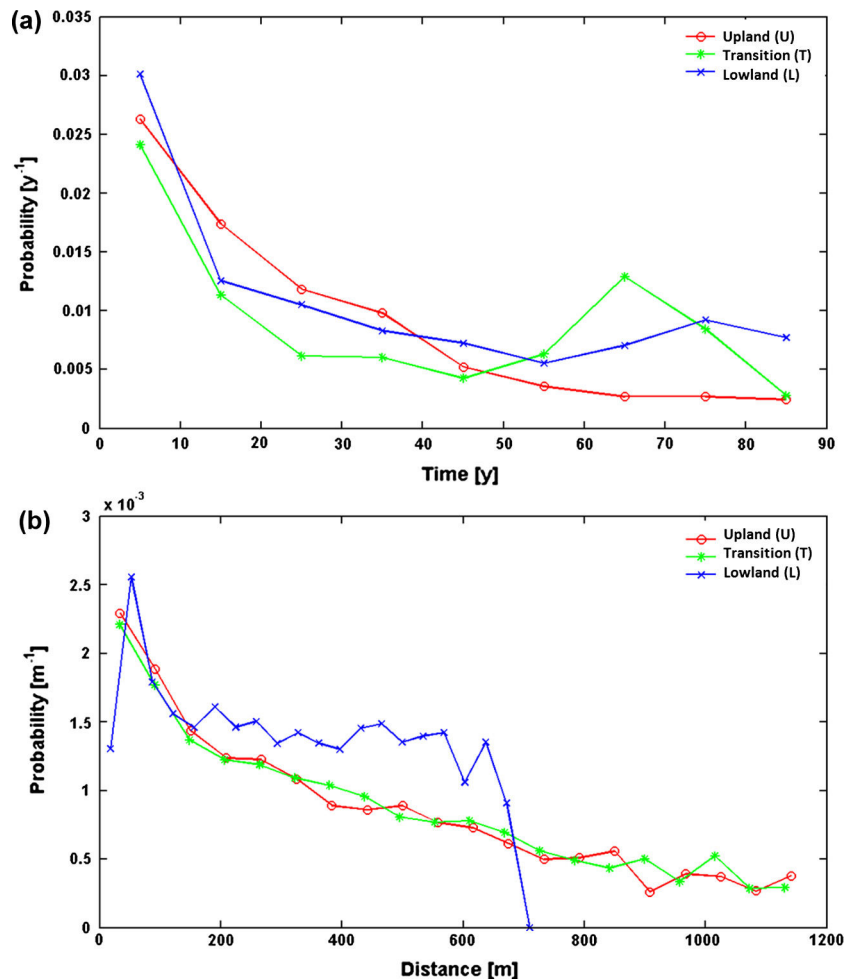


Fig. 9. Representative plots of (a) transit time distributions and (b) groundwater travel distance distributions taken from three sampling zones each belonging to a different catchment area (upland, transition, lowland). The transit time is defined as the time a water molecule spends between the recharge location and the sampling zone. Transit times show an exponential-like distribution. The groundwater travel distance distribution was shorter in the lowland area than in the upland and transition area.

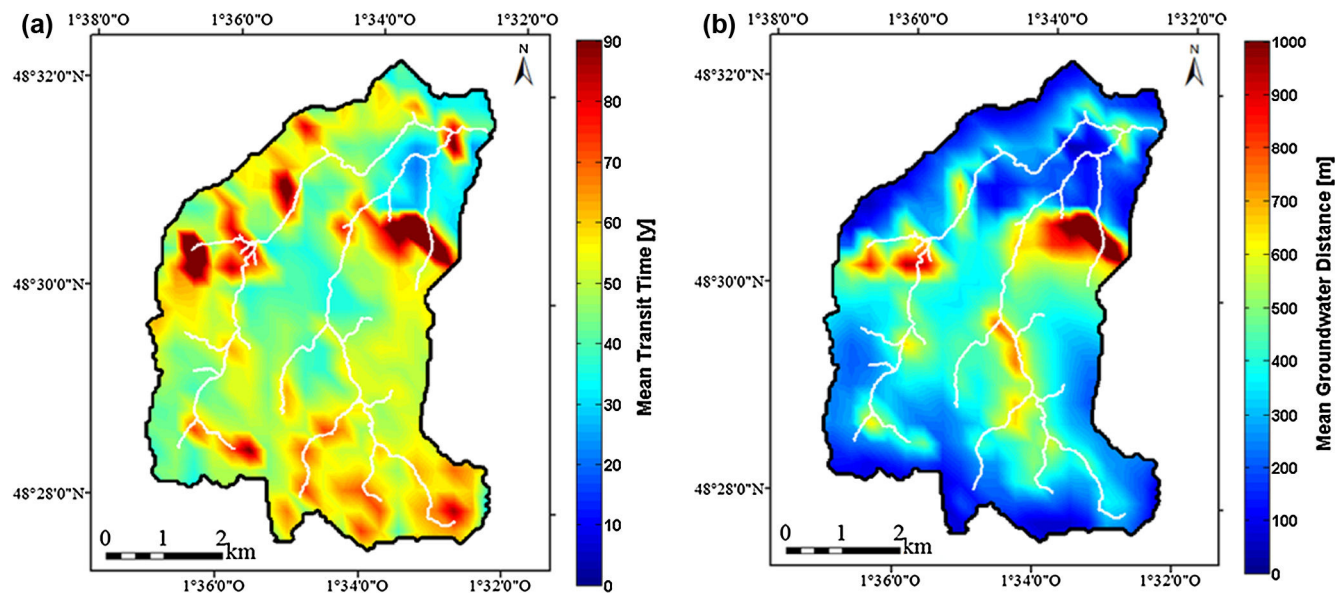


Fig. 10. Spatial analysis of the Pleine-Fougères aquifer in regards to (a) mean transit times, and (b) mean groundwater travel distances, obtained by interpolating the results of 278 sampling zones. The transit time is defined as the time a water molecule spends between the recharge location and the sampling zone. Contours of the maps correspond to the catchment boundaries (black polygons).

the upland and lowland area without going under a stream, indicating a dominance of local, rather than intermediate or regional flow. Groundwater flow lines were generally oriented along the east–west direction, except in the transition zone where flow moved primarily from south to north (Fig. 6). Some flow lines intersected the surface along the stream network or just down-slope of the steep transition, consistent with observations of springs and surface water in the catchment. The groundwater table was close to the surface, showing groundwater outcropping at 80% of the total length of the stream channel throughout the catchment, though the groundwater table was more connected with the land surface in the lowland than upland area (Table 4). Some long groundwater flow lines crossed the boundary of the hydrological catchment, but they did not approach the boundary of the modeled domain (Fig. 6).

3.2. Groundwater circulation and $r_{\text{GW-LOCAL}}$

For the whole aquifer, groundwater circulation remained local with larger groundwater travel distances than the reference distances. Fig. 11 shows the three representative sampling zones for the upland, transition and lowland area of the reference model with the origin of the groundwater and reference flow lines. For the lowland and transition sampling zone, both recharge areas partially overlapped with a larger groundwater recharge area. For the upland sampling zone with higher topographical gradients, recharge areas only overlapped at the sampling zone showing groundwater flow lines and reference flow lines coming from an

opposite direction. This is possible because this sampling zone was not in the seepage area and all cases of overlapping and non-overlapping may occur.

The relationship between the ratio $r_{\text{GW-LOCAL}}$ (mean groundwater travel distance divided by the mean of the reference distance) and the proportion of saturated fraction related to the subsurface volume of the reference model revealed different controls for the upland and lowland area (Fig. 12). In the upland area, the saturated fraction filled less than 95% of the subsurface volume with a ratio $r_{\text{GW-LOCAL}}$ of 1.6. The groundwater table was recharge controlled showing larger distances with deeper circulations than in the lowland area. The groundwater flow in the upland area was more influenced by the hydrogeological conditions than the topographical gradients. Groundwater flow was limited by the fresh bedrock which prevented larger circulation. In the lowland area the groundwater table was limited by the topography with the saturated fraction filling more than 95% of the subsurface volume and a ratio $r_{\text{GW-LOCAL}}$ of 1.3. Due to the high groundwater table elevation, the groundwater flow was mainly affected by the topography. Flow lines were shallow and they followed the topographical gradients from the closest topographical height (the recharge location) to the discharge location (sampling zone). For the whole aquifer, $r_{\text{GW-LOCAL}}$ was 1.7, meaning that the mean groundwater travel distances were nearly twice as long as the mean of the local reference distances.

3.3. Alternative models

To test how our model assumptions influenced the results of the reference model, which indicated that groundwater circulations were local (<1 km) and mean transit times were quite long (51 years), we ran simulations of the four alternative models presented in Section 2.2. Our comparison was based on the characteristic mean transit times and mean groundwater travel distances for the full aquifer and the individual upland, transition, and lowland area (Table 3). Despite structural differences, the five models gave similar groundwater table heights, with a maximum mean difference of 2.2 m between the most different models (REF and AHC), meaning that all five models had a similar aquifer volume.

Table 4

Intersection rate of the groundwater table with the surface at stream channels for the five models (REF: reference model, THICK: model with thicker weathered zone, THIN: model with thinner weathered zone, AHC: model with higher hydraulic conductivity in granite, HOM: homogeneous model). Rate is expressed as the percentage of the connected length to the full stream length.

	REF	THICK	THIN	AHC	HOM
Catchment (%)	77	85	85	68	82
Upland (%)	97	94	98	100	96
Lowland (%)	70	82	79	56	76

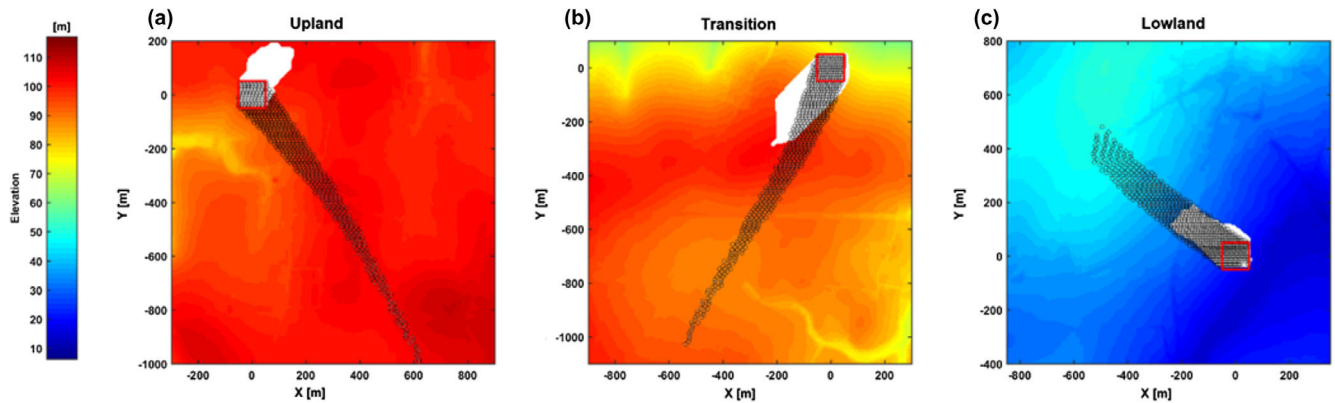


Fig. 11. Groundwater contributing areas (black circles) to the sampling zones (red squares): (a) upslope, (b) transition, and (c) downslope. White recharge areas are derived from the local reference distances. For each of the three plots, the corresponding elevation of the land surface is presented in colors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

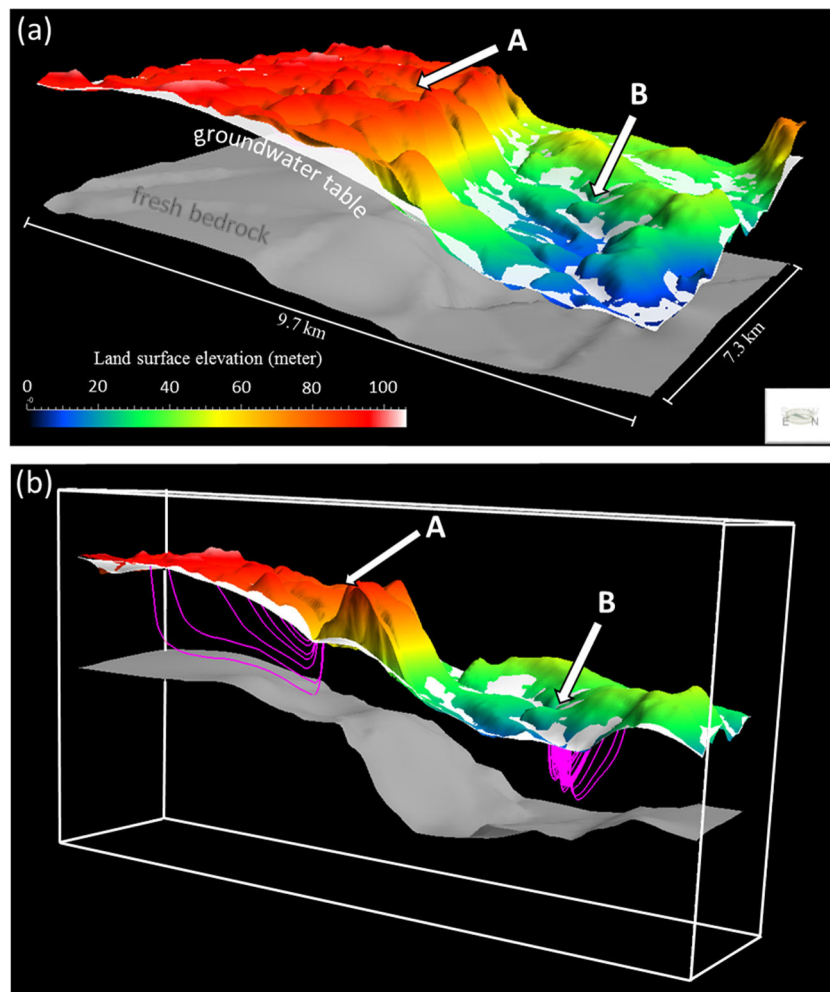


Fig. 12. Land surface (in color), groundwater (white) and fresh bedrock elevation (grey) of the model domain. Flow lines are presented for the lowland area, which had a topography controlled groundwater table, and the upland area, which had a recharge controlled groundwater table. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Mean transit times of the aquifer, like aquifer volumes, given by the five models were less variable than mean groundwater travel distances influenced by permeability and topography structures. Except for the homogeneous model (HOM), mean transit times were similar between models both for the whole aquifer and the

individual upland, transition, and lowland areas, though this result is not surprising since all models were calibrated using the same groundwater age data. HOM was different because sampling was performed over the full depth of the model (90 m), whereas the other models were limited by the impervious bedrock, resulting

in a shallower aquifer thickness (around 60 m; Table 3), and in mean transit times that were substantially larger for HOM. While mean transit times were highly sensitive to the overall aquifer volume, mean groundwater travel distances were consistent between models, showing greater sensitivity to topography and geological structure. The alternative hydraulic conductivity model (AHC), which had highly pervious granite upland and less pervious schist lowland showed much larger mean groundwater travel distances upland than the reference model (566 m for AHC and 326 m for REF; Table 3). Higher permeability in the upland area decreased hydraulic head gradients, resulting in a lower water table for AHC. Consequently, topography played a smaller role and groundwater distances were larger upland. The abrupt reduction of permeability by a factor of 10 from upland to lowland shortened the mean groundwater travel distance in the transition area from 576 m to 398 m. In the THICK model, with a thicker weathered zone, there was marginally more circulation through the transition area relative to the reference model (639 m versus 576 m) and the opposite effect was observed for the THIN model. However, mean groundwater travel distances were the same or smaller relative to REF in the upland area for both the THICK and THIN model (REF = 326 m, THICK = 296 m, THIN = 313 m).

4. Discussion

In this study we used groundwater flow models of a crystalline unconfined aquifer in Brittany, France to investigate the importance of local flow paths and to identify groundwater table controls at the small catchment scale. We hypothesized that relatively old groundwater would have traveled long distances from the recharge location to the sampling zone with increasing distances towards the catchment outlet. Contrary to our hypothesis we found highly local groundwater flow, with groundwater traveling less than 500 m on average (Table 3), and groundwater travel distances decreasing moving lowland (Table 3). To localize the flow circulation we used the ratio of groundwater travel distances derived by the numerical model to reference distances from the DEM. Topographical gradients were the major controls on groundwater flow in the lowland area whereas recharge dynamics governed the groundwater table in the upland area with a strong influence of the hydrogeological conditions on groundwater circulation. These results represent a departure from the historical conceptualization of the small-catchment hydrology (Tóth, 1963, 2009) with potentially important water source and water quality implications.

4.1. Patterns of groundwater circulation in shallow aquifers

Circulation was highly local for all models across a range of weathered and fractured zone thicknesses, not extending below stream beds, indicating a general lack of intermediate and regional flow paths (Gburek and Folmar, 1999). We were particularly interested in identifying mechanisms underlying this behavior, because local groundwater flow is sensitive to local permeability and topography structure, which can be very diverse at the sub-kilometer scale. Several dynamics could explain the contrasting circulation pattern we observed in the upland and lowland area of all models, including the limited aquifer thickness, topographical gradients and groundwater table configuration. The ratio $r_{\text{GW-LOCAL}}$ clearly showed a stronger influence of the topography on the flow circulation in the lowland area than in the upland area. Whether linked groundwater travel distances and topographical gradients promote short groundwater flow lines is readily testable and should be confirmed with a more systematic study on synthetic topographical structures (Crave and Davy, 2001; Lague

et al., 2000) and by comparing trends in multiple catchments (Thomas et al., 2016b).

Based on the reference model (REF) we wanted to demonstrate how the ratio $r_{\text{GW-LOCAL}}$ and the proportion of the saturated fraction in relation to the subsurface volume evolve under varying recharge and constant hydraulic conductivity conditions (Fig. 13). To analyze the change between recharge and topographical control, we performed simulations with several recharge rates ranging from 1/10 average recharge (16.7 mm a^{-1}) to 4 times average recharge (668 mm a^{-1}). Fig. 13 shows how groundwater flow circulation change depending on the groundwater table configuration which is in general related to hydraulic conductivity and the recharge rate. For a four-fold higher recharge rate (Fig. 13a) the groundwater table moved closer to the land surface and flow lines got shorter over the whole domain than for the initial recharge rate R (Fig. 13b), especially in the upland area. Also the flow lines followed more topographical gradients. Under a lesser recharge rate (Fig. 13c) the groundwater table is deeper and less connected to the land surface inducing longer groundwater travel distances. Most of the flow lines that started in the upland area traveled longer distances towards the lowland area. For the three example recharge rates we presented, not only the length of the groundwater travel distances, but also flow directions changed. Under topography controlled conditions ($4R$, Fig. 13a) flow lines are more east–west oriented due to local topographical roughness, whereas under recharge controlled conditions ($R/10$, Fig. 13c) flow lines follow the steep slope in south–north direction, again demonstrating the link between hydrogeological and topographical controls. The extent of the hydrogeological active zone varied proportionally to the induced recharge rate and the limiting depth coming from the unaltered bedrock. Particularly in the upland area, the groundwater table elevation was more susceptible to changes in recharge and deeper flow lines were limited by the fresh bedrock.

We propose the ratio of groundwater travel distance to reference distance ($r_{\text{GW-LOCAL}}$) as a useful tool to quantify the spatial extent of the groundwater circulation. The evolution of $r_{\text{GW-LOCAL}}$ with the proportion of the saturated fraction in relation to the subsurface volume at differing recharge levels give an indication of the recharge versus topography controls on the groundwater table and therefore on flow dynamics (Fig. 14). The ratio $r_{\text{GW-LOCAL}}$ decreased as the saturated fraction increased, reaching 1 when the saturated fraction exceeded 95% of the subsurface volume. This meant that when the aquifer filled the whole subsurface volume (groundwater table at the land surface), groundwater distances became similar to reference distances derived by the DEM, and topography mainly influenced the groundwater circulation. By contrast, a recharge controlled regime developed as the saturated fraction decreased and $r_{\text{GW-LOCAL}}$ became larger than 1. $r_{\text{GW-LOCAL}}$ decreased linearly with an increase of the saturated fraction despite increasing dispersion, i.e. longer flow lines due to greater distances between the land surface and the water table. The ratio $r_{\text{GW-LOCAL}}$ showed a distinct asymptotic behavior for the upland and lowland area. While the overall pattern was similar, the ratio $r_{\text{GW-LOCAL}}$ responded more strongly to changes in the extent of the saturated fraction in the upland area. This suggest two distinct regimes, one for the upland and the other for the lowland area (Fig. 14). The ratio $r_{\text{GW-LOCAL}}$ varied strongly ranging from 0.03 to 7.47 (lower quartile = 1.0 and upper quartile 2.2) dependent on the applied recharge rate, though the groundwater travel distance with their respective transit times remained larger than the reference distances in most areas. These results underline the need for a local analysis of groundwater table controls in small catchments and provide the ratio $r_{\text{GW-LOCAL}}$ to perform this analysis. While the criterion of Haitjema and Mitchell-Bruker (2005) is relevant to quantify topography and recharge controls at larger scales, our criterion is appropriate at smaller scales and for shallow aquifers.

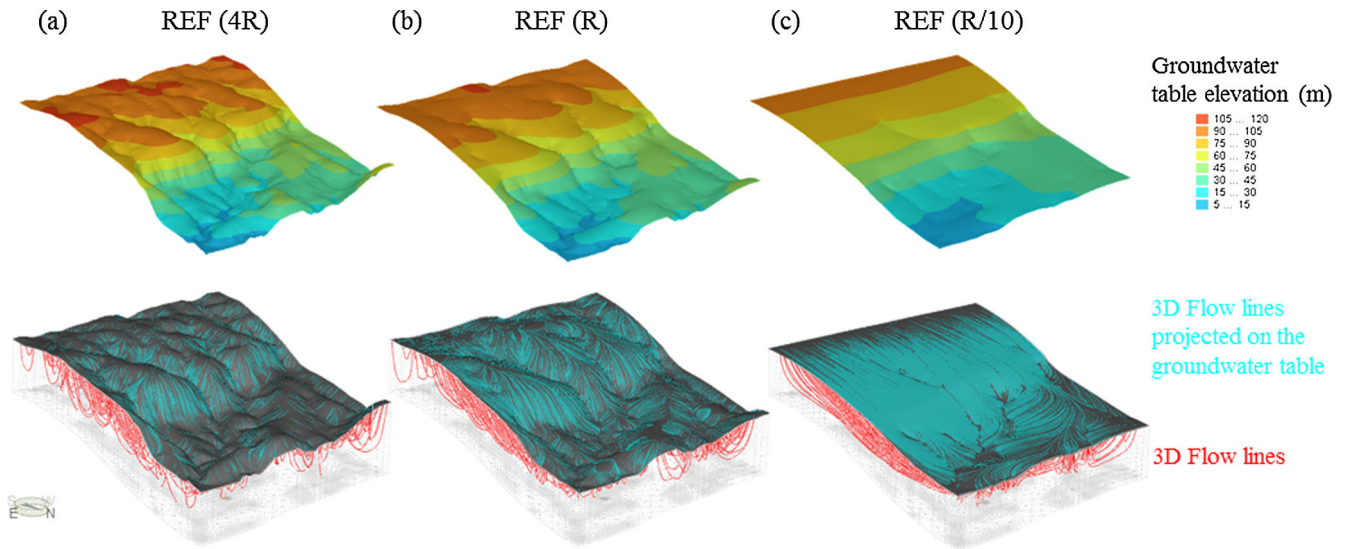


Fig. 13. Groundwater table elevations (colored plane) and 3D flowlines for the reference model (REF) with different recharge rates: (a) 668 mm y^{-1} , (b) 167 mm y^{-1} , and (c) 16.7 mm y^{-1} . 3D flowlines are represented in red in the flow domain and in blue projected on the top of the model i.e. the free surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

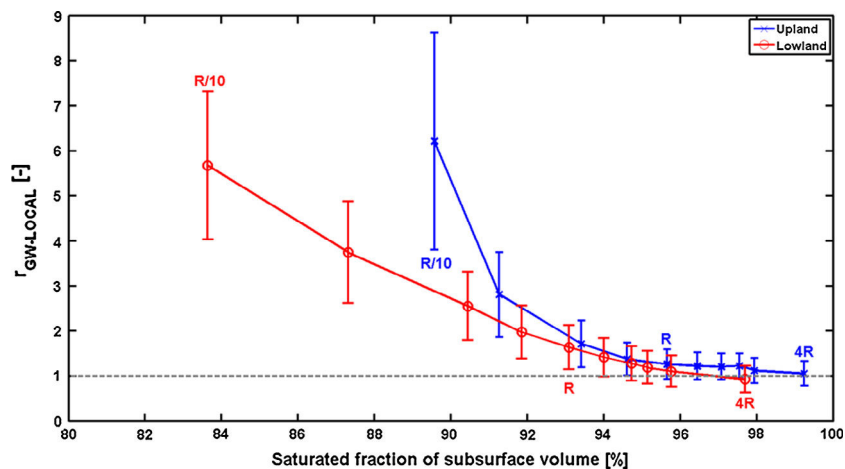


Fig. 14. Ratio $r_{\text{GW-LOCAL}}$ [-] of groundwater distance over local reference distance as a function of the proportion of the saturated fraction in relation to the whole subsurface volume [%] for the upland (red circled line) and lowland areas (blue crossed line). Mean values with their standard deviation are given for recharge rates from $R/10$ to $4R$. The grey line indicates a ratio $r_{\text{GW-LOCAL}}$ equal to 1 corresponding to topography controlled conditions. As the Recharge increases from $R/10$ to $4R$ both zones become topography controlled with a saturated zone filling more than 95% of the subsurface volume. Below 95% the groundwater table is recharge controlled. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.2. What does old and local flow mean for water quality?

Our results revealed that groundwater mean transit times and groundwater travel distances in this aquifer do not fit within the concept of local, intermediate and regional groundwater flow (Tóth, 1963, 2009) but that the majority of groundwater occurred within the shallow, weathered zone. While flow remained local, mean transit times were surprisingly long with mean transit times greater than 50 years. These mean transit times are much larger than values typically used in models forecasting water quality in shallow aquifers (Ayraud et al., 2008; Molénat et al., 2013). One of the implications of this finding is that any changes in land use or agricultural practice may take decades to influence groundwater quality. This time-lag between changes in management and potential improvements of water quality, complicates the evaluation of the efficacy of efforts to protect water quality such as fertilizer reduction or land cover change because cause and effect are so

temporally separated. Current water quality should therefore be related to past land-use and the duration of monitoring programs should be scaled depending on the distribution of transit times. Another implication of the long mean transit times observed here is that trends in groundwater quality could be influenced by long-term changes in water balance. Because the rate of recovery of a polluted aquifer depends largely on water turnover time, changes in groundwater recharge resulting from shifts in precipitation and evapotranspiration could strongly influence groundwater chemistry independent of any changes in land management. Marked latitudinal differences in climate projections of water balance in Europe (Forzieri et al., 2014) suggest a shortening of transit times (and associated recovery times) in northern Europe and a lengthening of transit times in southern Europe.

The second finding, that most groundwater stays highly local, traveling an average of less than 500 m from where it entered the aquifer, reinforces the importance of addressing groundwater

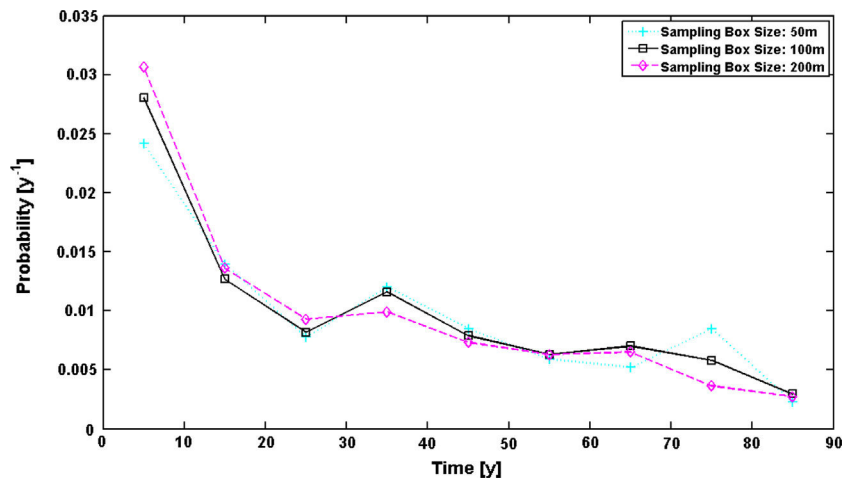


Fig. A.1. Transit time distributions for 50×50 m, 100×100 m, and 200×200 m sampling zone sizes showed no significant variations. Three sampling zones, centered at the same location, are designed to sample the entire groundwater column.

quality at highly local scales including plot-level scales of individual fields. The topography and recharge control on the groundwater table and therefore on groundwater travel distances during high and low flows, suggests that a reconsideration is warranted of the role of landscape features such as riparian zones, hedgerows, and groundwater surface water exchange zones in mitigating diffuse nitrogen pollution originating from groundwater via a temporally dynamic modeling approach. On a general note, it is worthwhile to notice that the transit time and travel distance distributions could not have been derived from each other because of their different shapes (i.e. independent modeling of these parameters were necessary). Only both distributions together reveal detailed information about the water source and the time spent in the aquifer.

Our results highlight several interesting phenomena regarding groundwater dynamics in shallow aquifers. In surface waters such as rivers and streams, water comes from large catchments very quickly, while groundwater systems in small catchments have old water coming from very local sources. The surface water contributing area increases moving downstream as catchment size increases. Conversely, from our study and other recent work (Gburek and Folmar, 1999), groundwater “catchments” seem to stay the same size or even decrease moving downslope, due to shifts in topographical controls and recharge dynamics. These distinct hydrological and landscape-level patterns mean that surface waters are more likely to be impacted by acute or diffuse pollution since they drain a larger region, but that quick transit time and small water volume mean contaminants can quickly be transported away or diluted. Groundwater systems are much more modular and are therefore potentially less likely to experience pollution. However, if there is a local contaminant source, long transit times and limited long-distance water exchange means that the impact may be extreme and long-lasting.

5. Conclusion

The comprehensive analysis of several numerical groundwater flow models developed for a shallow hard-rock aquifer in Brittany, France gave insights in internal flow structures that are impossible to measure in the field. The unconfined aquifer was dominated by local flow circulation that was more vulnerable to contamination than deeper flows. The mean length of groundwater flow paths was limited to a few hundred meters (334 m), while the mean

transit times were on the order of decades (51 y). A clear distinction could be drawn between the upland, transition, and lowland area for flow circulation and mean transit times, with greatest mean transit times and mean groundwater travel distances in the transition area followed by the upland and then the lowland area. Transit time distributions had an exponential-like distribution in the upland and lowland area, whereas the transition area showed a bimodal distribution. An examination of circulation in the upland and lowland area revealed distinct controls on the groundwater table and therefore on the flow behavior despite identical recharge conditions. We proposed the ratio $r_{\text{GW-LOCAL}}$ as an index of whether the groundwater table is limited by the topography or determined by the recharge rate at the small catchment scale, complementing the regional criterion of Haitjema and Mitchell-Bruker (2005; see Eq. (1)). At this site, the ratio $r_{\text{GW-LOCAL}}$ has proved a robust tool to describe the extent of groundwater circulation, and its generality should be tested between catchments (Thomas et al., 2016b).

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Appendix A

See Fig. A.1.

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3.3 Bilan

A travers l'analyse spatialisée des circulations souterraines et l'inférence des temps de résidence associés à ces circulations, ce chapitre montre bien que la grande majorité des écoulements souterrain en milieu cristallin sont locales et que les aquifères cristallins sont majoritairement drainés par la rivière la plus proche. Les écoulements souterrains ont donc lieu au sein d'un même versant. L'emboîtement des circulations souterraines qui peut survenir dans des aquifères sédimentaires relativement homogènes avec des profondeurs de sédimentation conséquente [Toth, 1963] ne sont pas représentatives des écoulements en milieu cristallin typique de la Bretagne. Cependant, dans le même temps, les temps de résidence associés à ces mêmes circulations sont, de manière contre intuitives, relativement longues (plusieurs décennies).

Les processus d'écoulements en milieu cristallin fracturé sont donc assez locaux (l'ordre d'une distance ligne de crête à la rivière soit en Bretagne une distance de l'ordre du km) mais relativement long. Cette information sur les processus d'écoulement trace une voie intermédiaire d'articulation entre données et modèles, qui tire parti de l'influence majeure de la topographie sur les écoulements souterrains dans les aquifères de proche subsurface. Cette voie se situe à mi-chemin entre, d'une part, les approches semi-explicites développées dans cette partie au Chapitre 1 et au Chapitre 2 et d'autre part, les approches explicites distribuées développées dans ce chapitre. Cette voie, c'est celle d'une modélisation semi-distribuée à l'échelle du versant, du fait de l'observation faite précédemment, qui est que les écoulements souterrains, dans leur majorité, n'excèdent guère le versant. Cette voie, c'est aussi celle d'une inférence de propriétés sur les données et de leur reproduction via des modèles et des expériences synthétiques pour en tirer une compréhension des processus. En effet, la calibration est coûteuse à développer ne serait-ce que pour un site comme celui de Pleine Fougères et pour un nombre de données relativement limité (données d'âge de l'eau, débit en régime permanent, données spatialisées topographiques et géologiques). L'intégration des données en grand nombre et particulièrement des observations de télédétection, ne peut se faire qu'avec des modélisations spatialisées, rendant compte de la diversité des sites d'étude, mais qui soit en même temps, suffisamment versatile pour être applicable à large échelle sur un grand nombre de versant. C'est donc l'objectif des modèles développés dans la troisième partie.

Partie III Stratégie de modélisation du flux et du transport à l'échelle du versant : un modèle à base physique parcimonieux

Modéliser de manière mécaniste les écoulements de l'eau dans un bassin versant demeure la méthode de choix pour comprendre, comparer et prédire l'importance des différents contrôles qui jouent pour former la qualité de l'eau en rivière. Cependant, comme cela a été déjà évoqué dans le chapitre précédent, ce type de modélisation se heurte à la complexité induite par le déploiement de modèles distribués à l'échelle globale ou même à l'échelle régionale [Fatichi et al., 2016; Paniconi and Putti, 2015]. Ce type de modèle lorsqu'ils existent concernent la plupart du temps des étendues relativement homogènes et non pas des géologies cristallines à la topographie menant à de petits bassins versants de l'ordre de quelques centaines de kilomètres carrés comme c'est le cas en Bretagne (Figure 22). L'intégration d'un grand nombre de données hétérogènes dans ce type de modèle par le moyen de la calibration se heurte ainsi à de nombreux défis (voir Partie IV Chapitre 5) [Goldstein and Coco, 2015; Hinnell et al., 2010; Kirchner, 2006]. En effet, l'intégration de chaque type de données requiert la description mécaniste du ou des processus conduisant à l'observation de ces données. L'ajout d'une paramétrisation adaptée à chaque processus engendre ainsi un nombre important d'inconnus dans le cadre d'une modélisation distribuée (menant à des problèmes équi-finalité [Beven, 2006]). D'autre part, une fois calés, ces modèles ne font presque jamais l'objet d'une actualisation grâce aux données qui ont été récemment collectées dans le cadre de programme de suivi.

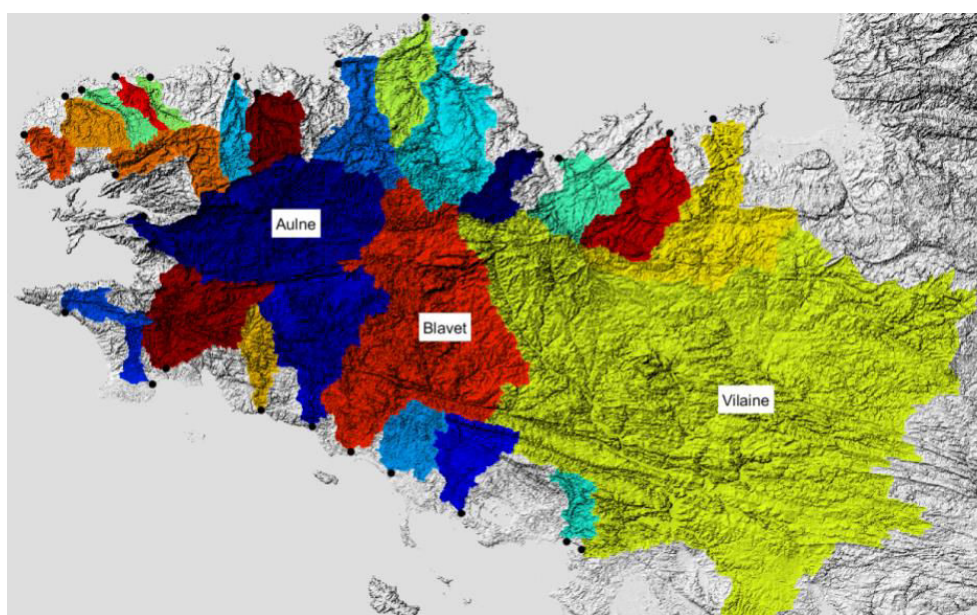


Figure 22: Découpage de la Bretagne en bassins versants. Hormis la Vilaine, le Blavet et l'Aulne, la Bretagne se caractérise par de petits bassins versants côtiers (quelques centaines de kilomètres carrés). D'après [Courtois et al., 2018].

La calibration ne permet donc que difficilement, et avec un coût important, une intégration massive des données collectées. Par exemple pour les données de géochimie introduites au chapitre précédent (CFCs, ^{85}Kr , DSI), la seule intégration de données géochimiques qui a été réalisée dans le modèle est l'intégration de données géochimiques supposés conservatives (et non réactives) comme les CFCs. L'utilisation de la silice pour dater les temps de résidence des circulations souterraines s'est ainsi faite avec un modèle implicite avec un priori basé sur la physique (le choix de l'inverse gaussienne comme LPM).

Nous proposons donc une démarche de modélisation intermédiaire, basé sur la physique des écoulements en milieu souterrain. Cette démarche de modélisation se base sur la représentation d'un processus clef pour la dynamique des écoulements en milieu souterrain, celui du partitionnement entre les écoulements de nappes, écoulements lents, et les écoulements de subsurface, écoulements rapides [Fan and Bras, 1998; Kirkby, 1985]. Dans le Chapitre 1, nous modélisons leur interaction via un processus à effet de seuil qui lie le volume stocké dans l'aquifère aux quantités de flux de subsurface pouvant être généré à travers la prise en compte de l'interaction entre le niveau de la nappe et la topographie. Plus le volume de l'aquifère augmente, plus le toit de la nappe est haute, plus l'aire de suintement sera étendue, plus la quantité de ruissellement sera important et plus la réponse du bassin versant aux précipitations sera « rapide ». Ce cadre de modélisation lie donc le stock au flux via un processus non linéaire simple (effet de seuil lorsque la nappe intersecte la topographie) qui pourrait être complexifié pour être plus réaliste.

D'autre part, cette démarche de modélisation repose sur une discrétisation du bassin versant avec des paramètres semi-distribués par rapport à des caractéristiques propres du bassin versant. Ces caractéristiques peuvent par exemple être la manière dont ce bassin versant est organisé par rapport à son réseau de rivières (e.g. largeur du bassin versant en fonction de la distance à la rivière, profil de pente du bassin versant sur un transect évoluant perpendiculairement à la rivière). Cette modélisation présente l'avantage 1. d'être basée sur la physique et d'offrir une interprétation via l'explicitation des processus dominants ; 2. de conserver une certaine spatialisation des écoulements via l'intégration de modèles de versant discrétisés par rapport à la distance à la rivière. Ces modèles présentent enfin l'avantage de rester « tractable » numériquement.

C'est sur la base de ce modèle décrivant le flux dans l'aquifère et dans le sol par l'intermédiaire de ruissellements de subsurface que nous développons ensuite un schéma de suivi particulier (Chapitre 2). Ce schéma consiste à résoudre le transport conservatif de manière lagrangienne en injectant des particules proportionnellement au flux de précipitations nettes. Une fois ce transport advectif résolu, nous ajoutons quelques étapes de posttraitement pour prendre en compte la dispersion opérée par le milieu souterrain ainsi que les interactions entre la nappe et la surface qui conduisent à générer du ruissellement dans les horizons les plus perméables du sol.

C'est cette approche parcimonieuse et à base physique qui nous permettra dans le dernier chapitre de cette partie de simuler, après une étape de calibration minimale, les variations saisonnières de concentrations en silice observées dans des bassins versants bretons (Chapitre 3). C'est de cette confrontation entre modèles et données qu'on peut inférer des comportements sur la structure et le fonctionnement de la zone critique en général et de celle des bassins versants bretons représentatifs des milieux cristallins en particulier. Nous nous intéresserons en particulier dans ce chapitre à partitionner les écoulements en rivière entre eaux jeunes et eaux plus âgées.

Chapitre 1 Modéliser le flux : Couplage des écoulements souterrains en aquifères avec les écoulements de proche subsurface dus à des processus de ruissellements

1.1 Introduction

Un processus clef de l'écoulement en milieu océanique humide typique de la Bretagne est le partitionnement entre les écoulements de surface / subsurface et les écoulements de nappe. Ce partitionnement varie durant une année hydrologique à cause du battement saisonnier de la nappe. En effet, en hiver et au début de printemps, le toit de la nappe est haut puisque la quasi-totalité des précipitations contribuent à l'infiltration (très peu d'évapotranspiration). Ce faisant, la nappe intersecte les couches les plus perméables du sol et la zone altérée et favorise un ruissellement de surface / subsurface, alimenté par la nappe, aussi appelé suintement (*seepage* ou *return flow*). De plus, l'infiltration tombant directement sur ces sols quasiment saturés favorisent des écoulements de proche subsurface (*lateral flow*) ou de surface (*overland flow*) tous deux constituant le ruissellement (*runoff* ou *subsurface stormflow*) (Figure 23). Au contraire en été et en fin d'automne, la nappe est au plus bas (comme la période est plus sèche et la quasi-totalité des précipitations alimentent l'évapotranspiration) et la nappe soutient l'étiage. C'est cette variation saisonnière (Figure 23) dont on suspecte qu'elle contribue significativement à la variation intra-annuelle de la qualité de l'eau dans les cours d'eau (Figure 24).

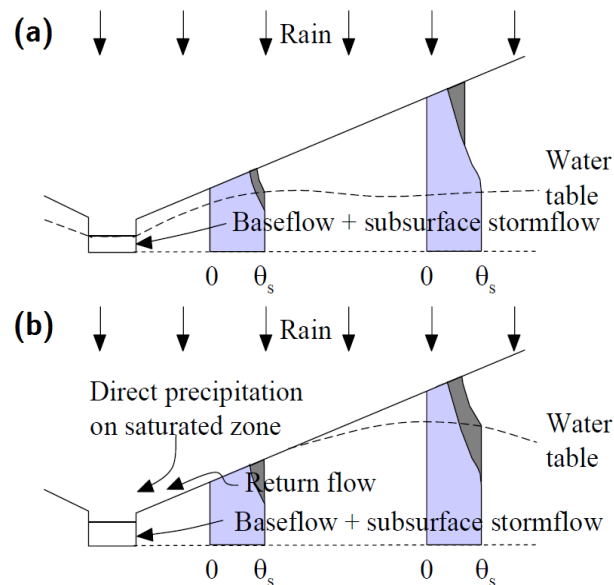


Figure 23: Variation saisonnière entre écoulements rapides, temporaires de ruissellements et écoulements lents, pérennes de nappes. D'après [Kirkby, 1985].

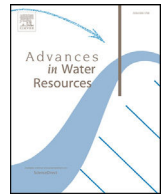
Cependant, cette interaction entre écoulements rapides et écoulements lents est difficile à modéliser parce que c'est un effet de seuil. Numériquement, ces équations sont souvent instables à résoudre. Ceci est également dû au fait que ce système d'équations aux dérivées partielles sont dites à surface libre, c'est-à-dire que la position de la nappe n'est pas prescrite *a priori* ce qui ne facilite pas la résolution de l'équation. De plus, à une distance x de la rivière (i.e. à un endroit donné), le changement de régime hydrologique se traduit par un changement de système : lorsque la nappe n'intersecte pas la surface, c'est un système différentiel qui régit l'évolution du stock d'eau et du débit dans l'aquifère ; lorsque la nappe intersecte la topographie, le stock de l'aquifère à cet endroit reste constant et c'est un système

algébrique qui régit la quantité de suintement qui ruisselle. De plus, étant donné que le stock d'eau à cet endroit est fixé et à son maximum, le débit souterrain est aussi à son maximum. Par conséquent, le ruissellement se détermine algébriquement en fonction de la quantité d'infiltration qui tombe (ruissellement direct ou « *overland flow* ») et de l'éventuel « rétrécissement » de la nappe (latéralement ou verticalement) qui induit un flux de suintement (« *return flow* ») (Figure 23).

Dans cette partie, nous établissons donc un système d'équations différentielles algébriques qui décrivent l'écoulement en milieu souterrain à l'aide des équations de Boussinesq et le processus de ruissellement par un effet de seuil. Nous proposons une méthode de régularisation pour résoudre ce système d'équations différentielles algébriques et résolvons ce système en flux et en volume à l'aide d'une discrétisation avec des éléments mixtes hybrides. Cette méthode de résolution avec régularisation est appliqué aux équations 1D « *hillslope storage Boussinesq* » mais pourrait être appliqué à des modèles 2D [Troch et al., 2003].

Nous vérifions la capacité de ce modèle à conserver la masse à la fois globalement et à l'échelle locale des éléments discrétisés. Cette propriété est due à la discrétisation en éléments finis mixtes hybrides. D'autre part, nous étudions les propriétés de convergence spatiale de ce modèle ainsi que la convergence par rapport au paramètre de régularisation. Enfin, nous évaluons la robustesse de cette formulation à l'aide d'une étape d'expériences numériques intensives réalisées à partir d'une analyse des versants classiquement rencontrés en Bretagne et avec des chroniques de pluie enregistrées sur des observatoires Bretons.

1.2 Article: Dynamic coupling of subsurface and seepage flows solved within a regularized partition formulation



Dynamic coupling of subsurface and seepage flows solved within a regularized partition formulation



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ABSTRACT

Hillslope response to precipitations is characterized by sharp transitions from purely subsurface flow dynamics to simultaneous surface and subsurface flows. Locally, the transition between these two regimes is triggered by soil saturation. Here we develop an integrative approach to simultaneously solve the subsurface flow, locate the potential fully saturated areas and deduce the generated saturation excess overland flow. This approach combines the different dynamics and transitions in a single partition formulation using discontinuous functions. We propose to regularize the system of partial differential equations and to use classic spatial and temporal discretization schemes. We illustrate our methodology on the 1D hillslope storage Boussinesq equations (Torch et al., 2003). We first validate the numerical scheme on previous numerical experiments without saturation excess overland flow. Then we apply our model to a test case with dynamic transitions from purely subsurface flow dynamics to simultaneous surface and subsurface flows. Our results show that discretization respects mass balance both locally and globally, converges when the mesh or time step are refined. Moreover the regularization parameter can be taken small enough to ensure accuracy without suffering of numerical artefacts. Applied to some hundreds of realistic hillslope cases taken from Western side of France (Brittany), the developed method appears to be robust and efficient.

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1. Introduction

Under the same term, runoff gathers several processes of different origins including infiltration excess overland flow and saturation excess overland flow (Bonell, 1998; Freeze and Harlan, 1969; Horton, 1933; Kirkby, 1978; McGlynn et al., 2002). While infiltration excess overland flow is controlled by rainfall intensity and surface properties like roughness (Darboux et al., 2002; Horton, 1933; Smith and Goodrich, 2006), saturation excess overland flow is generated by subsurface flow and saturation dynamics (Dunne and Black, 1970; Sophocleous, 2002). It occurs locally in so-called saturated source areas (Ogden and Watts, 2000) when the soil column is saturated up to the surface (Dunne, 1978; Musy and Higby, 2004). It comes from precipitation that cannot infiltrate (sometimes called direct precipitations onto saturated areas) and from

subsurface flows that exfiltrate and return to the surface, i.e. seepage flow or return flow (Dunne and Black, 1970). Once the soil column remains fully saturated, the subsurface flux stabilizes, remaining equal to the product of the soil transmissivity by the local hydraulic gradient. At the surface, fluxes can be highly variable depending on exfiltration and precipitations dynamics. Saturated source areas are found at the bottom of slopes, in the vicinity of rivers, in wetlands where water table can quickly rise up to the surface as well as upslope in slope hollows that force flowpaths to converge and exfiltrate (Birkel et al., 2015; Brutsaert, 2005; Fan and Bras, 1998; Torch et al., 2002). Subsurface and saturation excess overland flow have been proven to be important for providing water for evapotranspiration (Maxwell and Condon, 2016), enhancing erosion (Fox and Wilson, 2010), increasing groundwater flooding risks (Bauer et al., 2006; Habets et al., 2010; Holman et al., 2009; Kreibich and Thieken, 2008; Miguez-Macho and Fan, 2012), shaping the residence time distribution (Harman, 2015; Rinaldo et al., 2015; Tetzlaff et al., 2014) maintaining anoxic conditions in the soil and promoting denitrification hotspots (Pinay et al., 2015).

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There is a sharp transition when infiltration and subsurface flows do no longer sustain the full saturation of the soil column (Vivoni et al., 2007). Overland flow vanishes, a partially saturated area develops in lieu of the saturated source area, the water table falls down below the surface and subsurface flow becomes dynamic and non-linearly dependent on saturation. Such transitions between so-called fully saturated and partially saturated regimes are spatially variable and dynamic. They have been modelled by coupling shallow water and groundwater equations (Barthel and Banzhaf, 2016; Camporese et al., 2010; LaBolle et al., 2003) either by an exchange of fluxes (Govindaraju and Kavvas, 1991; Markstrom et al., 2008; Panday and Huyakorn, 2004) or by assigning the shallow water equations as a boundary to the groundwater equations (Kollet and Maxwell, 2006). Another method is to solve the groundwater equations for a prescribed position of the saturated source areas (Beaugendre et al., 2006; Bresciani et al., 2014; 2016) and to iterate until convergence is met (Diersch, 2013; Harbaugh, 2005). The seepage front (defined as the intersection of the subsurface water table with the land surface) is deduced accordingly (Anderson et al., 2015; Batelaan and De Smedt, 2004) and saturation excess overland flow is eventually derived from mass balance computations.

While these integrated hydrological surface-subsurface models (for a comprehensive review, see Fatichi et al., 2016) are adapted to well instrumented catchments or critical zone observatories, they require high computation capacities (Putti and Paniconi, 2004) and a lot of data to be calibrated with (Reggiani et al., 1998) making them difficult to parametrize because of their long run time. They are also prone to equifinality issues (Beven, 2006) and are sometimes subject to numerical instabilities (Doherty and Christensen, 2011). For applications where the only available information are a DEM, the rainfall time series and a discharge time series, non intensive process-based models have been proposed (Broda et al., 2012; Troch et al., 2003) but, to the best of our knowledge, they do not take into account the non linearity, described above, coming from the dynamic interactions between the water table and the land surface.

Here, we propose an integrated approach to simultaneously solve the subsurface flow, locate the potential saturated source areas and deduce the generated saturation excess overland flow. This approach is well suited to the sharp transitions presented previously. We hypothesize that surface processes can be simplified as follows. We assume instantaneous flood routing as surface flows are some orders of magnitude faster than subsurface flows (Dunne and Black, 1970; Fan and Bras, 1998). We consider infiltration processes as negligible. In temperate climates, most of the saturation excess overland flow occurs downhill and only a small amount of this flow is likely to infiltrate (Musy and Higy, 2004).

We model subsurface flow with the Boussinesq hydraulic groundwater theory based on Darcy's law and Dupuit–Forchheimer assumption (Boussinesq, 1877; Brutsaert, 2005; Troch et al., 2013). It expresses that hydraulic head responds to flow through transmissivity feedbacks without inertial effects (Bishop et al., 2011; Rodhe, 1987). We work at the hillslope scale with the hillslope storage Boussinesq equations (Troch et al., 2003), which include the geologic, pedologic and geomorphologic controls on subsurface flow dynamics (Bachmair and Weiler, 2012; Freer et al., 1997; Lanni et al., 2013; Savenije, 2010). They indeed model subsurface flow at the soil/bedrock interface (Freer et al., 2002; Tromp-van Meerveld and McDonnell, 2006), which is the most likely to generate saturation excess overland flow in humid and steep terrains with conductive soils (Weiler et al., 2006). They have also been extended to model the coupling between shallow and deep groundwater flow (Broda et al., 2012).

First, we describe the partially saturated and fully saturated flow regimes that can be encountered on hillslopes following the

two cases of Fan and Bras (1998) (Section 2.1) and combine them in a partial differential system deriving from partition considerations (Section 2.2). We regularize this system for numerical integration, discretize it spatially with a mixed finite element scheme and obtain a system of differential equations (Section 2.3). Second, we validate the method and analyse its convergence properties (sections 3.1 and 3.2). Finally we discuss its efficiency and robustness on realistic hillslope cases (Section 3.3).

2. Methods

We first recall the hillslope storage Boussinesq equations (Hilberts et al., 2004; Paniconi et al., 2003; Troch et al., 2003) and add to them the overflow condition when saturation reaches the surface. We show how the two regimes of partial and total saturation are generally formalized and further propose an alternative integrated partition formulation. The issued differential discontinuous equations are then regularized for numerical integration and spatially discretized with a mixed finite element scheme.

2.1. Hillslope storage Boussinesq equations

2.1.1. Case 1: subsurface flow only

Below land surface, when the soil is not fully saturated, only subsurface flow occurs. Hillslope storage Boussinesq equations physically describe the relation between subsurface flow and saturation (Troch et al., 2003, case 1 of Fig. 1a). Following Dupuit–Forchheimer assumption, discharge is proportional to the saturated thickness. Discharge is further integrated transversally to the main slope direction to yield a 1D continuity problem where discharge is also proportional to the width w (m) of the transect profile (Fig. 1b). The other key physical characteristic of the hillslope is its slope θ (rad) describing the mean evolution of the soil layer height. The integrated flux over the transect $Q(x, t)$ ($\text{m}^3 \text{s}^{-1}$) is linked to the subsurface water storage $S(x, t)$ (m^2) through the following set of equations:

$$\begin{cases} \frac{\partial S}{\partial t}(x, t) = -\frac{\partial Q}{\partial x}(x, t) + N(t)w(x) \\ Q(x, t) = -\frac{kS(x, t)}{f} \left(\cos \theta \frac{\partial}{\partial x} \left(\frac{S}{fw} \right)(x, t) + \sin \theta \right) \\ 0 \leq S(x, t) \leq S_c(x) \\ S(x, t) < S_c(x) \text{ or } -\frac{\partial Q}{\partial x}(x, t) + N(t)w(x) < 0 \end{cases} \quad (1)$$

where x (m) represents the distance to the channel varying between 0 at the river and L at the water divide, N (m s^{-1}) is the infiltration, k (m s^{-1}) is the hydraulic conductivity, f (-) is the drainable porosity. The subsurface water storage $S(x, t)$ is defined in Troch et al. (2003) by $S(x, t) = fw(x)h(x, t)$ where h is the groundwater elevation height (m) (Fig. 1). $S(x, t)$ cannot exceed the maximum subsurface water storage S_c (m^2) defined by $S_c(x) = fw(x)d$ where d (m) is the soil depth. For illustration purposes and with no loss of generality, we assume in what follows that k , f , θ and d are constant. The first equation of system (1) is the mass balance equation stating that the temporal variation of storage results from the local variation of subsurface flows and from the infiltration. The second line is Darcy's equation, integrated vertically and laterally, written as a function of the subsurface water storage S . The third equation just reminds that S is positive and cannot exceed the maximum subsurface water storage S_c . This system applies as long as the condition of the fourth line is fulfilled,

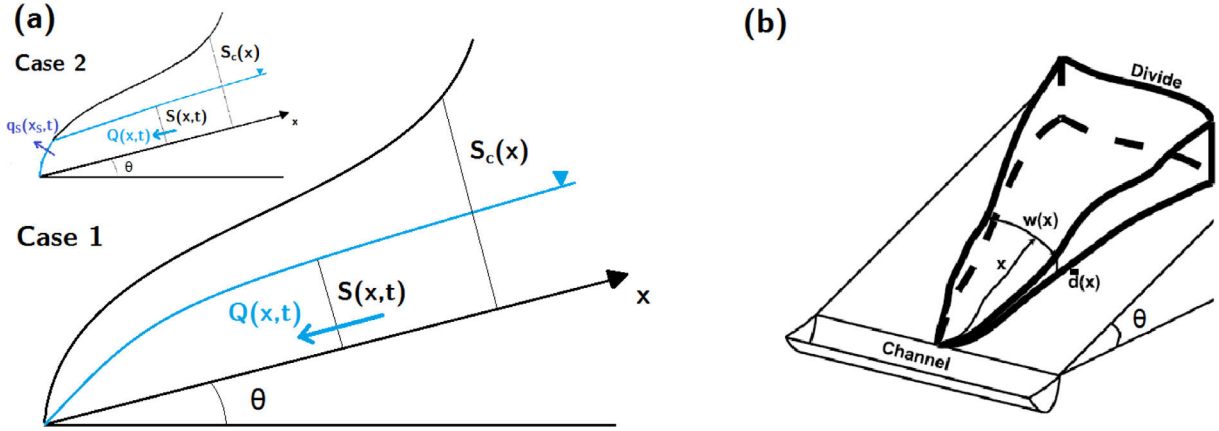


Fig. 1. (a) Cross-section view of the hillslope with a constant slope θ . The water table location $S(x, t)$ is indicated in blue. The subsurface flux $Q(x, t)$ is marked by the blue arrow. The saturation excess overland flow $q_s(x_s, t)$ (case 2) is materialized by the purple arrow and the surface by $S_c(x)$. Cases 1 and 2 represent partially saturated and locally fully saturated hillslopes respectively. (b) 3D view of the hillslope with an illustration of the width function $w(x)$ (Adapted from Troch et al., 2003). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

i.e. for partially saturated soil columns ($S(x, t) < S_c(x)$) or for fully saturated soil columns desaturating ($-\frac{\partial Q}{\partial x}(x, t) + N(t)w(x) < 0$).

2.1.2. Case 2: subsurface flow and dynamic saturation excess overland flow

If, at the location x_s , the soil is fully saturated and there is a positive flux balance, the excess in the flux balance is identified to the saturation excess overland flow q_s ($\text{m}^2 \text{s}^{-1}$) as it cannot be assigned to storage temporal variations ($\frac{\partial S}{\partial t}(x_s, t) = 0$, case 2 of Fig. 1a). The system of equations becomes:

$$\begin{cases} q_s(x_s, t) = -\frac{\partial Q}{\partial x}(x_s, t) + N(t)w(x_s) \\ \frac{\partial S}{\partial t}(x_s, t) = 0 \\ Q(x_s, t) = -\frac{kS_c(x_s)}{f} \left(\cos \theta \frac{\partial}{\partial x} \left(\frac{S_c}{fw} \right)(x_s, t) + \sin \theta \right) \\ S(x_s, t) = S_c(x_s) \text{ and } -\frac{\partial Q}{\partial x}(x_s, t) + N(t)w(x_s) \geq 0. \end{cases} \quad (2)$$

The fourth line ensures that the soil is fully saturated and that there is a positive flux balance ($-\frac{\partial Q}{\partial x}(x_s, t) + N(t)w(x_s) \geq 0$). As shown by the first equation, saturation excess overland flow is made up of two terms representing the seepage flow ($-\frac{\partial Q}{\partial x}$) and the direct precipitations onto saturated areas (Nw) (Dunne and Black, 1970).

Solving the dynamic transition between these two regimes (essentially due to interactions between the soil water table and the land surface) requires to change of system of equations (system (1) or (2)) depending on the state of saturation and subsurface flow (S and Q). It is the last equation in systems (1) and (2) that controls the transition.

2.2. Partition problem

To avoid switching between regimes and equation sets, we propose an alternative partition formulation. This formulation reconciles systems (1) and (2) in a single system by partitioning the incoming flux $-\frac{\partial Q}{\partial x} + Nw$ in the variation of the subsurface water

storage $\frac{\partial S}{\partial t}$ and in the saturation excess overland flow q_s :

$$\begin{cases} \frac{\partial S}{\partial t}(x, t) + q_s(x, t) = -\frac{\partial Q}{\partial x}(x, t) + N(t)w(x) \\ q_s(x, t) = \mathcal{G}\left(\frac{S(x, t)}{S_c(x)}\right) \mathcal{R}\left(-\frac{\partial Q}{\partial x}(x, t) + N(t)w(x)\right) \\ Q(x, t) = -\frac{kS(x, t)}{f} \left(\cos \theta \frac{\partial}{\partial x} \left(\frac{S}{fw} \right)(x, t) + \sin \theta \right) \\ 0 \leq S(x, t) \leq S_c(x). \end{cases} \quad (3)$$

$\mathcal{G}$ (Fig. 2a) is the function defined in $[0, 1]$ by $\mathcal{G}(u) = \mathcal{H}(u - 1)$, $\mathcal{R}$ is the ramp function (Fig. 2b) defined in $\mathbb{R}$ by $\mathcal{R}(u) = u \mathcal{H}(u)$, where $\mathcal{H}$ is the Heaviside step function (Fig. 2c):

$$\begin{aligned} \mathcal{H}: \quad \mathbb{R} &\longrightarrow \{0, 1\} \\ u &\longmapsto \begin{cases} 0 & \text{if } u < 0 \\ 1 & \text{if } u \geq 0. \end{cases} \end{aligned} \quad (4)$$

In fact, system (3) can be readily expressed as a partition formulation by rewriting its first two equations:

$$\begin{cases} \frac{\partial S}{\partial t}(x, t) = \left(1 - \mathcal{G}\left(\frac{S(x, t)}{S_c(x)}\right) \mathcal{R}\left(-\frac{\partial Q}{\partial x}(x, t) + N(t)w(x)\right) \right) \left(-\frac{\partial Q}{\partial x}(x, t) + N(t)w(x) \right) \\ q_s(x, t) = \left(\mathcal{G}\left(\frac{S(x, t)}{S_c(x)}\right) \mathcal{R}\left(-\frac{\partial Q}{\partial x}(x, t) + N(t)w(x)\right) \right) \left(-\frac{\partial Q}{\partial x}(x, t) + N(t)w(x) \right). \end{cases} \quad (5)$$

It is the quantity $\mathcal{G}(S/S_c) \mathcal{R}(-\partial Q/\partial x + Nw)$ that triggers the dynamic transitions between the two regimes. When it is null, system (3) reduces to (1). When it is equal to 1, system (3) reduces to (2).

The fourth line of system (3) ensures that the subsurface water storage S remains positive and lower than S_c .

2.3. Numerical methods

System (3) is a set of partial differential equations with discontinuous right-hand sides which can be formally defined in the weak sense of distributions. To solve the partial differential system (3) numerically, $\mathcal{G}$ is challenging because of its discontinuity at

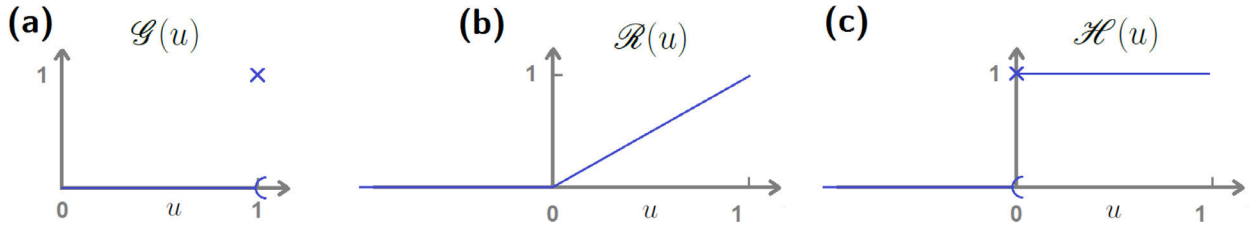


Fig. 2. Illustration of (a) the discontinuous function $\mathcal{G}$ (b) the ramp function $\mathcal{R}$ (c) the Heaviside function $\mathcal{H}$ defined by Eq. (4).

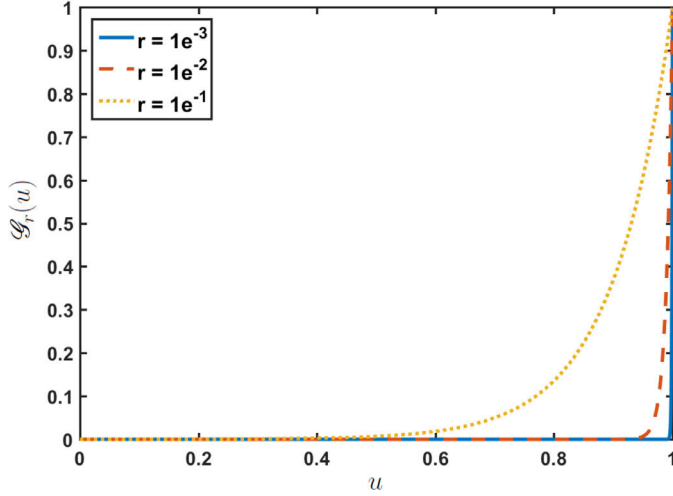


Fig. 3. Function $\mathcal{G}_r$ regularized from function $\mathcal{G}$ (Fig. 2). Function $\mathcal{G}_r$ is defined by Eq. (6) and represented for different values of the regularization parameter r .

$u = 1$. Various numerical techniques exist to handle the discontinuous functions present in partial derivatives systems (Agosti et al., 2015; Bouillard et al., 2007; Hoffmann et al., 2016; Kumar et al., 2014). System (3) can be rewritten, still in a weak sense, as a non linear complementarity problem, solved with a semi-smooth Newton method (De Luca et al., 1996; Pang and Gabriel, 1993). Here, to solve system (3), we choose to regularize the discontinuous function $\mathcal{G}$, discretize in space using a mixed finite element method and use classic methods for temporal integration (variable-step, variable-order solver).

2.3.1. Regularization

To smoothen the transition between partially and fully saturated regimes, we use the convex function $\mathcal{G}_r$ (Haddou and Migot, 2015) defined by:

$$\mathcal{G}_r : [0, 1] \longrightarrow [0, 1]$$

$$u \longmapsto \exp\left(-\frac{1-u}{r}\right) \quad (6)$$

where $r > 0$. The regularized function $\mathcal{G}_r$ converges to $\mathcal{G}$ when r tends to 0. The function $\mathcal{G}_r$ is continuous in $[0, 1]$, convex and differentiable in $[0, 1]$. The left derivative in 1 ($\lim_{x \rightarrow 1^-} \mathcal{G}_r'(x) = \mathcal{G}_r'(1^-) = \frac{1}{r}$) ensures a sharp transition between the partially and fully saturated regimes. The regularization coefficient $r > 0$ controls the stiffness of the transition between the two states (Fig. 3).

Replacing the discontinuous function $\mathcal{G}$ by its continuous counterpart $\mathcal{G}_r$ leads to the system:

$$\begin{cases} \frac{\partial S}{\partial t}(x, t) + q_S(x, t) = -\frac{\partial Q}{\partial x}(x, t) + N(t)w(x) \\ q_S(x, t) = \mathcal{G}_r\left(\frac{S(x, t)}{S_c(x)}\right) \mathcal{R}\left(-\frac{\partial Q}{\partial x}(x, t) + N(t)w(x)\right) \\ Q(x, t) = -\frac{kS(x, t)}{f} \left(\cos\theta \frac{\partial}{\partial x}\left(\frac{S}{f_w}\right)(x, t) + \sin\theta\right) \\ 0 \leq S(x, t) \leq S_c(x) \end{cases} \quad (7)$$

2.3.2. Space and time discretization

We discretize the 1D hillslope in N_x elements and use a mixed finite element method to derive from the system (7) estimates of the soil storage S , the subsurface flux Q and the excess overland flux q_S (Douglas and Roberts, 1985). S and q_S are discretized at the cell centres and Q at their edges following the classic mixed finite element methodology. As for regular grids, finite differences lead to the same expression as mixed finite element (Chavent and Roberts, 1991), we express spatial derivatives by their finite difference approximation. In practice, the continuity equation (third equation in system (7)) is discretized at the cell centres and the integrated Darcy equation (second equation of system (7)) is discretized at the edges. Q and $\frac{\partial}{\partial x}\left(\frac{S}{f_w}\right)$ are defined at the cell edges by imposing their continuity between two adjacent cells. The multiplicative factor $\frac{kS}{f}$ at the cell edge is taken as the arithmetic average between the neighbouring cell centres. The discretization in space of the system (7) eventually leads to a semi-discrete system of ordinary differential equations. We use the variable time step and variable order ode15s MATLAB® solver based on the backward differentiation formulas (BDF) of orders 1–5 (Shampine et al., 1999).

2.3.3. Metrics for convergence analysis

We define the metrics for the convergence analysis of the discretization scheme using a discrete L^2 norm. Let $\{t_i, i = 1, \dots, N_t\}$ a set of given times in $[0, T]$ with $t_0 = 0$ and $\{x_k, k = 1, \dots, N_{ref}\}$ a set of given points in $[0, L]$ with $x_0 = 0$. We define the discrete norm of a function $f(x, t)$ with given values $f(x_k, t_i)$ by:

$$\|f\|^2 = \sum_{i=1}^{N_t} \sum_{k=1}^{N_{ref}} |f(x_k, t_i)|^2 (t_i - t_{i-1}) (x_k - x_{k-1}) \quad (8)$$

In order to compare a function f with a reference function g , we introduce the relative error metric ϵ_f defined by:

$$\epsilon_f = \frac{\|f - g\|}{\|g\|} \quad (9)$$

with adapted computations when f and g display different spatial discretization schemes. In practice, the times t_i are provided by user-defined external time-steps and the points x_k are cell centres or cell edges of a reference mesh.

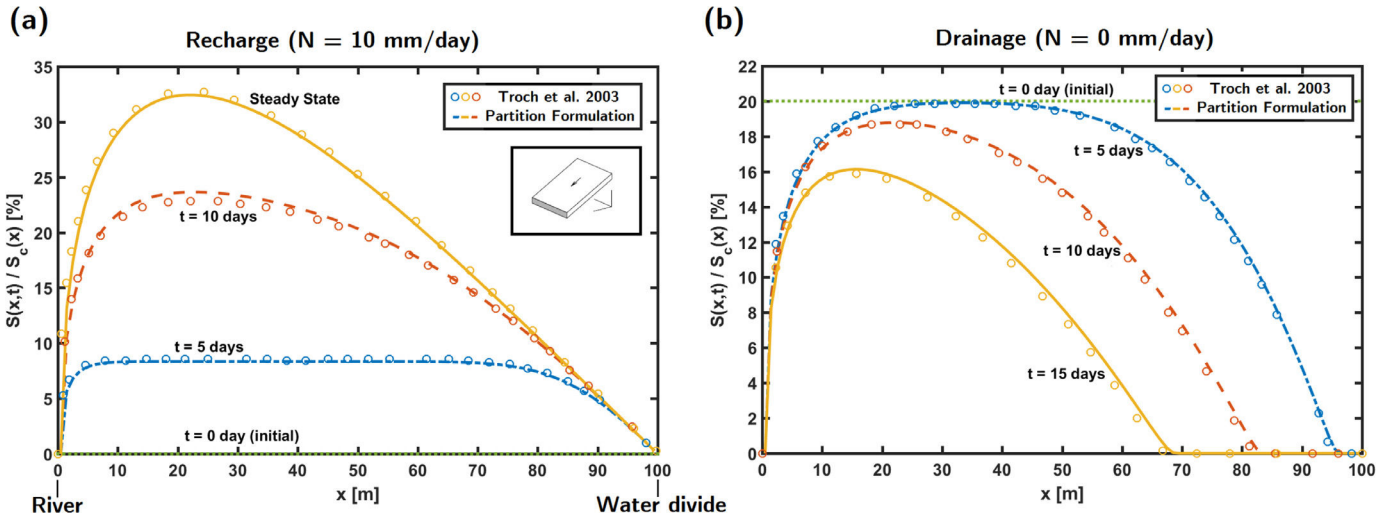


Fig. 4. Relative subsurface water storage $S(x, t)/S_c(x)$ (expressed in %) along the hillslope for the (a) recharge and (b) drainage experiments. Insert shows a sketch of the hillslope of slope 5% (Troch et al., 2003).

3. Results

We assess the partition formulation (7) discretized with a mixed finite element scheme on several numerical experiments. We use two numerical experiments of Troch et al. (2003) without any overland flow generated for the first one, and with locally saturated hillslope for the second one. We also design experiments with transitions from purely subsurface flow dynamics to simultaneous subsurface and saturation excess overland flows. On this latter experiment, we exhibit that the choice of the discretization scheme preserves the mass balance, we determine the convergence of the spatial discretization scheme, analyse the internal time steps influence and assess the sensitivity of the partition formulation to the regularization parameter r . Third we carry extensive numerical testing to assess the robustness of the regularized partition formulation on realistic experiments.

3.1. Comparison with previous numerical experiments

3.1.1. Case without overland flow

We check the partition formulation (7) on the numerical experiments of Troch et al. (2003). We choose the straight hillslope experiments with a slope of 5% as it is the less likely to fully saturate the soil column and to generate saturation excess overland flow. For this case, boundary conditions are $S(x=0, t)=0$ at the channel outlet and $Q(x=L, t)=0$ at the water divide. The hillslope is 100 m long, spatially discretized with $N_x=100$ elements. We apply a regularization parameter $r=1 \times 10^{-3}$ and consider two infiltration cases. The first case is a recharge experiment with a constant infiltration ($N=10 \text{ mm d}^{-1}$) on an initially dry hillslope ($S(x, t=0)=0$). The second case is a free drainage experiment ($N=0 \text{ mm d}^{-1}$) on a hillslope initially partially saturated (uniformly saturated at 20% of its maximum capacity i.e. $S(x, t=0)=0.2 \times S_c(x)$).

Fig. 4 shows a close agreement of the two methods in both recharge and drainage experiments with the marked storage accumulation near the river (left part of the graphs). The sharp saturation gradient next to the river comes from the imposed Dirichlet condition of zero storage at the river. This test demonstrates the consistency of our numerical approximation of system (7) with the method of Troch et al. (2003) which is based on the discretization of system (1).

3.1.2. Case with overland flow

We further assess the partition formulation on a steep convergent hillslope (insert of Fig. 5, slope of 30%, Troch et al., 2003). The hillslope saturates close to its outlet. It is initially partially saturated, $S(x, t=0)=0.2 S_c(x)$, and progressively drains to the river where the saturation remains imposed $S(x=0, t)=0$. Hillslope is limited on its upper side by a water divide condition $Q(x=L, t)=0$.

The saturation profiles and the subsurface flow to the river remain close to those of Troch et al. (2003) (Fig. 5). The main benefit of the partition formulation (7) is to provide the saturation excess overland flow generated both spatially and temporally, which amounts to 16% of the total outflow to the river (Fig. 5b). The river outflow is not bounded by the limited interface of the subsurface to the river in this convergent configuration. It may be significantly enhanced by the generation of saturation excess overland flow when the water table intercepts the land surface (Fig. 5b).

3.2. Saturation excess overland flow on a convergent hillslope

To check that the saturation excess overland flow is well modelled, we consider a steep periodic hydrologic forcing $N(t)$ on a hillslope with another convergent shape (shown in insert of Fig. 6, Troch et al., 2003). Both the convergence of the hillslope and the high value of infiltration tend to generate saturation excess overland flow with dynamically generated fully saturated areas. Boundary conditions are modified at the river to fully saturated soil ($S(x=0, t)=S_c(x)$) but remain no flow at the water divide ($Q(x=L, t)=0$). Initially, the hillslope is dry ($S(x, t=0)=0$). $N(t)$ is a square wave with a period of 10 days and values alternating between 0 and 30 mm d^{-1} . We spatially discretize the hillslope with $N_x=100$ elements and apply a regularization parameter $r=1 \times 10^{-3}$.

Starting from dry conditions, hillslope progressively fills with quickly rising saturation next to the river because of the convergence conditions (Fig. 6a or Video 1 in the supplementary material). The saturation profile at $t=12$ days does not show any seepage while at $t=26$ days and at $t=35$ days, an extended seepage front has developed in the 20 m next to the river. Even though saturation profiles are close at $t=26$ days and $t=35$ days, seepage is almost twice as large at $t=26$ days because of the presence of direct precipitations onto saturated areas (Fig. 6b or Video 1). At $t=35$ days, only seepage flow occurs. Breakdown of the mass

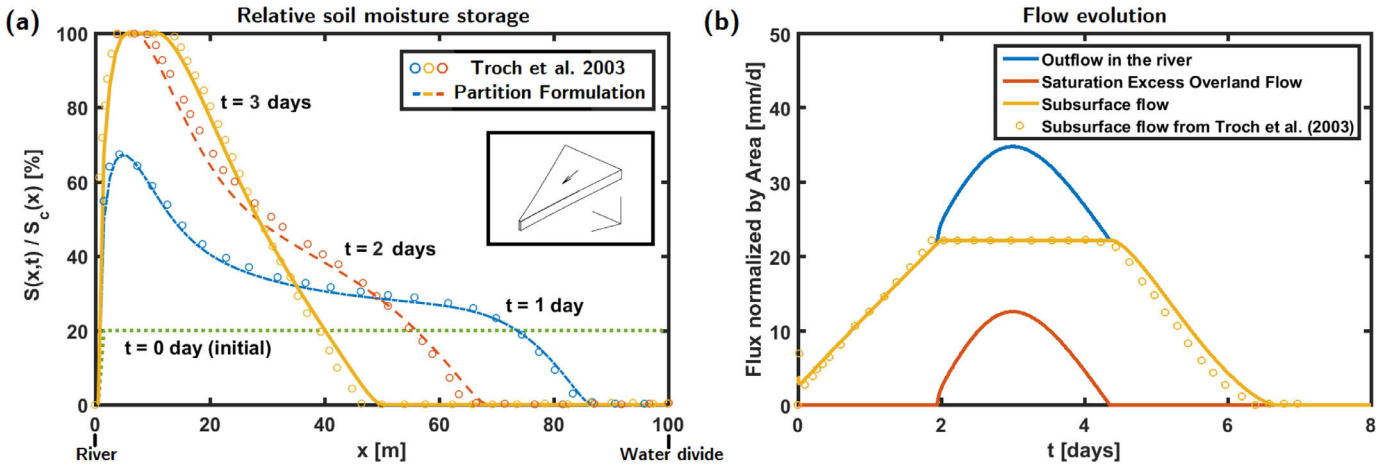


Fig. 5. (a) Relative subsurface water storage $S(x, t) / S_c(x)$ (expressed in %) along the 30% sloping convergent hillslope shown in the insert (Troch et al., 2003) during the drainage of partially saturated initial conditions. (b) Outflow evolution in the river for the same drainage experiment.

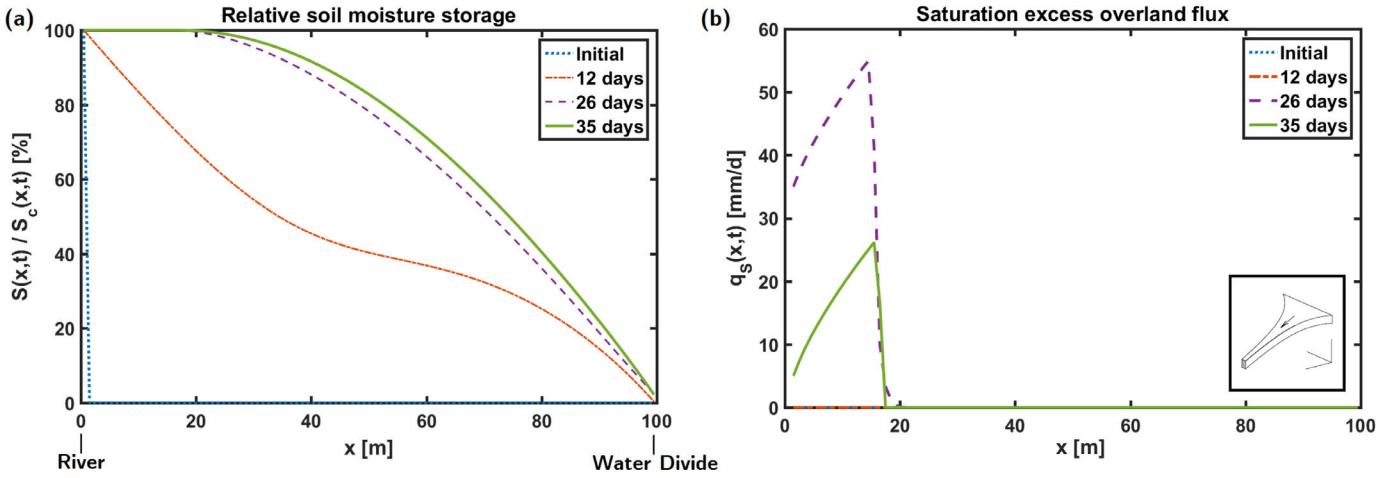


Fig. 6. (a) Subsurface water storage and (b) Saturation excess overland flow profile along a convergent hillslope. Sketch of the convergent hillslope is shown in the insert (Troch et al., 2003).

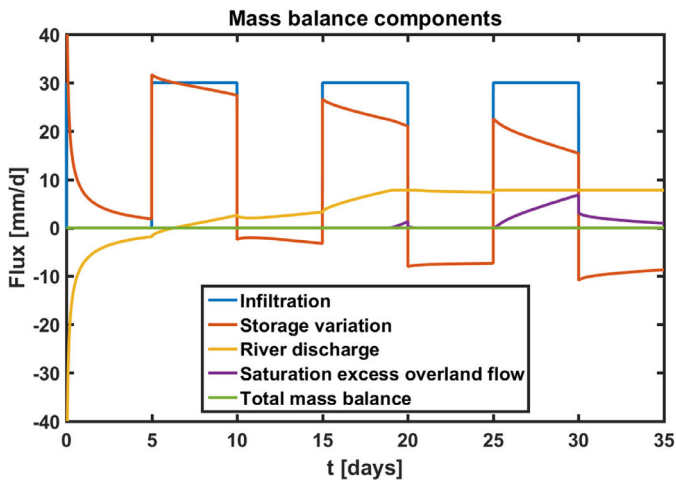


Fig. 7. Temporal evolution of the terms of the hillslope mass balance (first equation in system (7)) in terms of storage variation, river discharge and saturation excess overland flow. The sum of the terms (the mass balance error) remains equal to 0.

balance at the hillslope scale shows the partition of the incoming infiltration in global storage variations, saturation excess overland flow generated and outflow in the river (Fig. 7 or Video 1). Despite

the intermittent infiltration, the discharge in the river is steadily increasing because of the progressive filling of the hillslope after the dry initial conditions. Discharge in the river remains always larger than the saturation excess overland flow.

3.2.1. Mass balance error analysis

Interest of the mixed finite element scheme is to preserve mass balance at the scale of the discretized spatial elements. A detailed analysis of the local mass balance error with the numerical experiment described previously shows that statistics (mean and 99th percentile) carried on the spatial and temporal distributions of the mass balance errors are of the order of $10^{-13} \text{ m}^3 \text{ s}^{-1}$ and remain smaller than the tolerance of the ode15s solver (absolute tolerance fixed at $10^{-10} \text{ m}^3 \text{ s}^{-1}$). When normalized by the forcing terms (second line of Table 1), mass balance errors are not found significative (in average equal to 1.6×10^{-7}). Thus the applied spatial discretization scheme guarantees local mass conservation. At the scale of the entire hillslope, Fig. 7 illustrates this mass balance preservation globally.

3.2.2. Convergence with the spatial discretization

Following the convergence metrics defined in Eq. (9), we compare different simulations of the same numerical experiments with N_x varying between 300 and 700 to the reference simulation composed of 1100 cells. The regularization parameter r is fixed to

Table 1

First line: statistics on the mass balance error ($\text{m}^3 \text{s}^{-1}$) for the 100 discretized elements of the hillslope. Second line: mass balance statistics (-) normalized by the rainfall (30 mm d^{-1}). Absolute tolerance of the ode15s solver was set to 10^{-10} for this numerical experiment.

	Mean	Std	1st percentile	99th percentile
Mass balance ($\text{m}^3 \text{s}^{-1}$)	3.0×10^{-13}	6.0×10^{-12}	0	3.8×10^{-13}
Normalized mass balance (-)	1.6×10^{-7}	3.2×10^{-6}	0	2.0×10^{-7}

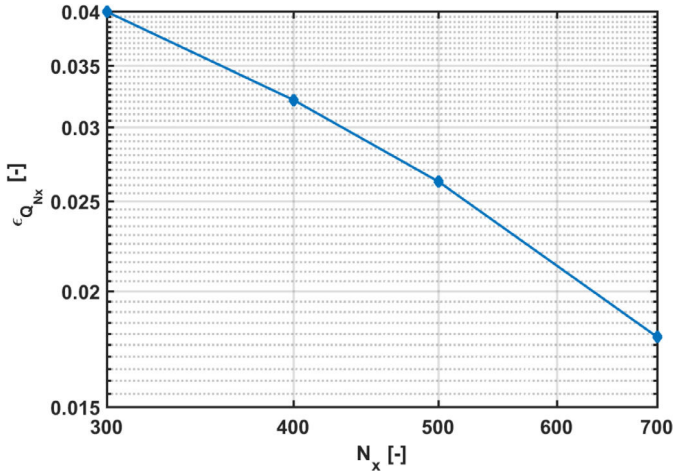


Fig. 8. Spatial convergence analysis of Q on the convergent hillslope. Simulations with N_x varying from 300 to 700 are compared to the reference simulation with $N_x = 1100$. The error metric $\epsilon_{Q_{N_x}}$ is defined by Eq. (9).

1×10^{-3} . Thus we determine the convergence rate $\epsilon_{Q_{N_x}}$ as a function of N_x . We show the convergence results only for Q (Fig. 8) as they are similar for S and q_s . It shows a fast increase in precision compared to the reference solution. The magnitude of the slope in a log/log scale is equal to -0.95 . Convergence rate is close to the theoretical rate equal to -1 demonstrated for linear and smooth problems, $\epsilon_{Q_{N_x}} = O(\frac{1}{N_x})$ (Chavent and Roberts, 1991).

3.2.3. Time steps analysis

Accuracy is also obtained by adapting the time step and the order of the scheme in ode15s to solve system (7). Fig. 9a shows that

the total number of internal timesteps n_t increases approximately linearly with N_x ($n_t \approx 40N_x$). The adaptive method used by ode15s is efficient to provide optimal balance between accuracy and efficiency. We cannot separate the effects of the spatial discretization from the number of computed internal timesteps on the gain in accuracy as we use the integrated solver ode15s which automatically adapts its timesteps. Fig. 9b highlights at which time ode15s refines its internal timesteps during the simulation. It shows the cumulated number of internal timesteps used by ode15s as a function of the time simulated for different spatial discretization (N_x between 100 and 700). The number of internal timesteps increases rapidly at the beginning of the simulation (for $t < 5$ days) and just after the infiltration events ($t \geq 10, 20$ or 30 days). These refinements are due to strong gradients appearing in the soil matrix at the beginning of the simulation when the hillslope discretized elements equilibrates with the fixed saturated channel bank and when the infiltration stops. The more the hillslope is discretized, the more pronounced is the refinement. This may be to satisfy the relative error tolerance which is more difficult to attain for finer discretizations.

3.2.4. Convergence with the regularization parameter r

We also determine the convergence rate of ϵ_{S_r} and $\epsilon_{q_{S_r}}$ as a function of the regularization parameter r (Eq. (9)) for a fixed spatial discretization with $N_x = 100$ (Figure 10). The number r varies between 0.2 and 10^{-6} and is compared to the reference solution with $r_{ref} = 2 \times 10^{-7}$ ($N_{ref} = N_x = 100$). We only consider ϵ_{S_r} and $\epsilon_{q_{S_r}}$ since the regularization parameter controls the presence or absence of saturation excess overland flux depending on soil saturation. ϵ_{S_r} and $\epsilon_{q_{S_r}}$ scale with $r^{1.4}$ and $r^{0.94}$ demonstrating the fast convergence with the regularization parameter r . The built-in ode15s solver performs well even with stiff partition functions ($r = 2 \times 10^{-7}$).

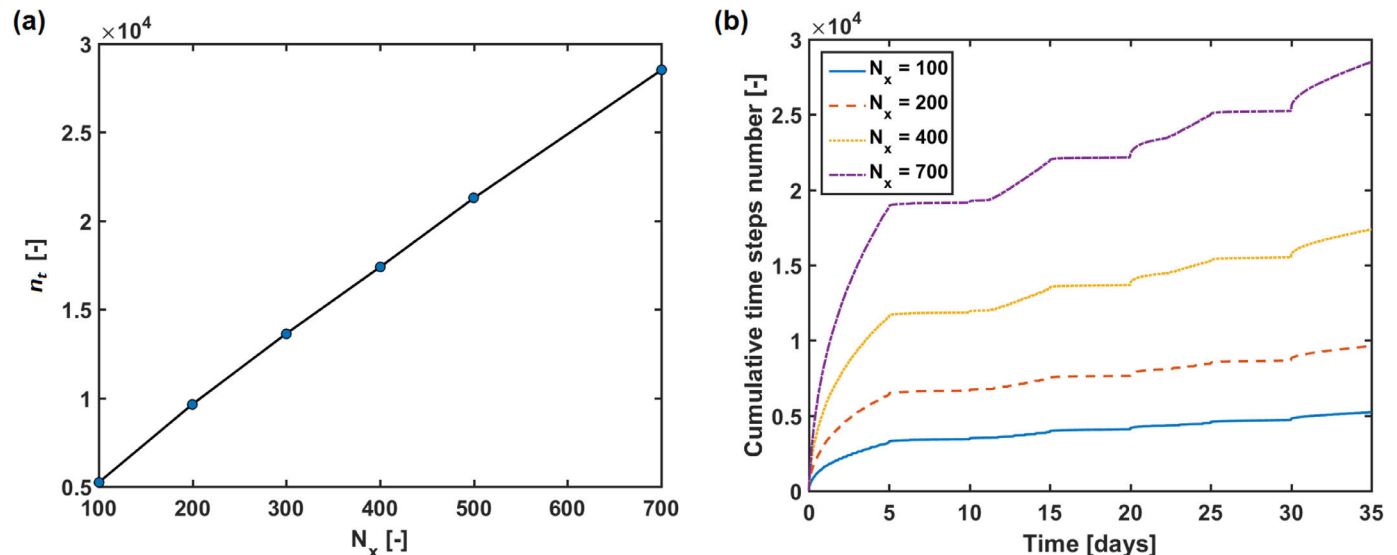


Fig. 9. (a) Total number of internal timesteps n_t used by ode15s as a function of the number of the elements N_x used to discretize the hillslope. (b) Evolution of the cumulative number of internal timesteps used by ode15s during a simulation for different numbers of cells N_x .

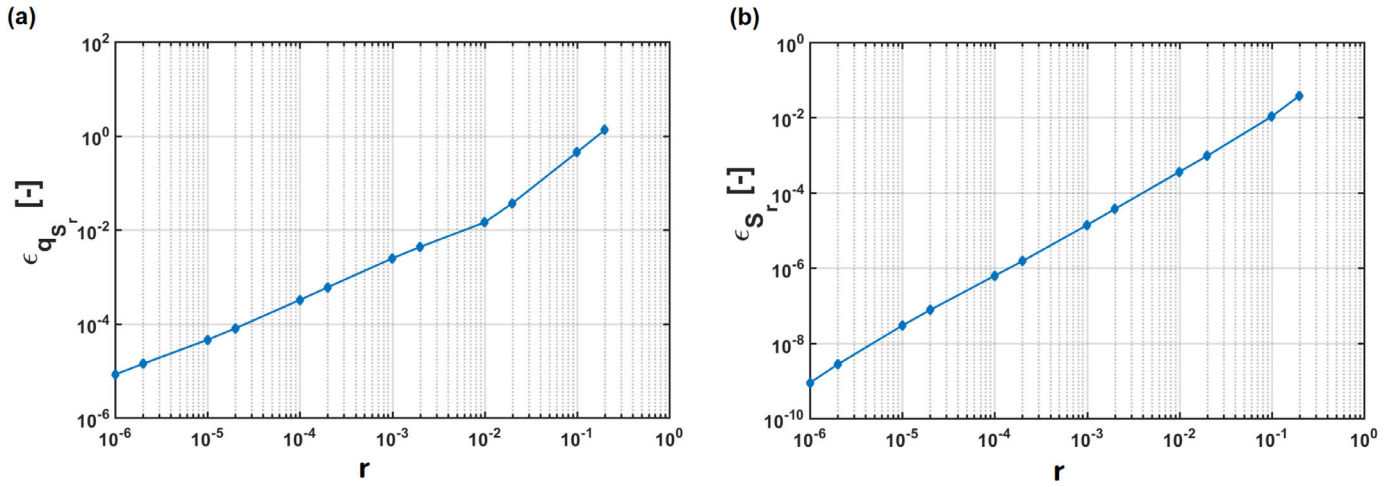


Fig. 10. Convergence of (a) q_s and (b) S with the regularization parameter r . Errors are compared to the reference solution taken at $r = 2 \times 10^{-7}$.

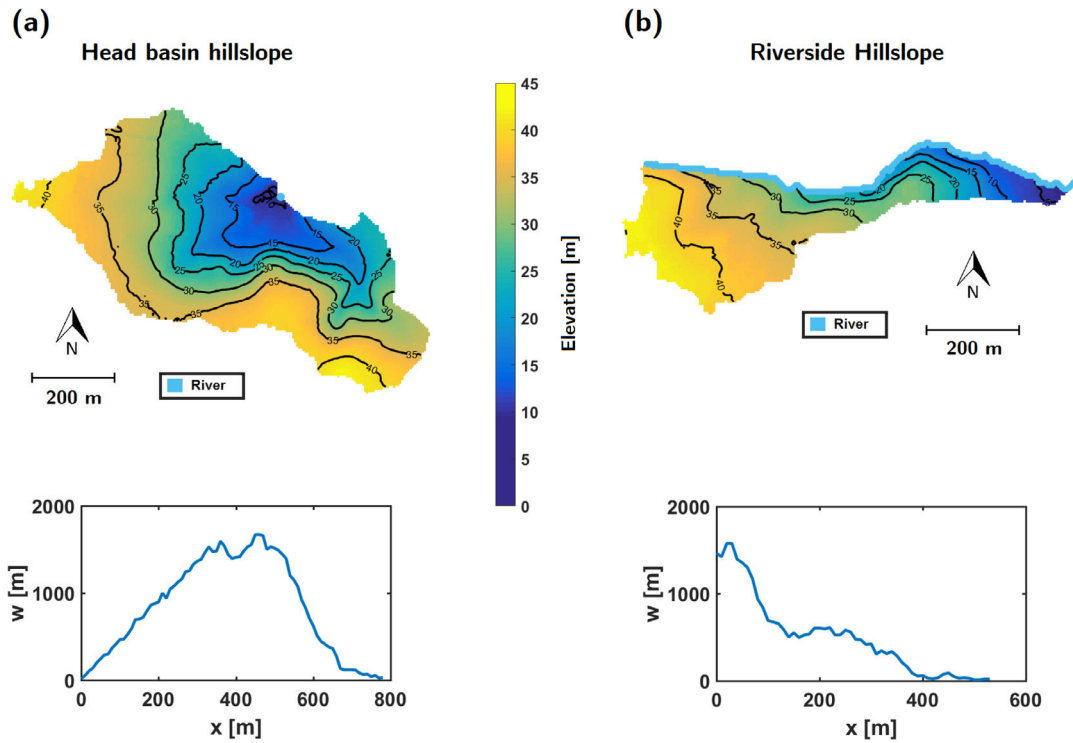


Fig. 11. Two major classes of hillslopes: (a) Head basin hillslopes located at the spring of river. (b) Riverside hillslopes located along the river channel. Notice the different behaviour of their width functions.

We have assessed the numerical methods proposed in Section 2.1. The mixed finite element method gives an accurate estimation of fluxes and subsurface water storage, as shown by the comparison with the previous results of Troch et al. (2003). It ensures accurate local and global mass balance preservation. The partition formulation with discontinuous functions and the proposed regularization are relevant methods to account for seepage in efficient and simple ways. They are well suited to follow dynamic transitions between partially and fully saturated regimes. They show good convergence rates with the regularization parameter and lead to problems that can be integrated with classic ordinary differential equation solvers.

3.3. Extensive testing for robustness evaluation

To evaluate the robustness of the method, we run realistic simulations on 1109 real hillslope shapes, with varied geologic parametrizations and with five different infiltration time series. This represents 8320 simulations. Hillslope structures are extracted from a 5m LiDAR Digital Elevation Model of Brittany. Hillslope shapes can be classified in the two categories of the head basin hillslopes (Fig. 11a) and the riverside hillslopes (i.e. the hillslopes located along river channels, Fig. 11b). Head basins hillslopes have a typical divergent and then convergent shape favouring the apparition of saturated source areas near the streams. Hillslopes located along river channels are mainly divergent. Both hillslope types display some complexities in their width functions. Several

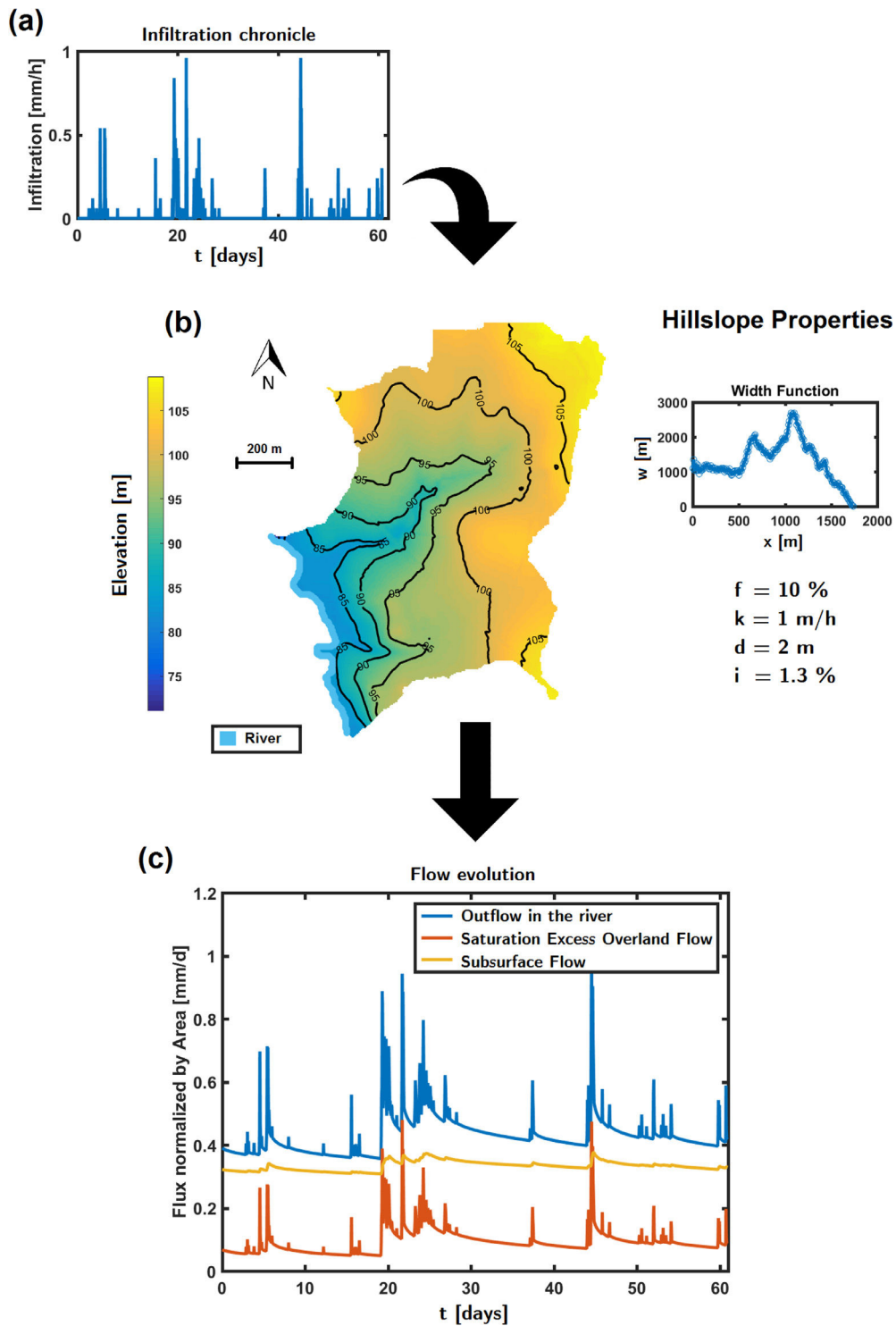


Fig. 12. Results of the simulation for a real hillslope from a catchment in Brittany (France) (Kolbe et al., 2016) with (a) the infiltration chronicle, (b) the hillslope shape and properties (width function and pedologic parameters) and (c) the hillslope response as subsurface and saturation excess overland flow and the sum of both (outflow in the river).

geologic parametrizations are tested with different values of hydraulic conductivities, soil depths and drainable porosities. These parameters are drawn from truncated lognormal distributions for the hydraulic conductivity and the soil depth and from a truncated normal distribution for drainable porosity (Table 2). Infiltration time series are taken as simple synthetic cases or deduced from real precipitations. The two synthetic cases are a steady infiltration time series of 0.75 mm d^{-1} and a square periodic (period

of 10 days) infiltration time series of 35 days varying between 0 and 1.5 mm d^{-1} . Three realistic infiltration cases are derived from three different precipitation chronicles of 15, 61 and 365 days. For the steady infiltration time series, we start the simulation from an initially dry soil profile. For the other infiltration time series, we take the steady subsurface water storage profile under the average infiltration of the time series as initial conditions.

Table 2

Parameters of the truncated distributions used for the parametrization of the geological properties f (drainable properties), k (hydraulic conductivity) and d (soil depth). Intervals indicate the truncation range.

Parameters	Distribution type	Mean	Std	Interval
f (%)	Normal	30	10	[5,50]
k (m h ⁻¹)	Log normal	1	10	[0.05,15]
d (m)	Log normal	1	10	[0.2,11]

Fig. 12 illustrates the simulation methodology for a 1 km² hillslope of the Pleine Fougères watershed (Kolbe et al., 2016) located in North Brittany (Fig. 12a) with the realistic 61 days infiltration time series (Fig. 12b). Hydraulic conductivities, soil depth and drainable porosity are respectively set at 1 m/h, 2 m and 10%. The simulation exhibits a coexistence of subsurface flow along with saturation excess overland flow with two different dynamics (Fig. 12c). Subsurface flow dynamic displays smooth response following infiltration events while saturation excess overland flow, made up of both seepage flow and direct precipitations onto saturated areas, responds instantaneously to infiltrations with highly peaked flows. Out of the 8320 cases tested, no errors were reported by the MATLAB® ode15s solver. These extensive numerical experiments on contrasted hillslopes with sharp infiltration time series demonstrate the robustness of the numerical methods proposed, even in the case of steep rainfall time series (Fig. 12).

4. Conclusion

Hillslope response to precipitations is characterized by sharp transitions between two different regimes defined as a function of soil saturation. For partial soil column saturation, flows are restricted to the subsurface. For fully saturated soil column, flows occur both in the subsurface and on the surface as saturation excess overland flow. The hillslope response is highly impacted by the dynamic transition between these regimes. We propose a partition formulation with a mass balance equation where the storage variation is equal to the sum of the local variation of the infiltration and the subsurface flow minus the overland flow. We derive a regularized model which can be discretized in space and time by classic schemes. We choose a mixed finite element method which ensures local and global mass balance preservation along with an implicit temporal scheme to deal with sharp transitions.

The regularized discrete scheme has been validated against previously published results without saturation excess overland flow. With saturation excess overland flow, additional numerical experiments on a convergent hillslope show good convergence properties for both flow and saturation. Extensive tests on 8320 cases with different hillslope shapes and infiltration time series demonstrate the overall robustness of the method. The regularized and discretized partition formulation thus appears accurate and robust.

This model may be especially relevant for hillslopes with steep, shallow and conductive soils on top of poorly weathered bedrocks that promote the generation of saturation excess overland flow in riparian areas where surface flow routing can be neglected (Weiler et al., 2006). These conditions are typically encountered in Brittany (Merot et al., 2003; Montreuil and Merot, 2006). Integrating this model at the regional scale requires to subdivide the watershed into representative sub-units hillslopes. This can be done by automatically extracting contour-based hillslopes (Moretti and Orlandini, 2008) based on the representative elementary watersheds (Reggiani et al., 1998).

More generally this formulation provides a well-established mathematical formulation for dynamic transitions between partially and fully saturated regimes. It might be extended to 2D shal-

low aquifers. Adapted partition conditions might also be formulated for shallow water equations on top of 2D Boussinesq subsurface flows with the additional capacity to account for infiltration processes.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at [10.1016/j.advwatres.2017.09.008](https://doi.org/10.1016/j.advwatres.2017.09.008).

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1.3 Bilan

Dans cette partie, nous avons donc développé un modèle basé sur les équations de Boussinesq qui repose elle-même sur l'hypothèse de Dupuit-Forchheimer (équilibre hydrostatique ou champs de vitesse horizontal et constant sur la verticale). Ce modèle prend en compte l'interaction du toit de la nappe avec la topographie qui génère des zones de suintements. Ce modèle est donc conçu pour être capable de rendre compte des forçages climatiques et topographiques sur l'écoulement des eaux dans un aquifère de proche subsurface. Nous avons pu voir à travers une modélisation systématique que ce modèle respecte les attendus de conservation de masse. Il est aussi robuste puisqu'il a été testé sur des milliers de réalisations représentatives de la topographie bretonne.

Avec ces milliers de réalisation représentatives du climat et de la topographie bretonne, il est également possible de s'intéresser aux déterminants physiques qui conditionnent l'existence de zones saturées sur un versant. En effet, classiquement, l'indice topographique, utilisé pour prédire la saturation en un point, se heurte à sa trop grande simplification et a fait l'objet d'un grand nombre d'études [Beven and Kirkby, 1979; Merot *et al.*, 2003; Quinn *et al.*, 1995]. En particulier, nous étudions ce type d'indice sous l'angle d'un modèle à base physique. A l'aide de ces simulations numériques, nous esquisserons donc une méthode visant à retrouver les déterminants qui expliquent la saturation dans notre modèle (cf. Partie IV Chapitre 1).

D'autre part, la théorie de Boussinesq est attractive pour ouvrir la voie à une modélisation à base physique parcimonieuse qui soit représentative des écoulements dans les aquifères de proche subsurface. En effet, que ce soit pour l'analyse de récessions comme pour le développement de modèles pluie-débit, les applications de Boussinesq sont nombreuses et toujours d'actualité [Brutsaert and Nieber, 1977; Troch *et al.*, 1993; Troch *et al.*, 2013]. Cette « force » de la théorie de Boussinesq provient du fait que cette description 1D de l'écoulement tient compte de certaines propriétés clefs de l'écoulement en milieu souterrain : lien entre stock et flux via la loi de Darcy, écoulements éventuellement gravitaires via la prise en compte d'un substratum de l'aquifère penté. Le fait de considérer un aquifère à nappe libre permet d'une part, une variation de la transmissivité avec le stock d'eau présent dans l'aquifère ; d'autre part, il permet de représenter l'interception de la nappe avec la surface, ce qui engendre une non linéarité supplémentaire qui reflète la dynamique rapide des écoulements.

Cependant, pour représenter le transport à l'échelle d'un versant, les descriptions mécanistes de type Boussinesq ne permettent en général que de représenter des transports parfaitement mélangés dans la colonne d'eau. En effet, la théorie de Boussinesq est basée sur une homogénéisation des champs de vitesse sur la verticale [Dupuit, 1863]. Ainsi, les solutions analytiques visant à solutionner les distributions de temps de résidence à l'aide d'une hypothèse type Dupuit-Forchheimer conduisent à retrouver une distribution de temps de résidence exponentielle caractéristique des milieux parfaitement mélangés [Chesnaux *et al.*, 2005; Haitjema, 1995].

Pour cette raison, nous développons dans le chapitre suivant un formalisme de transport reposant sur la résolution du flux à l'aide de la théorie de Boussinesq mais à même de rendre compte de la stratification verticale des écoulements en milieu souterrain.

Chapitre 2 Modéliser le transport : Développement d'un modèle parcimonieux semi-explicite à l'échelle du versant

2.1 Introduction

Dans cette partie, nous développons un schéma de suivi lagrangien de particules pour solutionner les équations de transport conservatif sur un versant. Cette méthode vise en effet à compléter la résolution du flux opéré avec le modèle de type Boussinesq, présentée dans la partie précédente. Au préalable, nous décrivons également une méthode pour calculer le routage appliqué au flux de suintement généré sur le versant, routage nécessaire pour calculer le temps nécessaire à ce suintement pour rejoindre la rivière.

La méthode de suivi particulaire développée repose sur l'utilisation du champ de vitesse 1D dans l'aquifère qui peut être obtenu par résolution du système de Boussinesq présenté dans le chapitre précédent. En effet, le champ de vitesse $v(x, t)$ dans l'aquifère, dépend du stock d'eau présent dans l'aquifère $S(x, t)$, et du flux d'eau $Q(x, t)$, via la relation : $v(x, t) = Q(x, t)/S(x, t)$. A partir de ce champ de vitesse, la trajectoire advective 1D des particules dans l'aquifère peut être résolue à chaque instant et pour toute localisation d'injection des particules. On injecte donc ces particules à chaque instant t présentant une recharge non nulle, et à chaque endroit du versant proportionnellement à la quantité de recharge tombée pendant la période Δt et proportionnellement à l'aire de versant représentée. Dans le cas où les particules seraient injectées sur une zone complètement saturée, les particules sont alors directement advectées via une procédure de routage modélisant le transport horizontal de subsurface dans la colonne de sol vers la rivière. Connaissant ces trajectoires 1D plusieurs étapes de post-traitement, basées sur des considérations physiques, sont réalisées pour obtenir une stratification des écoulements ainsi qu'une représentation de la dispersion caractéristique des milieux souterrains. Premièrement, pour tenir compte de la stratification qui s'opère en milieu souterrain, on adjoint à ces trajectoires 1D, le suivi de la trajectoire verticale $z(t)$ de ces particules en considérant la conservation de la masse à l'échelle locale (à l'échelle des éléments discrétisés qui ont servi à la résolution du flux) et à l'échelle infinitésimale, via la prise en compte du fait que deux lignes de flux ne peuvent se croiser (ce qui résulte de la conservation de la masse via l'équation $\text{div}(\rho \mathbf{v}) = 0$). Cette dernière prise en compte amène naturellement au fait que les lignes d'écoulements des particules « s'emboîtent » selon le principe que les particules d'eau les plus jeunes et rechargées en dernier viennent « pousser » vers le fond les particules les plus vieilles [Haitjema, 1987; Pollock, 1988; Strack, 1984]. Deuxièmement, cette stratification des écoulements amène également à considérer que dans les zones de suintement (ou « *return flow* ») ce sont les particules les plus jeunes situées au sommet de la colonne d'eau qui vont suinter en premier. La proportion de particules que nous faisons quitter l'aquifère pour alimenter le suintement dépend de la proportion de flux qui suinte par rapport au flux qui transite dans l'aquifère pour un instant et un endroit donné. Troisièmement, pour modéliser la dispersion qui s'opère en milieu souterrain, on ajoute à chacune de ces particules une dispersion longitudinale sous la forme d'une distribution inverse gaussienne [de Marsily, 1986]. La dispersion ajoutée dépend d'un coefficient de dispersivité qui dépend linéairement de la distance parcourue par les particules en milieu souterrain [Gelhar et al., 1992]. Ainsi les particules qui ont été injectées près de la ligne de partage des eaux auront plus dispersé que celles injectées à proximité de la rivière [Kirchner et al., 2001].

Dans la partie suivante, nous décrivons donc mathématiquement ce formalisme, nous l'illustrons sur quelques cas tests, vérifions quelques propriétés physiques préalables. Nous démontrons ensuite son intérêt pour obtenir un formalisme à base physique spatialisée capable de modéliser les distributions de temps de résidence et les distributions de temps de transit. Ce modèle à base physique permet non

seulement de modéliser les distributions de temps des circulations d'eau à l'échelle du versant mais permet surtout de modéliser le transport de soluté via différentes hypothèses, en se basant sur une équation de transport réactif basée sur le temps de transit :

$$C_{out}^A(t) = \int_0^{+\infty} C_{in}^A(t - \tau) r(\tau) p_Q(t, \tau) d\tau, \quad (5)$$

où τ est le temps de transit, $C_{out}^A(t)$ est la concentration en soluté A mesurée en rivière à l'instant t , $C_{in}^A(t - \tau)$ est la concentration d'entrée en soluté A , définissant le chargement en soluté A (sous forme de concentration) qui a été appliqué à l'instant $t - \tau$ dans le bassin versant (historique des chargements en nitrates par exemple), p_Q est la distribution de temps de transit, temporellement variable et r est la réactivité, qui traduit la proportion de solutés restant en solution au bout d'un temps de transit τ . Cette réactivité est donc supposée dépendre uniquement du temps de transit τ (par exemple via une loi cinétique de premier ordre, voir partie Partie IV Chapitre 4).

2.2 Article: Coupling hillslope transfers and biogeochemical reactivity within a parsimonious and physically-based catchment model

Commentaire : cet article n'a pas encore été soumis dans une revue à comité de lecture. Pour cette raison, il apparaît encore sous la forme d'une version préliminaire avant le dépôt du manuscrit final pour soumission.

Coupling hillslope transfers and biogeochemical reactivity within a parsimonious and physically-based catchment model

A catchment scale, reactive transport model with a spatially-explicit time-based approach

Abstract

Understanding the fate of contaminants in catchments is essential to predict the impacts of growing anthropogenic pressure on groundwater resources and to assess the resilience of freshwater ecosystems. Soils and shallow aquifers constitute two major hydrologically and biogeochemically active compartments with characteristic flow paths of widely differing transit times. We develop a Boussinesq-based flow and solute transport model accounting for the interactions between groundwater flows, storage capacities and subsurface stormflow. For solute transport, we reconstitute the natural stratification of groundwater flow paths based on flow continuity and develop a forward advective dispersive particle tracking scheme representing the conservative transport of water parcels inside the soil and in the aquifer. With an additional time-based reactive framework, we model time-varying residence time distributions, transit time distributions and induced variations on simple inert and reactive tracers. Illustrated on a realistic case (Guillem catchment, France), a calibrated flow model shows how the structure of the catchment conditions the partition between groundwater and subsurface stormflows in the streamwater, its seasonal variability, and the broad range of transit times to the river.

Keywords: Reactive transport models; Lagrangian methods; Particle tracking; Advective dispersive framework; Boussinesq equations; Travel time distributions; Streamwater age; Groundwater age.

1 Introduction

Understanding the fate of terrigenous and anthropogenic elements transported by water inside a catchment is of critical importance to predict human impacts on aquatic ecosystems (Kirchner et al., 2000; Rockstrom et al., 2009; Steffen et al., 2015). Climate change, land use evolution and eutrophication alter the cycle of major elements (N, C, P, Si) in aquatic and continental ecosystems (Bennett et al., 2001; Galloway et al., 2004; Lal, 2004). Soils and aquifers intervene in these element cycles because of their extensive fluid / solid interface and high heterogeneous

30 reactivity (Pinay et al., 2015; Seitzinger et al., 2006). Impact of subsurface transfers in inert and
31 reactive elements must be quantified for the large-scale assessment of the sequestration of
32 carbon, of the removal of excess nutrient like nitrate and of the contribution of weathering and
33 buffering processes on the overall element cycles (Brantley et al., 2007; McClain et al., 2003;
34 McDonnell and Beven, 2014).

35 Modeling fluxes inside catchments has been approached by a diversity of methods from the
36 advanced integrated hydrologic models that represent explicitly physical processes in the
37 vadose and saturated zones (Ashby and Falgout, 1996; Fatichi et al., 2016; Maxwell, 2013;
38 Therrien and Sudicky, 1996) to the simpler and parsimonious models representing catchments
39 as series of compartments with non-linear storage discharge relationships (Perrin et al., 2001;
40 Perrin et al., 2003). An intermediary vertically integrated approach has been proposed by
41 Boussinesq with an important number of applications due to its physical relevance and its
42 parsimonious description (Boussinesq, 1877). Applications concern for example recession
43 analyses to rainfall-runoff (Troch et al. 2013), as Boussinesq theory reproduces accurately the
44 recession of the water table after an infiltration event (Brutsaert and Nieber, 1977; Guérin et
45 al., 2014). Boussinesq theory relies on the Dupuit-Forchheimer assumption according to which
46 the resistance to flow in the vertical direction can be neglected for thin unconfined aquifers of
47 vertical dimension much smaller than their horizontal extension (Dupuit, 1863). As a
48 consequence of vertical integration, vertical fluxes are not solved in Boussinesq models leading
49 to a uniform horizontal velocity field over the whole water column.

50 The vertical integration of flows inherently precludes any stratification of solute transport.
51 Thus, when considering impact of flow on transport consideration, Boussinesq theory has been
52 limited to 1D and 2D cases, such as the transfer from an aquifer to a stream or to a well
53 (Chesnaux et al., 2005). In the absence of stratification, for steady state conditions, the transit
54 time distribution remains close to an exponential characteristic of well-mixed aquifers
55 (Haitjema, 1995). However, growing evidences show that well-mixed systems cannot account
56 for preferential and stratified flows, which result in distributions of transit times broader than
57 the classical exponential and closer to gamma functions (Benettin et al., 2017; Berghuijs and
58 Kirchner, 2017; Beven, 2010; Godsey et al., 2010; Harman, 2015). Stratification in unconfined
59 aquifers occurs naturally following the evenly-distributed recharge processes at the water table
60 (top of the aquifer). Upstream, infiltrating water getting at the water table “pushes” down the
61 water already in the aquifer (Haitjema, 1987; Pollock, 1988; Strack, 1984), with a consecutive
62 increase of residence times with depth (Vogel, 1967). Downstream, in seepage areas, the return

flow (from the aquifer to the surface) is made up first of younger waters, which remained close to the water table, and, second, of older waters coming from deeper layers of the aquifer. In addition to this return flow, direct precipitation on these saturated soils is generated and is quickly routed to the stream network, representing an additional source of young waters. Both of these subsurface stormflow processes increase the proportion of smaller times in the transit time distributions leading to distributions more peaked towards the smaller times than the classical exponential distribution.

Here, we propose a parsimonious stratified transport model for Boussinesq groundwater flows, which additionally accounts for the dynamical interactions between water table and land surface (Marçais et al., 2017), and the routing of the runoff to the streams. We propose a vertically integrated, forward advective particle tracking technique, postprocessed to introduce the vertical stratification of the aquifer with an *ad hoc* vertical particle location derived from mass and flux conservations. Solute diffusion and dispersion are implemented for each particle as an inverse Gaussian distribution parametrized by the transit time. The Boussinesq-based groundwater flow method coupled with a gravity driven routing strategy and the adapted transport framework are described in sections 2 and 3. In section 4, we discuss how this formalism can provide time-varying transit time distributions of streamwater and time-varying residence time distributions of groundwater. These distributions obtained with parsimonious physically-based techniques can eventually be used to implement time-based and spatially explicit reactive frameworks (Maher and Druhan, 2014a) as well as transport of groundwater age tracers (Leray et al., 2014; Marçais et al., 2015). Finally, a real test case representative of Brittany rivers (France) is presented (section 5) with the eventual discussion on the flux and the transport models (section 6).

2 Flow model and methods

In this section, we recall the flux formalism relative to the hillslope storage Boussinesq equation modified to include return flow and subsurface flow generation (Marçais et al., 2017; Troch et al., 2003). We introduce a postprocessing step to model subsurface stormflow routing at the soil/bedrock interface. Overall, this formalism is aimed at simulating seasonal interactions between the water table of shallow aquifers and the soil/bedrock interface (Figure 1). All methods are developed here for the 1D hillslope Boussinesq equations (Troch et al., 2003). Without any specificity to the 1D system, they can be applied to any 2D Boussinesq systems.

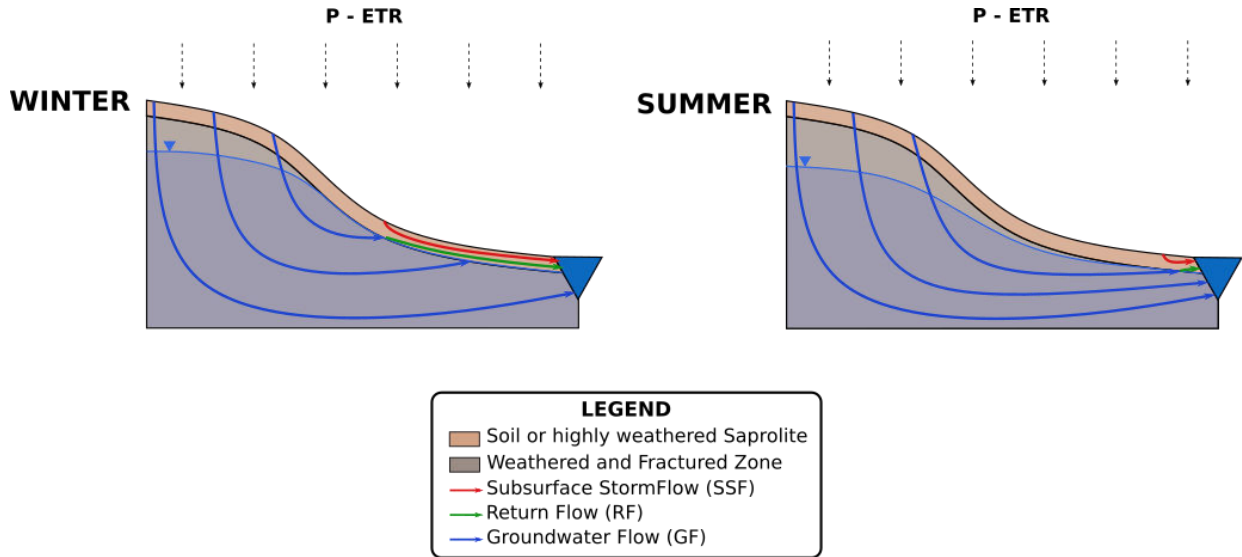


Figure 1: Sketch of the modeled process. When the water table intersects the interface between the soil and the deeper layer (e.g. bedrock, weathered zone), it generates a gravity driven flow. In the aquifer, groundwater flow is modeled with a Boussinesq formulation. The transition between these two states is achieved through a regularized threshold formulation. Note the decrease of runoff (red and green arrows) from winter to summer.

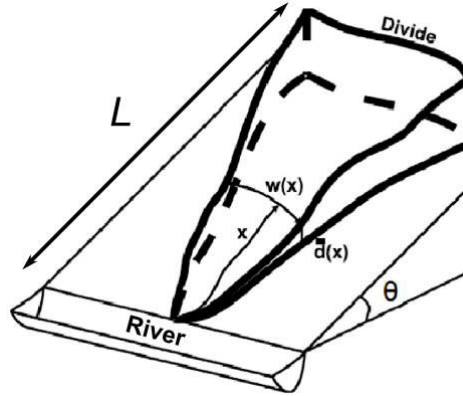
2.1 Subsurface flow model

This subsurface flow model is based on a Boussinesq formalism for unconfined shallow aquifers. Developed in previous articles (Paniconi et al., 2003; Troch et al., 2003), we only recall its assumption and resulting equations. For a hillslope typically described by the width function $\omega(x)$, the slope of the hillslope bedrock θ (Figure 2), and its hydraulic parameters, the porosity f and the hydraulic conductivity k , groundwater flow in a shallow aquifer draining to a stream can be described by Boussinesq equations:

$$\begin{cases} \frac{\partial S}{\partial t}(x, t) = -\frac{\partial Q}{\partial x}(x, t) + N(t) \omega(x) \\ Q(x, t) = -\frac{kS(x, t)}{f} \left(\cos \theta \frac{\partial}{\partial x} \left(\frac{S}{f\omega} \right) + \sin \theta \right) \end{cases}, \quad (1)$$

where t is the time, x is the distance to the channel varying from 0 at the river to L at the water divide and $N(t)$ is the infiltration time series. S is the subsurface water storage, defined as the aggregated groundwater stored at a distance x of the river: $S(x, t) = f\omega(x)h(x, t)$ (with $h(x) \leq d(x)$ where $d(x)$ is the aquifer maximum depth). This subsurface water storage verifies the conservation of mass (first equation of system (1)). $Q(x, t)$ is the integrated flux over the

112 transect constituted of a Darcy flow driven by the gradient of storage and of a gravity flow
 113 function of the bedrock slope (second line of the system (1)).



114

115 Figure 2: 3D view of the hillslope with an illustration of the width function $\omega(x)$ and of the function $d(x)$.
 116 Adapted from (Troch et al., 2003).

117 As saturation reaches the upper soil layer (when $h(x, t) = d(x)$ and $S(x, t) = S_c(x)$),
 118 groundwater flows trigger seepage and induce direct precipitations onto the saturated areas.
 119 Therefore, the system of partial differential equations (1) has been extended to take account for
 120 the dynamical interactions between the water table and the land surface and the apparition of
 121 the subsurface stormflow $q_s(x, t)$:

$$\left\{ \begin{array}{l} \frac{\partial S}{\partial t}(x, t) + q_s(x, t) = -\frac{\partial Q}{\partial x}(x, t) + N(t) \omega(x) \\ q_s(x, t) = G\left(\frac{S(x, t)}{S_c(x, t)}\right) R\left(-\frac{\partial Q}{\partial x}(x, t) + N(t) \omega(x)\right), \\ Q(x, t) = -\frac{kS(x, t)}{f} \left(\cos \theta \frac{\partial}{\partial x} \left(\frac{S}{f\omega} \right) + \sin \theta \right) \\ 0 \leq S(x, t) \leq S_c(x, t) \end{array} \right. \quad (2)$$

122 where G and R are functionals based on Heaviside step function to control the partition between
 123 groundwater flow and subsurface stormflow as functions of relative saturation and flow balance
 124 on the water column (Marçais et al., 2017). Considering that $S(x, t)$, $Q(x, t)$ and $q_s(x, t)$ are
 125 fully defined by equation (2), i.e. that runoff is bottom-up controlled by the aquifer saturation,
 126 a routing strategy is added for the subsurface stormflow generated.

2.2 Surface flow model

We add to the system (2), a postprocessing step to take into account the routing of this runoff constituted of seepage and of direct infiltration onto the soil/bedrock interface together promoting the apparition of subsurface stormflow at the soil/bedrock interface. To rout runoff to the river, we adopt a gravity-controlled flux, driven by the soil saturated hydraulic conductivity and the local topographic gradient (Fan and Bras, 1998). For the soil layer, fluxes are routed at the velocity $v_{SSF}(x)$ defined by:

$$v_{SSF}(x) = k_{soil} \sin \theta_{soil} = \gamma k \sin \theta_{soil}, \quad (3)$$

where k_{soil} is the saturated hydraulic conductivity of the soil layer and γ is a coefficient linking the bedrock hydraulic conductivity k to the soil hydraulic conductivity k_{soil} (Fan and Bras, 1998). θ_{soil} is the slope of the soil. At the hillslope scale, it is assumed to be similar to the topographic slope. The river discharge $Q_{mod}^{flux}(t)$ results as the sum of the aquifer discharge outflow in the river $Q(x = 0, t)$ and the runoff flux integrated and routed over the hillslope:

$$Q_{mod}^{flux}(t) = Q(x = 0, t) + \int_0^L q_s \left(x, t - \int_0^x \frac{du}{v_{SSF}(u)} \right) dx. \quad (4)$$

Once released in the soil layer through seepage or direct infiltration onto saturated soil/bedrock interface, the subsurface stormflow is routed to the river with a time function of the distance between the release location and the river channel and function of the local subsurface stormflow velocity integrated over the water pathway in the soil layer. If instantaneous routing case is considered, equation (4) stays valid, assuming an infinite soil hydraulic conductivity. In this case all the subsurface stormflow generated is directly integrated without any delay to the river discharge.

In the Boussinesq approach for groundwater flows, celerity (flux response to precipitations) is dissociated from velocity (effective particles speed travel inside the aquifer). On the contrary, for runoff, the celerity of the flux coincides with the velocity of the particles inside the flux (McDonnell and Beven, 2014). Transport of solute is based on this flow structure fully described by equation (2), (3) and (4). This system of equation is discretized on a regular mesh of N_x elements characterized by their length Δx according to classical mixed finite element scheme (Marçais et al., 2017).

3 Transport model and method

We describe the Lagrangian transport scheme defining the trajectory of the flowlines in each of the subsurface compartment. Once the Boussinesq-threshold system (2) inside the aquifer has been solved, we use a Lagrangian formalism to derive the advective transport inside the aquifer defined by:

$$\begin{cases} S(x(t), t) \frac{dx}{dt}(t) = Q(x(t), t) \\ x(t_0) = x_0 \end{cases}, \quad (5)$$

where t_0 is the initial time, x_0 is the initial position of the flow line and $x(t)$ is its 1D trajectory in the aquifer. This system derives from the Lagrangian definition of velocity, $v(x(t), t) = \frac{dx}{dt}(t) = \frac{Q(x(t), t)}{S(x(t), t)}$, where the temporal derivative of the trajectory $x(t)$ is linked to the velocity field. Velocity is the ratio of the groundwater flux $Q(x(t), t)$ over the lateral amount of groundwater stored $S(x(t), t)$. The transport equation (5) is solved by a particle method. Each particle is seeded at the top of the saturated zone according to the infiltration flux and further transported laterally and vertically in the aquifer. It eventually gets out of the aquifer system either to be routed in the soil layer or to be directly transferred to the stream. We successively describe the injection procedure, the lateral and vertical transfers in the aquifer, and the eventual seepage, discharge and transfer in the soil layer to the river.

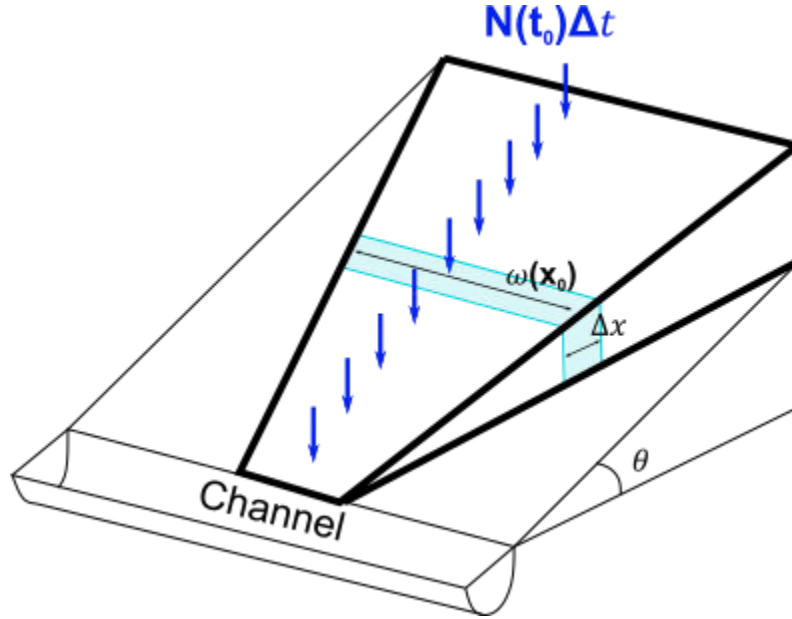
3.1 Flux-weighted particle injection

The time range over which transport is simulated is divided in N_t time steps of duration Δt . The N_p injected particles over the simulation period are distributed over the N_x different meshes of length Δx , and over the N_t time steps of duration Δt . Each particle i , injected at the time t_{inj}^i and at the location x_{inj}^i , carries a volume of water Ω_i , proportional to the surface over which it is injected equal to $\omega(x_{inj}^i) \Delta x$ and to the infiltration flux equal to $N(t_{inj}^i) \Delta t$ (Figure 3):

$$\Omega_i = N(t_{inj}^i) \Delta t \omega(x_{inj}^i) \Delta x. \quad (6)$$

Note that the infiltrating flux N is zero over the dry period and that it is homogeneous over the domain for precipitation events. With this weighting method, both the spatial and temporal discretization can be non-uniformly distributed over the domain.

177 Incoming volume of water are either infiltrated in the aquifer when $S(x_{inj}^i, t_{inj}^i) < S_c(x_{inj}^i)$
 178 (section 3.2) or routed in the soil layer to the stream otherwise ($S(x_{inj}^i, t_{inj}^i) = S_c(x_{inj}^i)$)
 179 (section 3.5). Reinfiltration downstream in the aquifer when saturation may be less is not
 180 accounted for, as this is a more specific hydrologic case that would induce a full coupling of
 181 the surface / subsurface systems with much higher computational costs (Kollet and Maxwell,
 182 2006; Putti and Paniconi, 2004).



183

184 Figure 3: Hillslope sketch: the hillslope storage Boussinesq equation models groundwater flow in 1D at the
 185 hillslope scale. The hillslope is described by the width function $\omega(x)$ and the slope of its bedrock θ . Particle
 186 injection strategy: each particle is weighted proportionally to the quantity of infiltrating water $N(t_0)\Delta t$ over
 187 the time step t_0 and the area $\omega(x_0)\Delta x$ it represents depending on the mesh discretization scheme chosen.
 188 Adapted from (Troch et al., 2003).

189 3.2 Lateral particle transport in the aquifer

190 Particle trajectories in the aquifer are computed by solving equation (5) with an explicit time-
 191 stepping algorithm. Particles are advected in the aquifer from their inlet time to their exit either
 192 by seepage (section 3.4) or directly to the river (section 3.5). It should be noted that their
 193 velocity along their trajectory can be significantly slower than the groundwater flux response
 194 to external forcing terms because of the groundwater storage $S(x, t)$ (equation (5)). It is not the
 195 case, however, in the soil layer where flux celerity and transport velocity are identical (see
 196 section 2.2) (McDonnell, 2017; McDonnell and Beven, 2014; van Verseveld et al., 2017).

Practically, we compute the aquifer trajectories $x_{GW}^i(t)$ for each of the N_p injected particles used for the solving of equation (5). This forward particle tracking method models the 1D lateral transport of conservative elements in the shallow aquifer.

3.3 Vertical particle transfer in the aquifer

For the vertical transfer of particles $z_{GW}(t)$ in the aquifer and the induced stratification of the groundwater flow lines, we propose an *ad-hoc* algorithm based on flow continuity and volume preservation. In fact, as Boussinesq equations rely on a vertical integration principle, they do not give any information on vertical transfers. Several methods have been proposed to retrieve the vertical velocity assuming either an instantaneous infiltration of water over the whole column of the aquifer with full mixing (Haitjema, 1995) or a linear decrease of vertical velocity with depth with a zero velocity at the aquifer bottom and a vertical velocity equal to the incoming infiltrating flux at the water table (Haitjema, 1987; Pollock, 1988; Strack, 1984).

We propose a different method to reconstruct the vertical particle trajectories $z(t)$ based on the assumption that vertical transfers are primarily limited by the continuity of flows. Infiltrating volumes first start at the top of the water column next to the water table and progressively get down as more recently water volumes are added up to the water column. Based on a conservation of volume principle, this method implicitly cumulates all the volumes contained in a water column. Even though it cannot be traduced in partial differential equations, it can still straightforwardly be translated in algorithmic terms. Each mesh cell j (interval $[X_j, X_{j+1}]$) corresponds to a water column, which contains the $N_p(X_j, t_k)$ particles at time t_k which position $x_i(t_k)$ fall in the range $[X_j, X_{j+1}]$. All of these particles are laterally advected at the same speed $Q(X_j, t_k)/S(X_j, t_k)$ and the sum of their volume (defined in equation (6)) is equal to the saturation $S(X_j, t_k)$:

$$S(X_j, t_k)dX_j = \sum_{i=1}^{N_p(X_j, t_k)} \Omega_i. \quad (7)$$

To get their vertical position, we order them by their travel time $t_k - t_{inj}^i$ starting from the particles with the largest time (and hence the most remote recharge location) at the bottom to the particles with the smallest time at the top of the water column next to the water table. The absolute position of the particle is deduced by discretizing the water column according to the volume of the particles Ω_i defined in equation (6). Particles are then distributed along the water

column from the aquifer bottom $z_b((X_j + X_{j+1})/2)$ to the water table elevation $h((X_j + X_{j+1})/2, t_k)$. The elevation of the water table can be expressed according to the saturation and to the hillslope width as:

$$h((X_j + X_{j+1})/2, t_k) = z_b((X_j + X_{j+1})/2) + \frac{S((X_j + X_{j+1})/2, t_k)}{f \omega((X_j + X_{j+1})/2)}. \quad (8)$$

The vertical position of the particle m is then given by:

$$z_m(X_j, t_k) = z_b((X_j + X_{j+1})/2) + \frac{\sum_{i=1}^m \Omega_i}{S(X_j, t_k) dX_j} h((X_j + X_{j+1})/2, t_k), \quad (9)$$

given that the particles have been ordered according to their travel time, oldest particles are at the bottom of the aquifer (for the first indices of m) and youngest particles are at the top of the aquifer (for the last indices m), according to the stratification of groundwater circulation (Figure 4). With this algorithm, particles representing the water column can go up and down depending on the shape of the substratum and on the boundary condition at the top of the water column.

3.4 Particle seepage to the soil layer

To respect the conservation of volume, particles are removed from the water column proportionally to the seepage flux $q_s(x, t)$ in the seepage areas identified by their full saturation $S(x, t)/S_c(x) = 1$. This seepage flux is the return flow from the aquifer to the soil layer. It concerns only the particles at the top of the water column. They are removed according to the ratio of return flow to groundwater flow. The number of particles removed from the water column to the return flow is in proportion of the return flow to the total flow (constituted of groundwater flow and of return flow):

$$r(x, t) = \frac{q_s(x, t) - N(t)\omega(x)}{q_s(x, t) - N(t)\omega(x) + Q(x, t)}. \quad (10)$$

Compared to other assumptions of full mixing over the water column, ordering particles in the water column has significant consequences on transit times as the “youngest” particles are the first to get out of the aquifer in the seepage areas. As seen previously, the oldest particles are at the bottom of the aquifer whereas the youngest are at the top of the water column.

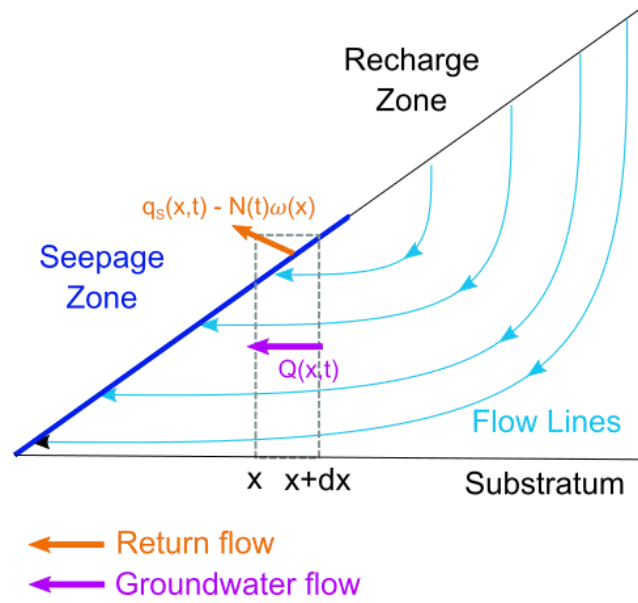


Figure 4: Sketch of the flow line distribution. The stratification of the particles proposed in section 3.3 respects the conservation of mass laterally (in the direction modeled by the flux equation (1)) and vertically through the premise of no-crossing between streamlines. This strategy can be summarized as “last in, first out” for the particles, therefore suggesting a process-based interpretation for the preferential selection of young water to be released to the stream.

3.5 Particle transfer to the river

Return flow generated in seepage areas are then advected laterally at the routing velocity $v_{SSF}(x)$ defined in equation (3), enabling to get their horizontal trajectory $x_{SSF}^i(t)$, for each particle seeped. Their vertical location is assumed to be at the soil / bedrock interface defined by the function $z_{top}(x)$.

Fluxes $Q_{mod}^{flux}(t)$ arriving at the river at time t are given by equation (4) summing up $Q(x = 0, t)$ and the seepage fluxes considering the delay of the routing in the soil layer. Its equivalent particle flux $Q_{mod}^{part}(t)$ can straightforwardly be expressed as the sum of the particles arriving between $t - \Delta t$ and t at the river:

$$Q_{mod}^{part}(t) = \sum_{i=1}^{N_{part}(t)} \Omega_i^{part}, \quad (11)$$

where $N_{part}(t)$ is defined as the cardinality of the ensemble of particles getting out of the aquifer or of the soil layer at time t defined as $\{P_i \mid x_{GW}^i(t - \Delta t) > 0 \ \& \ x_{GW}^i(t) =$

263 $0 \text{ OR } x_{SSF}^i(t - \Delta t) > 0 \text{ \& } x_{SSF}^i(t) = 0\}$ where P_i refers to particle i and Ω_i^{part} is defined by
 264 equation (6).

265 **4 Transit time distributions and reactive framework**

266 Several postprocessing methods are added to derive the transit time and residence time
 267 distributions as well as the transport of inert and reactive solutes.

268 **4.1 Modeling conservative solute transport from the particle tracking**

269 The numerical scheme presented in section 3 solves for the advective transport of water
 270 volumes under the flow condition given in section 2. It also corresponds to the advective
 271 transport of a solute without any diffusion nor dispersion. We introduce diffusive and dispersive
 272 processes by considering that each particle is a flow line over which transport times can be
 273 modeled by an Inverse Gaussian distribution accounting both for advective and
 274 diffusive/dispersive processes (Engdahl and Maxwell, 2014; Kirchner et al., 2001):

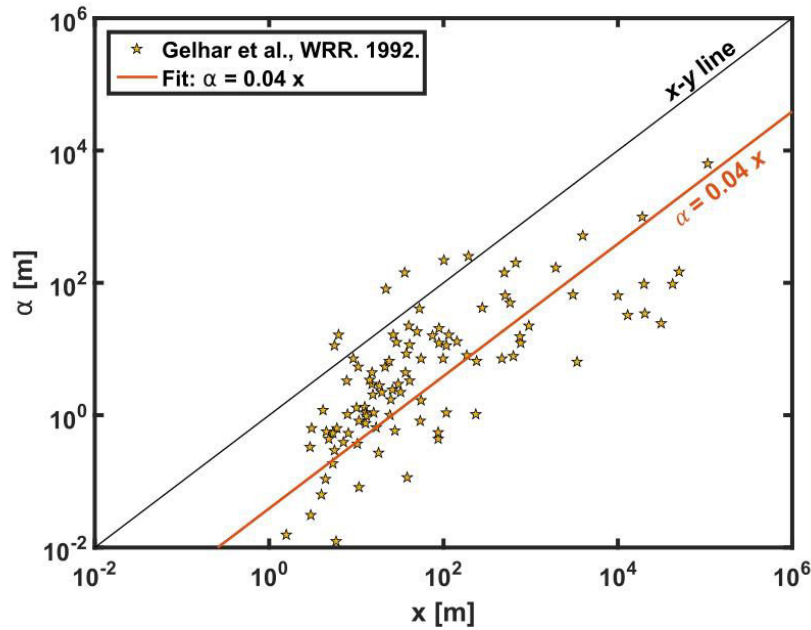
$$\begin{cases} p(t, x) = \left(\frac{x^2}{4\pi Dt^3} \right)^{1/2} \exp\left(-\frac{(vt - x)^2}{4Dt} \right) & \text{if } t \geq 0, \\ p(t, x) = 0 & \text{if } t < 0 \end{cases}, \quad (12)$$

275 where x is the distance that the particle has traveled since time t , v is the average velocity of the
 276 particle and D is the diffusion-dispersion coefficient due to velocity heterogeneities in the
 277 porous medium. This formalism implicitly assumes that the longitudinal dispersion, well
 278 represented here, is much larger than the transversal dispersion. If this may be justified in
 279 shallow hillslope systems, this assumption should be taken with care for larger systems. This
 280 kinematic dispersion effect classically depends on the average particle velocity v such that the
 281 dispersion coefficient is equal to $D = \alpha v + d$, where α is the dispersivity and d the diffusion
 282 (de Marsily, 1986; Pfankuch, 1963). Neglecting the diffusion d compared to the kinematic
 283 dispersion αv and rearranging this inverse Gaussian formula in a time-based framework with
 284 $D = \alpha v = \alpha \frac{x}{\mu}$, with μ the travel time over the flow line, leads to:

$$\begin{cases} p(t, x, \alpha, \mu) = \left(\frac{\mu}{4\pi \frac{\alpha}{x} t^3} \right)^{1/2} \exp \left(\frac{-(\mu - t)^2}{4 \frac{\alpha}{x} \mu t} \right) & \text{if } t \geq 0 \\ p(t, x, \alpha, \mu) = 0 & \text{if } t < 0 \end{cases} \quad (13)$$

285 Following the observation made by Gelhar et al. (1992) (Figure 5), we assume that the
 286 dispersivity α depends linearly on x with a coefficient typically equal to 1/25. We thus consider
 287 that the characteristic dispersivity encountered along the flowpaths is proportional to their
 288 length. The longer is the flow path, the longer will be the dispersivity, eventually leading to the
 289 following expression:

$$\begin{cases} p(t, \mu) = \left(\frac{25\mu}{4\pi t^3} \right)^{1/2} \exp \left(\frac{-25(t - \mu)^2}{4\mu t} \right) & \text{if } t \geq 0 \\ p(t, \mu) = 0 & \text{if } t < 0 \end{cases} \quad (14)$$



290

291 Figure 5: Longitudinal dispersivity α versus the typical longitudinal scale x (Gelhar et al., 1992). The fit gives
 292 a relation $\alpha = 1/25 x$.

4.2 Residence time distributions, transit time distributions and storage selection functions

The residence time distributions can be derived on the basis of the particles in the aquifer and soil layers and on the time that they have spent in it. The transit time distribution is defined from the travel time of the particles reaching the river in the associated time step. In both cases, the distribution of times is obtained by summing up the inverse Gaussian distributions associated with the travel time spent in the aquifer layer. Each distribution of the sum is weighted by the water volume associated to the particle (Ω) as defined by equation (6). This results in synthetic, physically-based transient residence time distributions $p_S(t, \tau)$ and transient transit time distributions $p_Q(t, \tau)$, where t is the sampling time and τ is the transit or residence time.

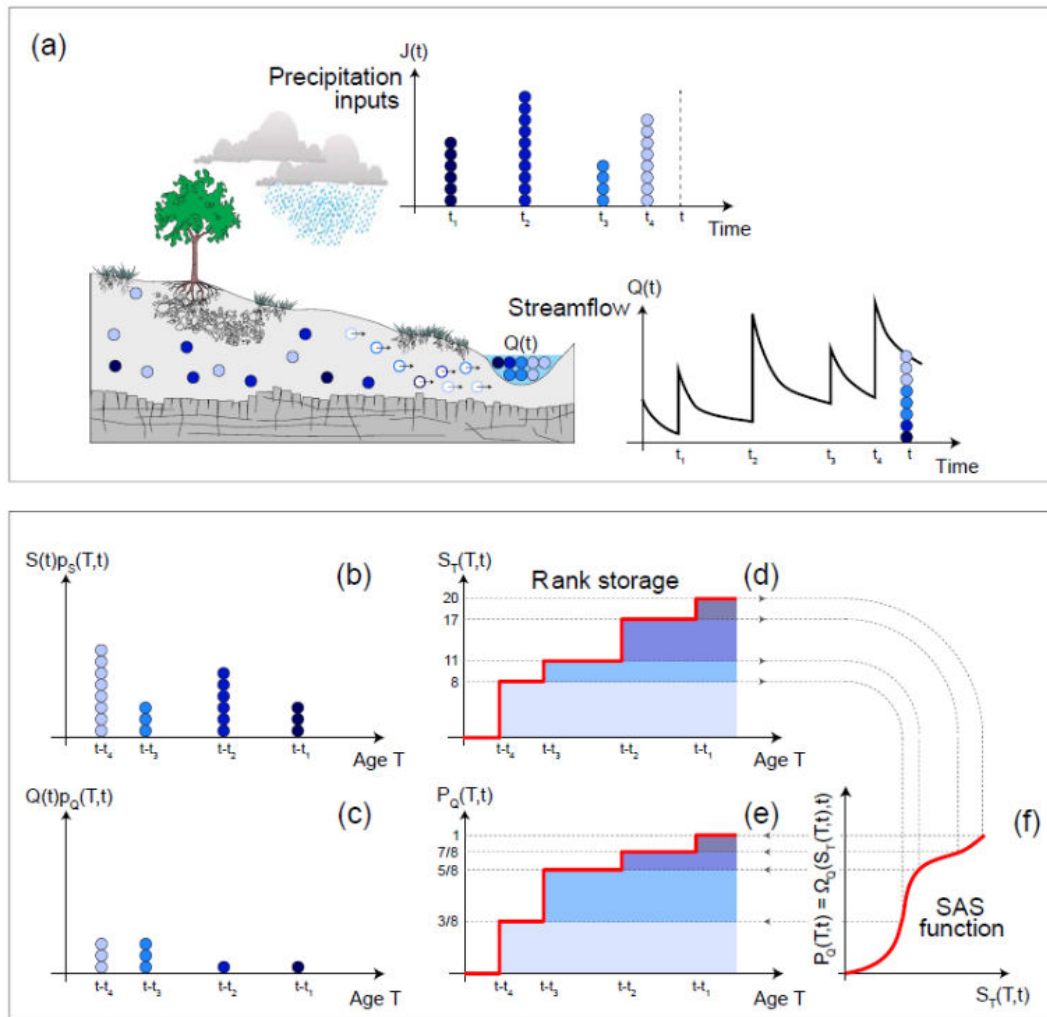


Figure 6: (a) Scheme illustrating the differences between the residence time distributions and the transit time distributions. Residence time distributions represent the age distributions of the particles stored within the

system whereas transit time distributions represent the age of the groundwater exiting the catchment towards the stream at the sampling time t . (b) to (d) illustrate the method to retrieve the storage selection function from the residence time distribution and the transit time distribution (from Benettin and Bertuzzo (2018)).

The comparison of these two distributions characterizes the “preference” of the catchment to release younger or older groundwater to the streams. Indeed, the transit time distribution is made up of the particles released to the river at a given sampling time t and is related to the residence time distribution corresponding to all the particles stored in the catchment (aquifer and soil layers) by the storage selection function:

$$\omega_Q(\tau, t) = \frac{p_Q(\tau, t)}{p_S(\tau, t)}. \quad (15)$$

With an adapted change of variable, the storage selection function can be expressed as a function of the dimensionless aquifer storage S , ordered from the youngest to the oldest ages. The change of variable is defined by:

$$S(\tau, t) = \int_0^\tau p_S(u, t) du, \quad (16)$$

and transforms $\omega_Q(S, t)$ in a probability distribution which rates the contribution of each stored water of a given age to the streamflow (Rinaldo et al., 2015; van der Velde et al., 2012).

4.3 Towards a time-based and spatially-based reactive framework

From these time distributions, simplified reactivity can be implemented. The temporal dependence of reactivity is the most classical assumption to model zeroth order or first order kinetically-controlled heterogeneous reactions at the catchment scale (Kolbe et al., in rev.; Maher and Druhan, 2014b). The spatial dependence of reactivity can also be modeled since transport is spatially explicit. For example, to model the variation of the solute species A in the river, the time-based framework could be traduced by the following convolution:

$$C_{out}^A(t) = \int_0^{+\infty} C_{in}^A(t - \tau) r(\tau, \beta) p_Q(t, \tau) d\tau, \quad (17)$$

where C_{out}^A is the concentration of element A in the river at sampling time t , C_{in}^A is the spatially uniform input time series of element A , for all potential times $t - \tau$ and r is one minus the

reactivity over travel time τ of the solute element A inside the catchment. With this framework, variable input time series can be considered as this has been the case for fertilizer application since the 1940s (Aquilina et al., 2012). Without any reactivity ($r=1$), equation (17) models the mixing of conservative solutes within hillslopes. For first-order kinetically-controlled reaction the reactive factor only depends on the travel time τ as:

$$r(\tau, \beta) = \exp(-\beta\tau), \quad (18)$$

where β is the characteristic reaction rate (Appelo and Postma, 1994).

Reactivity can alternatively be expressed as a function of the aquifer location both laterally and vertically. It would be the case for different kinetic reactions between soil and aquifer compartments or between fully saturated (potentially anoxic) and partially saturated zones (Ebrahimi and Or, 2015; Sexstone et al., 1985). It can also be applied to model vertically differentiated reactions as suspected in several studies (Kolbe et al., in rev.; Tesoriero and Puckett, 2011) as the vertical trajectory $z(t)$ of the particles is explicitly solved.

5 Catchment description, field data and modeling strategy

To illustrate the interest of this modeling framework, we assessed its relevance on the following real test case.

5.1 Catchment description

The tested case is the Guillec catchment located in western Brittany (France). This catchment has been chosen because it is relatively limited in size (73 km²) and because discharge data are available for 15 years. It is characterized by an oceanic temperate climate with an average precipitation of about 1000 mm/yr and a real evapotranspiration approximately equal to 600 mm/yr. Its geology is crystalline, mainly granitic, though some clastic sedimentary materials are present in the fluvial system due to the weathering of the crystalline bedrock. Topographical gradients are relatively limited with altitudes ranging between 7 and 125 m over 7 to 10 km (Figure 7a).

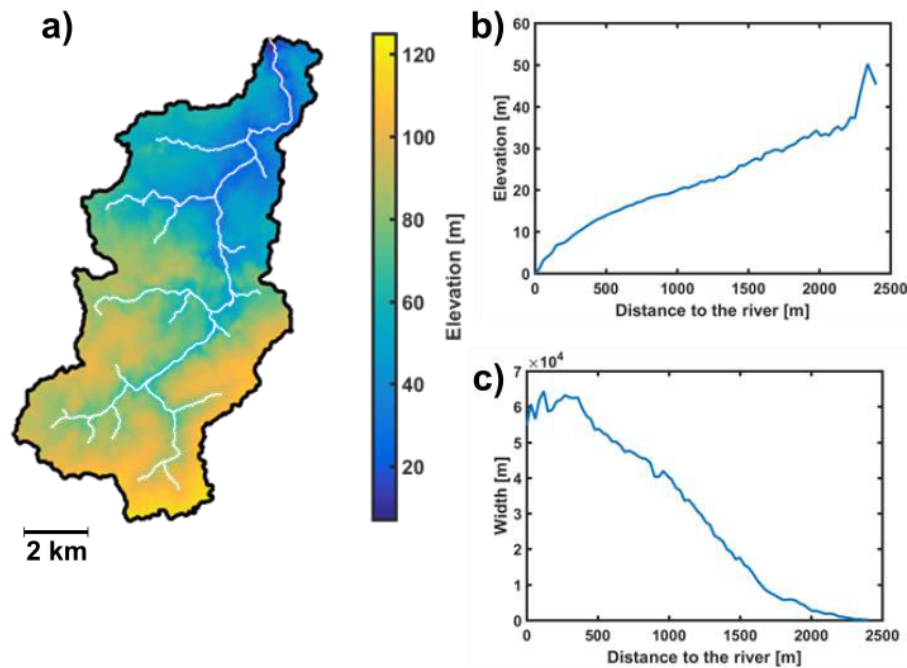


Figure 7: (a) 2D representation of the topography of the Guillec catchment. (b) Elevation function characterizing the average elevation of the catchment at a distance x from the river. (c) Width function characterizing the partial area distribution of the catchment as a function of the distance x from the river.

5.2 Precipitation, evapotranspiration and discharge data

A daily discharge time series is available over 15 years at the catchment outlet. In the objective of analyzing the interannual and seasonal fluctuations of discharge and time-varying transit time distributions, the monthly average of this time series was derived (Figure 8). The input meteorological forcing signal comes from rainfall and evapotranspiration data produced by the SURFEX program, a Meteo France model assimilating rainfall, temperature and wind data to produce unified national scale daily time series data on rainfall and real evapotranspiration at the grid scale of 8x8 km (Barbu et al., 2014; Boone et al., 2017; Faroux et al., 2013; Quintana-Seguí et al., 2008a; Quintana-Seguí et al., 2008b). Precipitation and evapotranspiration were obtained for the Guillec catchment by averaging the 64 km² grids covering the catchment proportionally to their relative area of the catchment at the month time scale (Figure 8).

The net precipitation is strongly correlated to the observed discharge in river with highest effective precipitations during the wet season when river discharge is at its maximum and zero effective precipitations during the dry season when river discharge is at low flows (Figure 8). However, the amplitude of the net precipitation events between the wet and the dry season is more important than the observed variations in river discharge suggesting that part of the net

precipitation falling in the wet season is recharging the aquifer. During low flows, this stored water is restituted to the stream leading to a typical recession in the discharge time series.

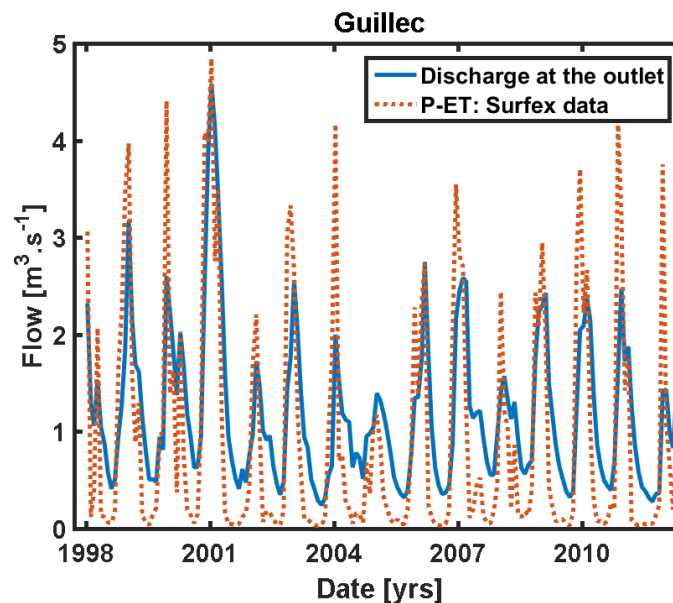


Figure 8: Monthly averaged discharge time series at the outlet of the Guillec catchment compared to the reconstructed net precipitation (precipitation minus evapotranspiration) derived from the French meteorological model.

5.3 Hillslope model

Hillslope model has been derived from the topographically defined catchment from the gauging station at the outlet. SRTM data were analyzed with the topotoolbox package (Farr et al., 2007; Schwanghart and Kuhn, 2010; Schwanghart and Scherler, 2014) under the assumption that the hydrological and hydrogeological catchments correspond (Gleeson and Manning, 2008; Haitjema and Mitchell-Bruker, 2005; Reggiani and Schellekens, 2003; Reggiani et al., 1998). This assumption is generally well verified in Brittany where crystalline bedrocks and low topographical gradients preclude the existence of significant regional groundwater circulation (Kolbe et al., 2016). We choose to rely on a representation of the catchment based on an equivalent hillslope representation characterized by its relative elevation to the river and equivalent structure (Loritz et al., 2017; Reggiani and Schellekens, 2003). This equivalent hillslope representation is obtained by aggregating the cells of the DEM in a 1D representation according to their distance to the river in the DEM. This 2D DEM-based analysis gives the width function $\omega(x)$ and the mean elevation function $z_{top}(x)$ at the scale of the catchment (Figure 7b and c). Assuming a flat bedrock located at the same elevation as the river outlet, the width and elevation functions characterize the storage capacity of the catchment as a function

of the distance to the stream: $S_c(x) = f\omega(x)z_{top}(x)$, where f is the porosity set to 20% as generally reported for the upper weathered zone of this crystalline area (Ayraud et al., 2008; Kolbe et al., 2016; Roques et al., 2014). Flows are modeled with the methods given in section 2 with $N_x = 100$ discretized mesh elements.

Two different models structure are compared, one with an instantaneous routing (which is equivalent to an infinite soil hydraulic conductivity) and one with limiting subsurface stormflow routing. Hydraulic conductivities for both of these models were calibrated by maximizing the Nash Sutcliffe efficiency based on the monthly discharge data (Nash and Sutcliffe, 1970). The Nash Sutcliffe efficiency compare the square difference between the real and the modeled discharge time series rated by the variance of the real time series:

$$NSE = 1 - \frac{\sum_{k=1}^{N_t} (Q_{mod}^{flux}(t_k) - Q_{real}(t_k))^2}{\sum_{k=1}^{N_t} (Q_{real}(t_k) - \overline{Q_{real}})^2} \quad (19)$$

The first model has only one parameter, which is the bedrock hydraulic conductivity. The second one has two parameters, the bedrock hydraulic conductivity and the soil hydraulic conductivity. Calibration was performed by systematically sampling the bedrock hydraulic conductivity in the range $[2.8 \cdot 10^{-8} \text{ m/s}; 2.8 \cdot 10^{-3} \text{ m/s}]$ and, for the simulation with the subsurface stormflow routing framework, the soil hydraulic conductivity in the range $[2.8 \cdot 10^{-6} \text{ m/s}; 2.8 \cdot 10^{-3} \text{ m/s}]$.

6 Results and discussion

We implement the flow and transport models presented in sections 2 and 3 on the Guillec catchment (section 5). The flow model is calibrated on the discharge flow data to illustrate the relevance of the modeled processes (surface / subsurface exchanges and flow routing). The particle tracking method is validated against the flow results. Adding diffusion and dispersion, transport simulations are eventually discussed for their contribution on residence time and transit time distributions defined in section 4. Finally, we model numerically nitrate solute evolution in rivers following the reactivity assumption described in section 4.3.

6.1 Calibration of hydraulic conductivity by discharge data

Hydraulic conductivities are calibrated by comparing the observed and simulated discharge data at the Guillec catchment outlet with the NSE metric introduced in equation (19). Both models

with instantaneous and limiting routing are evaluated with the same regular sampling optimization method. Models with instantaneous routing calibration leads to a bedrock hydraulic conductivity of $3.6 \cdot 10^{-5}$ m/s with a NSE of 0.69 (Figure 9). The relatively limited NSE value is linked to the difficulty of this model to account consistently for both the high flow and the low flow periods. The introduction of routing processes improves the simulation of discharge with a larger NSE value of 0.81. Both high flows and low flows are well represented with a smaller bedrock hydraulic conductivity of $2.0 \cdot 10^{-5}$ m/s compensated by a much larger soil hydraulic conductivity of $1.4 \cdot 10^{-2}$ m/s for the routing processes. The low flow periods are more consistently modeled by the lower bedrock hydraulic conductivity, which limits the transfers to the river in the dry periods. In the wet periods, the enhanced seepage induced by the smaller bedrock hydraulic conductivity is buffered by the routing limitations and does not translated in much higher discharges in the river.

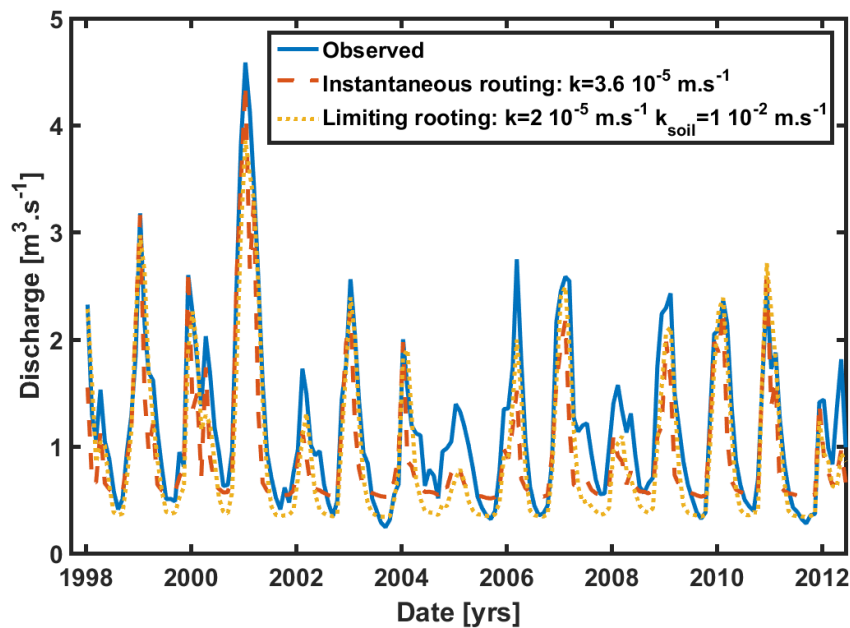


Figure 9: Observed versus modeled discharge shown for the Guillec catchment without routing (NSE=0.69) and with routing (NSE=0.81).

6.2 Numerical assessment of the particle tracking method

Following this flux calibration, we use the particle tracking scheme with an injection of 450 500 particles. To reach a representative sampling of the velocity field, the particle tracker is run on a 333 years period in steady state for initiation prior to the first date of sampling. We set this

duration so that the particle estimated discharge is equal to the discharge estimated with the flux method at the end of the steady-state simulation. This ensures that the injected particles have completed the sampling of the overall water catchment volume. The numerical consistency of the particle tracking scheme is verified by checking the conservation of mass. The flux $Q_{mod}^{flux}(t)$ representing the river discharge, obtained by solving the system of partial differential algebraic (2) and by computing the equation (4) is compared to the particle river discharge $Q_{mod}^{part}(t)$ defined in equation (11).

The comparison of flow and particle discharge does not show any systematic bias (Figure 10a). Some overestimation can be noted for the biggest flows larger than $3 \text{ m}^3/\text{s}$ (20% at most). The spread around the x-y line is due to the approximation made by generating fluxes with a discrete number of particles. Overall the particle tracking scheme respects the conservation of mass since it leads to the same discharge estimation as the discharge simulated by solving the system (2) potentially supplemented by the routing equation (3) (Figure 10b).

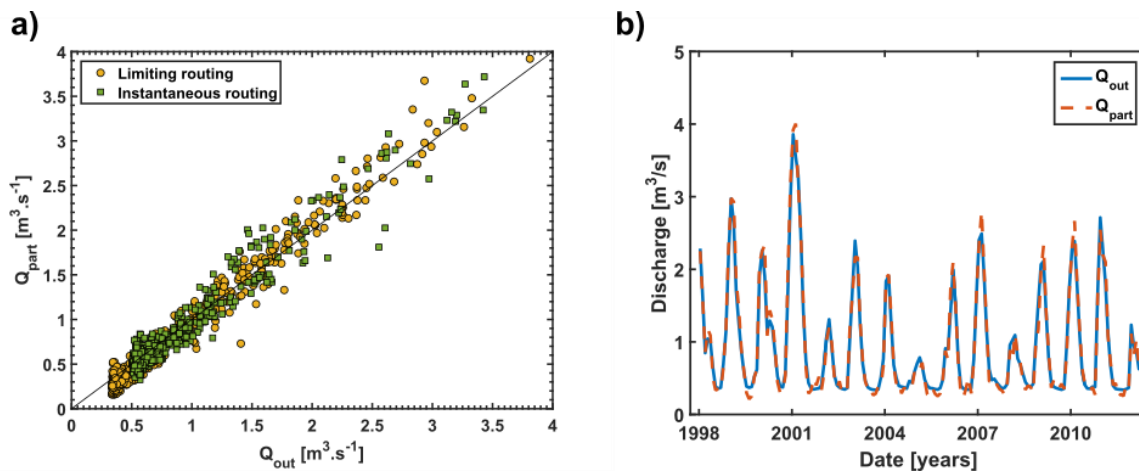


Figure 10: Comparison between river discharge directly modeled with system (2) and river discharge obtained with the particle tracking technique for the two models considered: with a routing and with instantaneous routing. a) Direct comparison of outflow fluxes. b) Comparison of the discharge time series for the model with subsurface stormflow routing.

6.3 Residence time distributions

Particle tracking results are postprocessed as detailed in section 3.3 to give the residence time everywhere in the groundwater system. We represent the cross section of the 1D aquifer of the equivalent hillslope considered with the stratification of the residence time for the two most contrasted hydrologic periods, i.e. the wettest event recorded in January 2001 and the driest event recorded in September 2003 (Figure 11). For the wettest event, the aquifer contains

substantial proportion of young groundwater (0-1 year) at the top of the aquifer. Due to the interception of the water table with the soil/bedrock interface, this young groundwater is rapidly advected through the stream with the subsurface stormflow. In the driest conditions, the water table is around 2 m below its level reached in the wettest conditions. The aquifer contains fewer young groundwater with only a thin veneer of young groundwater at the top of the aquifer. The amount of old groundwater (older than 35 years) is comparable for the two water periods considered.

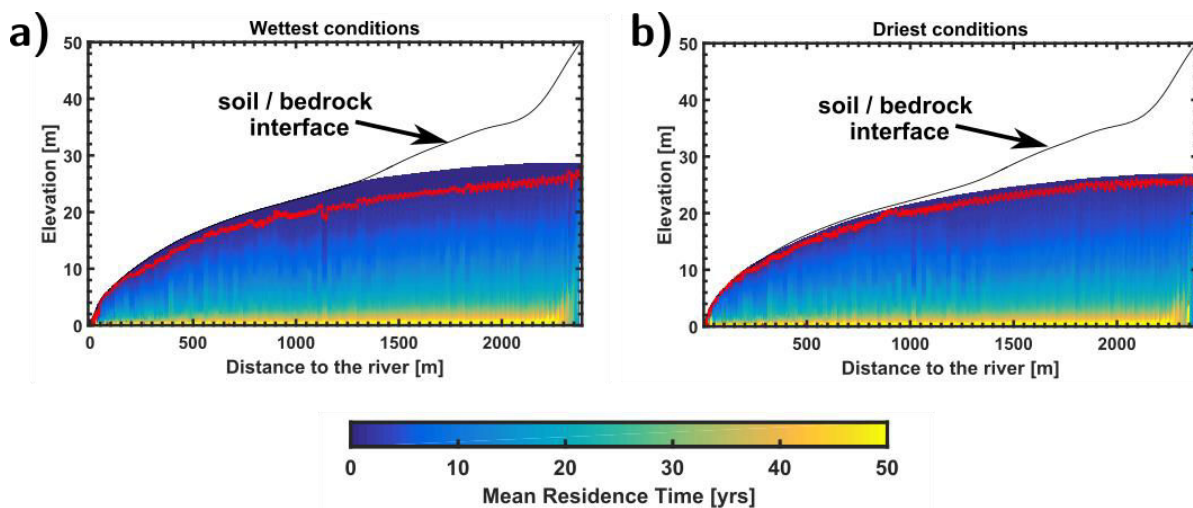


Figure 11: Residence time distributions in the aquifer for (a) the wettest (b) the driest conditions of the 1998-2012 period for the Guillec catchment. Model assumes an instantaneous soil routing process. Note the significant proportion of young groundwater in the aquifer in the wettest conditions (January 2001) while there is only a thin layer in the driest conditions (September 2003). The red line materializes the limit of the residence times less than one year old. The black line represents the soil/bedrock interface.

Even though the spatial patterns of the residence times vary between these two events, the residence time distributions have similar exponential shape (Figure 12). This is because the residence time distribution is weighted by the water stored inside the catchment which is predominantly made up of old waters located at the bottom of the aquifer. The exponential distribution represented in Figure 12 has a mean residence time of 18.7 years equal to the average of the two mean residence time for the wettest and the driest events (respectively equal to 18.1 and 19.3 years). For the model with instantaneous subsurface stormflow routing, the mean residence time is smaller, in average equal to 12.8 years (equal to 12.3 and 13.3 years respectively for the wettest and driest events). Overall, the residence time distribution is not significantly transient and can be assumed to be exponential.

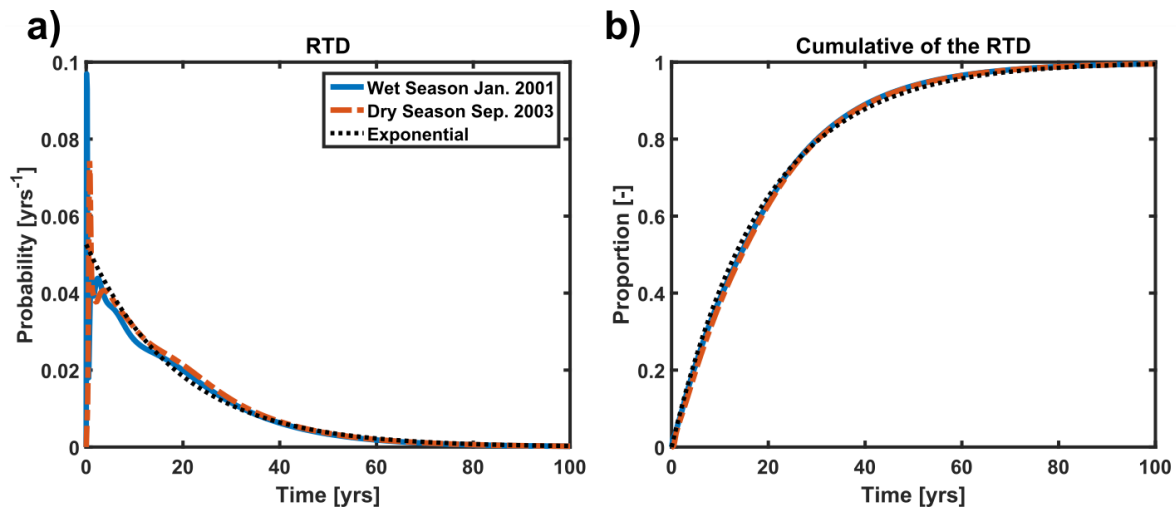


Figure 12: Residence time distributions obtained for the model with subsurface stormflow routing for the driest and wettest events of the time series. Both distributions are similar, close to the exponential distribution represented by the dotted line.

6.4 Transit time distributions

The transit time distribution is also derived at each time step from the particle tracking results to qualify the relative proportion of younger and older water discharged to the stream. It is fundamentally coming from the aggregated contributions of the saturated areas of the catchment, themselves strongly dependent on their distance to the stream. Figure 13 illustrates the typical weighted aggregation of the transit time distributions coming from the particles. These particles arrive in the same sampled time interval and come from different locations with different mean travel times and different dispersion (Kirchner et al., 2001).

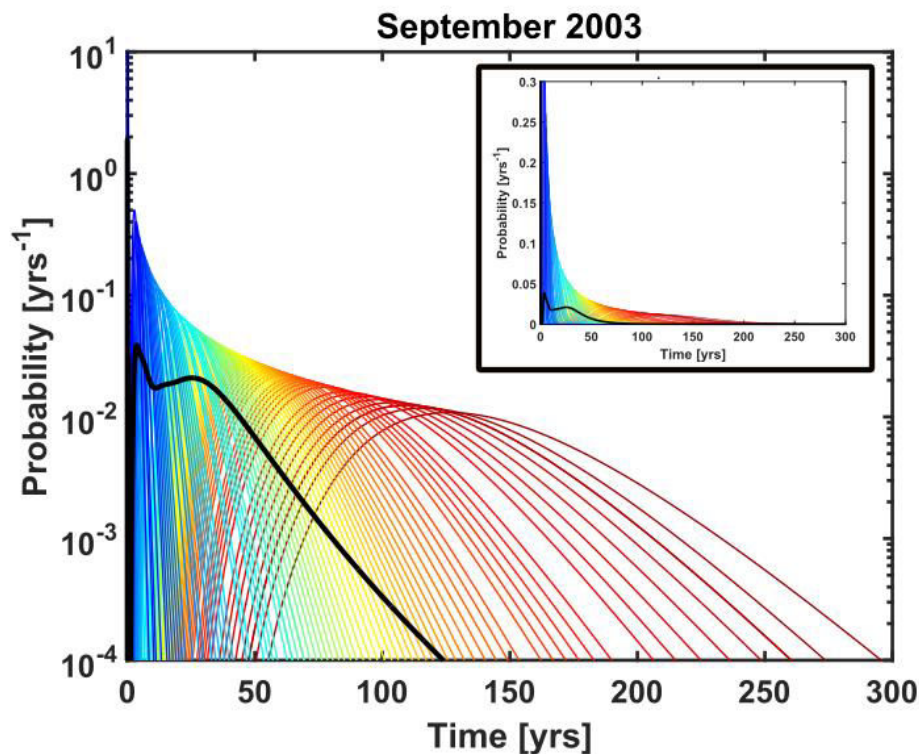


Figure 13: Aggregated transit time distribution (black line) from particles transit time distributions (color lines) at the end of the dry season, in September 2003 (semilog plot). Each color line corresponds to the distribution of a single particle. The mean transit time and the standard deviation of the transit time distribution depend on the starting location and on the starting time of the particle. In insert, same sketch plotted in linear plot. Note how the transit time distribution is peaked on the young transit time (less than 1 year) even for this month taken at the end of the dry season (September).

If the residence time distributions can be assumed to be non-transient (section 6.3), this is not the case for the time varying transit time distributions shown for the hydrologic year 2007-2008 (Figure 14). These transit time distributions reflect the climatic seasonal forcing typical of temperate climatic conditions. At the end of the dry season (September-October), the transit time distributions show a strong tendency towards the older ages (orange curves), whereas at the end of the wet season, when the water table is high, intersecting highly permeable horizons of the soil layer, transit time distributions show increased proportions of young groundwater (blue curves).

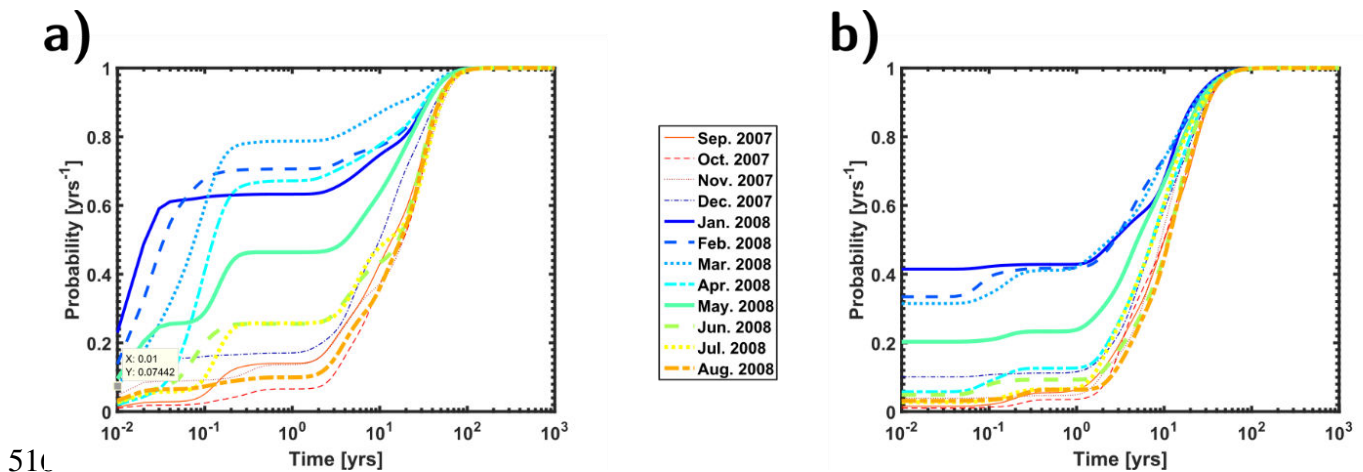


Figure 14: Cumulative of transit time distributions for the hydrologic year 2007 – 2008 for (a) the model with subsurface routing (b) the model with instantaneous subsurface routing. During the wet season the proportion of young water in the river increases significantly. Note the differences between the two sets of transit time distributions according to the choice of model representation.

Significant differences can be observed in the cumulative transit time distributions for the two different model structures during the wet season, whereas they are more consistent during the dry season. The model with subsurface stormflow routing (Figure 14a) is more seasonally dynamic than the model with instantaneous subsurface stormflow routing (Figure 14b). This is because the model with instantaneous routing has no processes able to represent the dynamic of fast hydrological flow paths below one month (which corresponds to 0.08 year) since the groundwater flow paths have a minimal transit times of some months. On the contrary, the model with a subsurface stormflow routing strategy models the very shallow subsurface flow paths that can be of the order of some days. Modeling these shallow subsurface flow paths might be essential to precisely model the discharge in the river as it has been shown in section 6.1 that the two models have significant differences in NSE.

Additionally, these models differ in terms of the proportion of young water. Especially, more young water proportion is generated during the wet year with the model with subsurface stormflow routing. This is because these two models have different structures (different bedrock hydraulic conductivities). Indeed, for the model with subsurface stormflow routing, the optimized bedrock hydraulic conductivity is smaller than for the model with instantaneous subsurface stormflow routing. This leads to the generation of more subsurface stormflow since small bedrock hydraulic conductivities induce a higher water table, which leads to more interaction between the water table and the land surface.

Overall, these seasonal patterns in young water proportion impact the temporal variability of the mean transit times (Figure 15). The model with subsurface stormflow routing displays a higher variability than the model with instantaneous subsurface stormflow routing. This is due to similar reasons than the one invoked for the increased variability in young water proportion. Indeed, the model with subsurface stormflow routing presents a smaller bedrock hydraulic conductivity which also leads to an increase in the volume stored inside the aquifer. This increase in volume is followed by larger mean residence times in the catchment (Figure 15, dashed lines). Therefore, in the dry season when there is only old groundwater discharged to the stream, the mean transit times of the model with subsurface stormflow routing are significantly older than the mean transit times of the model without subsurface stormflow routing. On the contrary, in the wet season, the two models generate subsurface stormflow in different proportions which exactly compensate their difference in mean residence times leading to similar mean transit times during the wet season.

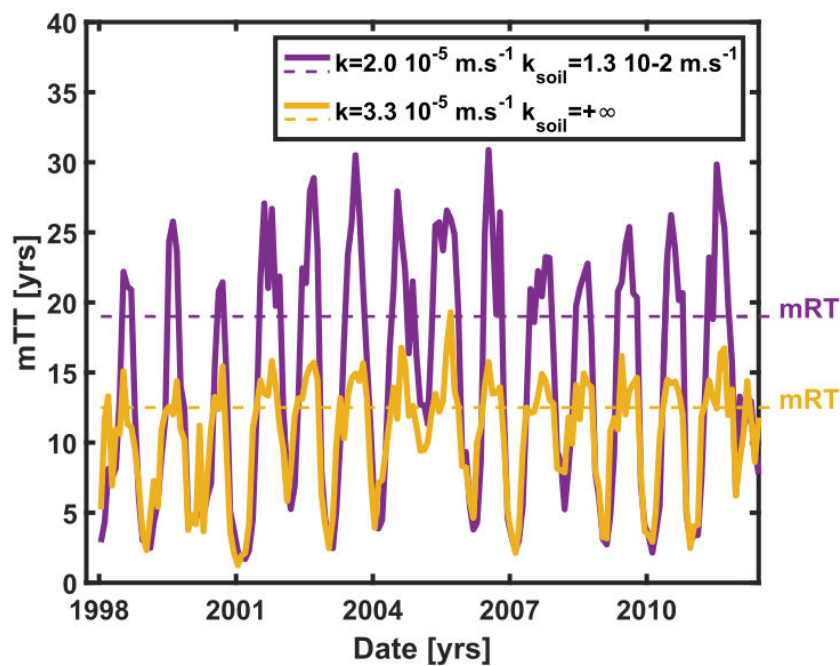


Figure 15: Temporal variation of the mean transit time variability for the two models considered (with and without subsurface stormflow routing). The mean transit time follows a typical seasonal variation with more young water during the wet season and less during the dry season. The corresponding average mean residence times for these two models are materialized by colored dashed lines. Note how the increase in mean residence time between the two different model structures is correlated with the variability in mean transit time.

6.5 Storage Selection Functions

To synthetically characterize the preference of the hillslope modeled to release young or old groundwater, storage selection functions are used. We represent this function for the two most contrasted months: the driest month in September 1992 and the wettest in January 2001 and for two months of the same hydrologic season: October 2007 and January 2008 (Figure 16). Compared to the perfectly mixed assumption which corresponds to a cumulative of the storage selection function on the x-y line (Figure 16, thin black dashed line), the storage selection functions for these two events are significantly driven towards younger ages for the wet season and towards older ages for the driest event (Figure 16, color lines). This pattern is supposed to be typical of catchments where the preference for releasing young waters stored in the catchment increases with the wetness of the catchment which promotes connectivity and the occurrence of fast, superficial flow paths in the subsurface (Benettin et al., 2017; Harman, 2015).

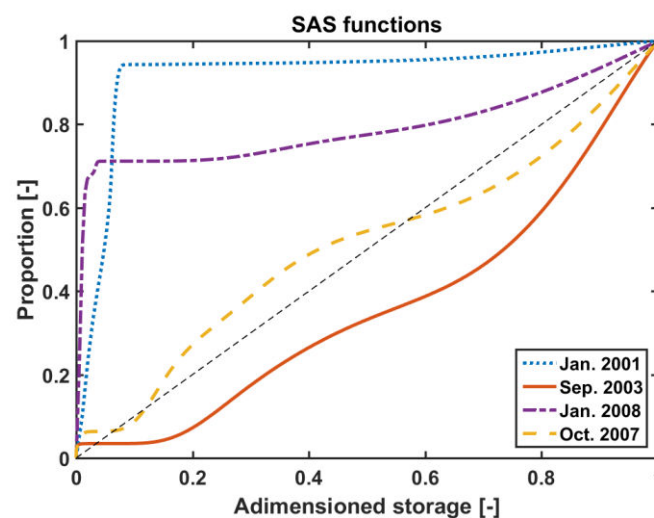


Figure 16: Cumulative storage selection functions for the model of the Guillec catchment with subsurface stormflow routing. The behavior of the catchment changes critically with the season. In the wet period, young waters are preferentially discharged to the stream. In the dry period, the representative hillslope model selects a larger proportion of old groundwater. The x-y line represents a random sampling characteristic of a random process.

6.6 Application: computation of different solute concentrations in the river discharge in the Guillec catchment

Temporal variability of different solute concentrations can be modeled assuming different hypotheses regarding the reactivity of these elements. For inert anthropogenic gases and nitrate

dissolved species, two different reactivity frameworks can be represented, one without any reactivity and another with a first order kinetic reaction (section 4.3). The first framework represents the effect of the mixing due to the stratification of transported elements thoroughly described in section 3.3 and 3.4. The second hypothesis assumes a first order kinetic reaction with $1/\beta = 20$ years. Indeed, previous studies have shown that this reactivity timescale is characteristic of some shallow aquifers in crystalline regions (Kolbe et al., in rev.; Tesoriero and Puckett, 2011).

Figure 17 shows the nitrate evolution in the Guillec river reproduced numerically when considering these two hypotheses for the two different model structures considered: a) with instantaneous routing in the soil layer and permeable weathered zone and b) with slower routing in the soil layer and less permeable weathered zone. The blue line represents the input nitrate time series representing the nitrate load remaining after the harvest.

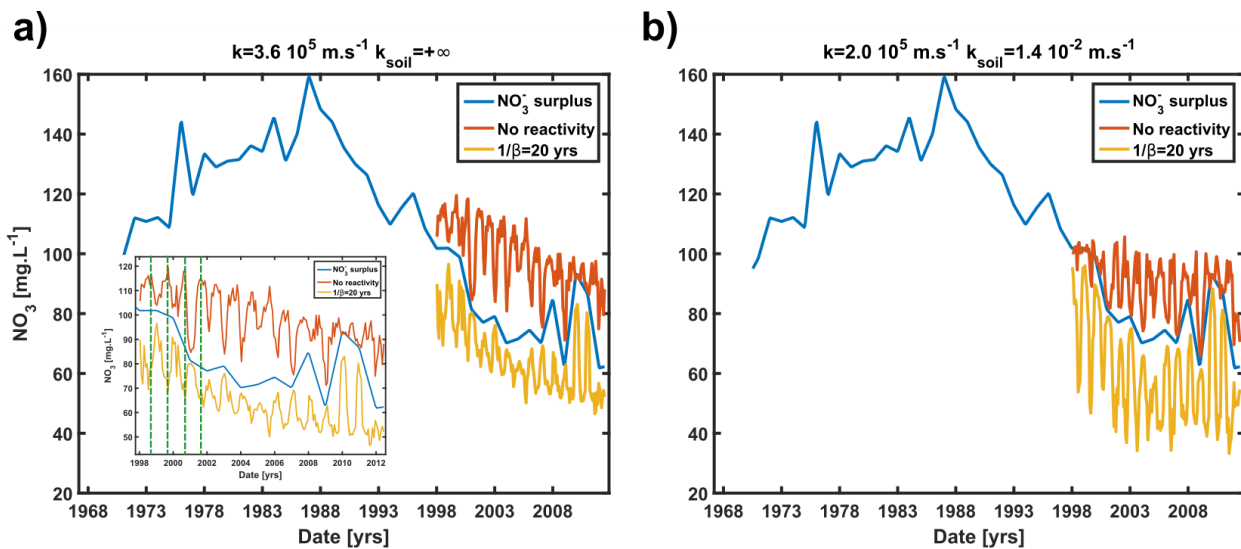


Figure 17: In stream modeled nitrate time series and input nitrate loads (in blue) for two different models structure: a) with a permeable weathered zone and an instantaneous routing in the soil layer. b) with a less permeable weathered zone and a routing in the soil layer with a saturated hydraulic conductivity of $1.3 \cdot 10^{-2} \text{ m.s}^{-1}$. In insert a zoom of the same numerical time series with vertical green dashed lines representing the wet season. Note the contrasted seasonal variations depending on the reactivity hypothesis.

This figure reproducing numerically in stream nitrate time series illustrates the so-called legacy or inheritance effect described in previous studies (Bouraoui and Grizzetti, 2011; Hrachowitz et al., 2015; Meter and Basu, 2017; Meter et al., 2016). Indeed, despite the strong reducing tendency in nitrate loading, nitrate concentrations remain high, sometimes, higher than current nitrate loading due to the memory effect of the catchment which contains decades year old

groundwater. These results show a decreasing tendency consistent with what have been observed in Brittany and more generally in western countries where public policies aiming at reducing nitrate loading have been applied (Bouraoui and Grizzetti, 2014). Obviously, considering that nitrates are removed according to a first order kinetically-controlled degradation (with a typical reaction time of 20 years) leads to reduced nitrate concentrations in the river compared to the no-reactivity hypothesis (yellow lines materializing the first order kinetically-controlled reactivity assumption are always below the red lines representing the no-reactivity assumption).

Additionally, nitrate concentrations show marked seasonal variations, consistently with previous observations (Figure 17a, insert) (Abbott et al., 2018). This is due to the seasonal variations of hydrological flow paths described with a time-based approach in the previous section (section 6.4 and 6.5). The no-reactivity assumption leads to maximum nitrate concentrations during the dry season (materialized by the green dashed lines in the insert) and minimal nitrate concentrations in the wet season. In the dry season, the stream is primarily constituted of old groundwaters, which have an age contemporary of the maximum inputs loads of the 1970s, therefore increasing the nitrate concentrations in the stream. In the wet season, a significant proportion of young subsurface flow paths are feeding the stream, therefore decreasing the nitrate concentrations due to the decrease in the input nitrate loading. However, when assuming a reactivity hypothesis, seasonal patterns observed in the simulated nitrate concentrations are reversed. With a first order kinetically-controlled reactivity, minimum (respectively maximum) nitrate concentrations are simulated during the dry season (respectively the wet season). With this assumption, the reactivity effect prevails over the mixing effect. Indeed, in the dry season, old groundwater feeding the stream are partially denitrified decreasing the nitrate concentrations whereas, in the wet season, subsurface flow paths are too young to get denitrified since the typical reactivity time scale is 20 years.

7 Conclusion and perspectives

We have developed a flux and transport model based on Boussinesq theory accounting for the interaction between the water table and the soil / bedrock interface. These dynamical interactions lead to the alternance between groundwater dominated and subsurface stormflow dominated flow paths to the stream at the seasonal time scale. We reconstruct the natural stratification of flow paths following flow and mass continuity principles and propose time-

based advective particle tracking scheme to simulate these processes. We introduce the effect of dispersive and diffusive processes by considering each particle as an inverse Gaussian distribution where dispersion is obtained by the product of a scale-dependent dispersivity and of the travel distance of the particle. We deduce the time-varying transit time and residence time distributions and illustrate them on a real test case, the Guillec catchment, with two different models (with instantaneous and time-limited routing). Both flow models are calibrated on the discharge time series. After validation of the transport algorithm, we show how stratification, surface/subsurface exchanges and routing shape the transit time and residence time distributions. While the residence time distributions can be assumed relatively stable with time, the young water proportion of the time varying transit time distributions is highly variable seasonally leading to pronounced seasonality in the mean transit times variations.

We have eventually shown with how the transport inert and simple reactive solutes can be simulated within a classical convolution approach to account for spatially explicit dependence of reactivity between different hydrological compartments (e.g. soils, aquifers). We discuss the interests of time-based descriptions with minimal spatial representation of the flow paths to test different approaches of reactivity structures in catchments.

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877

2.3 Bilan

Dans ce chapitre, nous avons décrit une méthode de suivi de particules injectées sur un versant en régime transitoire. Ce suivi de particule permet de reconstituer le temps de résidence des eaux qui sont stockées dans l'aquifère ou temporairement dans le sol lors des épisodes de ruissellements de subsurface. Il permet également d'avoir accès aux distributions de temps de transit représentant le mélange d'eaux de différents âges qui alimentent la rivière à l'instant t . Cette dernière distribution est, comme on l'a vu, éminemment variable saisonnièrement et dépend de l'état de saturation du versant ainsi que du forçage climatique. Ces distributions caractérisent en fait temporellement les chemins de l'eau empruntés dans le bassin versant et leur variabilité tout au long de l'année.

Avec ces distributions, on montre comment, à partir d'une donnée sur le chargement en nitrate du fait des forçages agricoles, on peut modéliser les variations de concentrations en nitrates en rivière. Ceci suppose de faire une hypothèse sur la réactivité qui a lieu dans le versant. Ici nous avons présenté une hypothèse de réactivité uniquement basé sur des considérations temporelles (loi cinétique d'ordre 1) [Kolbe *et al.*, in rev.]. Ce modèle permet d'envisager d'implémenter des concepts de réactivité plus complexes, soit basé sur le concept de temps d'exposition [Ginn, 1999], soit sur une description spatialisée de la réactivité : ajout d'une réactivité qui dépend de la profondeur (pour prendre en compte la disponibilité de minéraux réduits comme la pyrite dans les aquifères) ou qui dépend de la zone du versant (sols, aquifères, zone riparienne), voire de ses propriétés (e.g. état de saturation) (voir Partie IV Chapitre 4).

Ces expériences numériques qui ont permis de valider le schéma de suivi particulière montre, qu'avec ce formalisme, on peut donc envisager de prédire l'évolution des concentrations en nitrates sur un bassin versant suivant différents scénarios de réduction des intrants. Plus généralement, ce formalisme de modéliser l'évolution de la concentration en solutés en rivière, qu'ils proviennent d'éléments anthropogéniques ou issus de l'altération. Cependant, avant de s'intéresser à une réactivité aussi complexe, cela nécessite d'abord d'avoir un modèle qui a été calibré en flux et en transport. C'est l'objet de la prochaine partie de montrer comment arriver à une calibration *a minima* du flux et du transport, à l'aide de données de débit et de suivi de silice dissoutes en rivière en faisant une hypothèse minimaliste sur l'altération de la silice en milieu souterrain.

Chapitre 3 Comprendre le partitionnement entre eaux jeunes et eaux vieilles dans les cours d'eau à l'aide de données en silice et d'un modèle à base physique

3.1 Introduction

Dans cette partie, nous nous intéressons à comprendre les variations saisonnières de silice mesurées en cours d'eau et à évaluer leur potentiel pour estimer les temps de transit en rivière et leur variabilité intra annuelle. En effet, nous avons vu à la Partie II Chapitre 2 que la silice peut être utilisée en aquifère comme un traceur des temps de résidence. En effet, de par le fait que la silice est un produit de l'altération des roches cristallines, elle est en un marqueur du temps de contact entre l'eau et les roches et donc de leur temps de résidence. Si en aquifère, nous avons d'autres traceurs des temps de résidence, comme les CFCs ou le SF₆, ces traceurs sont des gaz dissous et ne peuvent pas s'utiliser en rivière car leur concentration s'équilibre rapidement avec l'atmosphère et ne permet donc plus d'avoir une indication sur l'âge moyen des eaux échantillonnées en rivière. Comme nous l'avons également vu dans la partie introductive (Partie I 1.2.2 et Partie I 2.1.2), les traceurs souvent utilisés en rivière comme le $\delta^{18}\text{O}$ ou le $\delta^2\text{H}$ ne caractérisent spécifiquement que la partie d'eaux jeunes de la distribution des temps de transit. La partie de la distribution des temps de transit composée des eaux plus vieilles est de ce fait mal caractérisée en rivière alors que c'est cette partie qui influence le plus le temps moyen. Certaines études recommandent ainsi de ne caractériser en rivière que la proportion d'eaux jeunes et non le temps de transit moyen quand on utilise des chroniques isotopiques en $\delta^{18}\text{O}$ ou en $\delta^2\text{H}$ [Kirchner, 2016]! Dans ce contexte, évaluer la possibilité d'utiliser la concentration en silice pour contraindre les temps de transit apparaît donc comme spécialement intéressante, surtout en considérant que la silice est un traceur spécifiquement sensible aux temps longs.

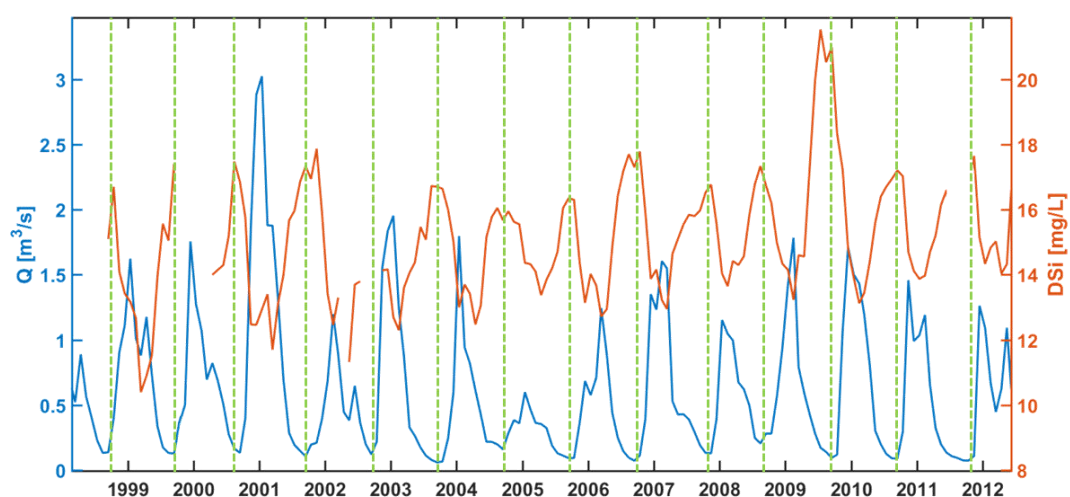


Figure 24: Evolution saisonnière de la concentration en silice dans un bassin versant breton (le Ris). Le débit est représenté en bleu (axe gauche) tandis que la concentration en silice est en orange (axe droit). Noter l'anticorrélation des deux types de données et le fait que les concentrations en silice atteignent leur maxima lors de l'étéage. Données représentées à l'échelle mensuelle provenant du programme de suivi Ecoflux.

Si on regarde une série temporelle mensuelle de concentrations en silice dans le bassin versant du Ris (Figure 1), on voit en effet que les *maxima* de concentrations sont atteints à la fin de la saison sèche, lorsque les étéages sont les plus marqués. Cette saison correspond au moment où les nappes souterraines

sont les plus sollicitées, et donc intuitivement, au moment où les eaux alimentant la rivière sont les plus anciennes.

Nous présentons donc un modèle qui relie les variations saisonnières mesurées en silice à la variation de temps de transit moyen en rivière. Ces variations de temps de transit sont une manière d'interpréter les variations de circulations hydrologiques en termes de temps de transit. Pour quantifier ce lien entre concentration en silice et temps de transit, nous reprenons le modèle présenté précédemment et y adjoignons une loi cinétique d'ordre 0 pour décrire la dissolution des roches silicatées. Nous évaluons la capacité du modèle à rendre compte des fluctuations saisonnières en silice, et présentons ensuite quelques implications sur la compréhension qu'un tel modèle engendre vis-à-vis de la variabilité des temps de transit en rivière.

3.2 Article : Partitioning young and old groundwater contributions to streams with integrated discharge and water quality data

Commentaire : cet article n'a pas encore été soumis dans une revue à comité de lecture. Pour cette raison, il apparaît encore sous la forme d'une version préliminaire avant le dépôt du manuscrit final pour soumission.

Partitioning young and old groundwater contributions to streams with integrated discharge and water quality data

Highlights

- Recharge and discharge variabilities informs the hydrological partitioning of streamflow.
- Seasonal dissolved silica variations reflect the variability of mean transit times.
- Old mean transit times in the watershed are driven by the groundwater flow.
- Young water proportion variabilities are due to ephemeral subsurface stormflow.

Abstract

If substantial proportions of river streamflows are constituted of water less than three months old, it is unknown how variable this proportion is according to time. We develop a parsimonious physically-based model informed by infiltration and discharge data time series to effectively partition the net precipitation (P-ET) into ephemeral subsurface stormflow and perennial groundwater flow. Both flow paths are defined with subsurface processes and made explicit in terms of transit times. We model the subsurface flow generating process by a threshold effect when the water table saturates the soil/bedrock interface. This dynamical interaction of the water table with the soil/bedrock interface drives the seasonal response of the watershed to net precipitation. We show that, once calibrated on outflow data, these models turn out to relevantly explain the seasonal variability in dissolved silica variability in streams. If young subsurface flow (less than 3 months) constitute 24% of streamflow in average, this contribution is highly variable between summer and winter ranging between 0% and 70%. This is due to the evolving flow structures following the seasonal climatic forcing and differences in the moisture conditions issued by the catchment heterogeneity. Even if the young subsurface stormflow is the most variable, the old groundwater flow (>5 years) contributes significantly to the streamflow, leads to mean transit times in average equal to 16 years and drives the occurrence of runoff processes, which rejuvenate streamwater.

Keywords: Time-varying transit time distributions; Groundwater residence time distributions; Storage Selection Functions; silicate weathering rates; Dissolved silica; Groundwater age.

1 Introduction

Understanding how water travels in a catchment, where and at which rate and what kind of minerals it solubilizes in its travel underground is central to quantify and predict human impacts on aquatic ecosystems [McDonnell and Beven, 2014; Pinay *et al.*, 2015; van der Velde *et al.*, 2010]. Monitoring water quality in groundwater as well as in streamwater requires to better understand these hydrologic flow paths location, timescale and variability and their overall consequences on reactivity [Abbott *et al.*, 2016; Beyer *et al.*, 2016; Kirchner and Neal, 2013]. Enhanced availability of water-quality datasets on different catchments has promoted the development of new concepts for explaining the multiscale temporal variability of water quality [Hornberger *et al.*, 2001; Martin *et al.*, 2004; McDonnell, 1990; Molenat and Gascuel-Oudou, 2002; Molenat *et al.*, 2008; Onderka *et al.*, 2012; Ronchi *et al.*, 2013]. Among them, the characterization of the transit time distribution, of the residence time distribution and of the relation linking them thanks to different tracers has been widely developed to relate water quality time series to physical transfer and processes [Aquilina *et al.*, 2012; Bolin and Rodhe, 1973; Botter *et al.*, 2011; McDonnell *et al.*, 2010; Soulsby *et al.*, 2009]. For water sampled in the river, the transit time distribution represents the distribution of travel times of the water in the catchment from the precipitation event to its discharge into the stream [Heidbuchel *et al.*, 2012; McGuire and McDonnell, 2006; Rinaldo *et al.*, 2011]. For water sampled in the aquifer, the residence time distribution represents the age distribution of the water stored inside the same catchment [Bethke and Johnson, 2008; Cornaton and Perrochet, 2006; Etcheverry and Perrochet, 2000; Leray *et al.*, 2016].

These two transit time and residence time distributions present marked differences with mean residence times typically of the order of some decades to centuries and mean transit times of the order of hundred days to some years [Ayraud *et al.*, 2008; Gleeson *et al.*, 2016; Hrachowitz *et al.*, 2009; Hrachowitz *et al.*, 2010; Kolbe *et al.*, 2016; Leray *et al.*, 2012; Tetzlaff *et al.*, 2009]. While mean transit and residence times have been characterized for decades [Maloszewski and Zuber, 1996; Maloszewski *et al.*, 1992; McGuire *et al.*, 2005; Nyberg *et al.*, 1999], the effective partitioning of younger versus older streamwater or groundwater has attracted more attention only recently [Jasechko, 2016; Kirchner, 2016]. The proportion of streamwater less than 3 months old has been shown to represent in average 30% of the river discharge at the global scale [Jasechko *et al.*, 2016] while significant amounts of old streamwater are also present due to the long tailing in the transit time distribution [Morgenstern *et al.*, 2010; Peters *et al.*, 2014]. Similarly, for groundwater, aquifers contain at the same time fossil waters and very young

waters [Gleeson *et al.*, 2015; Jasechko *et al.*, 2017]. The significantly younger water in the streams has been interpreted as the illustration of catchment heterogeneity, which stores groundwater with a broad range of residence time and which releases preferentially young water [Harman, 2015; Rinaldo *et al.*, 2015; van der Velde *et al.*, 2012]. However, it is unknown 1. how catchments can release such young streamwater while they are constituted predominantly of older groundwater? 2. how this young streamwater proportion can be temporally so variable? and 3. what are the processes able to sustain large age contrasts and temporal variabilities? Some studies have addressed these questions separately from river time series with data-based models to infer the variable proportion of younger and older groundwater directly [Benettin *et al.*, 2017]. Other studies have addressed the contrasting age paradox between stored and travelling waters with conceptual and process-based models [Danesh-Yazdi *et al.*, 2018]. Very few studies however looked into the underlying physical processes able to explain patterns found in real datasets [Kaandorp *et al.*, 2018; Yang *et al.*, 2018].

Several processes have been invoked to promote the simultaneous occurrence of young and old water fractions in the river discharge and in the aquifer for such an important timescale. Fundamentally, the internal heterogeneity of the catchment partially mixes waters of different ages and promotes the apparition of heterogeneous flow paths connecting different groundwater compartments and aquifers to the sampled stream or groundwater areas [Berghuijs and Kirchner, 2017; Bolin and Rodhe, 1973; Eriksson, 1961; Eriksson, 1971]. For the residence time distribution corresponding to the groundwater stored inside the aquifer, age distributions are also widened by dual porosity storage and by hydraulic conductivity decrease with depth [Ameli *et al.*, 2016a; Ameli *et al.*, 2016b; Haggerty, 2001; Haggerty and Gorelick, 1995; Haggerty *et al.*, 2000]. For the transit time distribution, macropore flows and stratification in the catchment properties (porosity, hydraulic properties) also lead to enhanced age dispersion [Beven, 2010; Kirchner *et al.*, 2001; Rinaldo *et al.*, 2011]. Part of the age variability comes from and thus can be informed by the relative importance of subsurface and groundwater flows. Runoff processes are of particular interest because 1. they are known to vary importantly during the year with strong impact on the variability of solute time series monitored in rivers 2. they promote the apparition of fast surface and/or subsurface flow together with the occurrence of slow groundwater flow, which could explain differences observed in mean residence time and mean transit time as well the important partitioning observed both in transit time distributions and residence time distributions [Beven, 2010; McDonnell, 2013; McDonnell and Beven, 2014]. Additionally, runoff is known to be driven by the climatic variability and by the amount of

water stored inside the catchment (moisture conditions) promoting fast connectivity of different water pools [Freeze, 1972; Penna *et al.*, 2011; Stieglitz *et al.*, 2003; Tromp-van Meerveld and McDonnell, 2006a; b]. These two patterns (climatic variability and moisture conditions) have been invoked as drivers for time series variability [Benettin *et al.*, 2013; Hrachowitz *et al.*, 2010; Tetzlaff *et al.*, 2014]. Indeed, during the wet season, when the water table of the aquifer intersects permeable horizons of the soil, gravity-driven subsurface stormflow is generated because of the saturation of this soil interface. This subsurface stormflow is constituted of both return flow, coming from the seeping groundwater and infiltration occurring on this saturated soil layer. On the contrary, during the dry season, the water table of the aquifer remains below the more pervious layers and no runoff is generated.

In this context, we develop a process-based framework to model this dynamical interaction between fast subsurface stormflow runoff and slow groundwater flow. We hypothesize that interactions are driven by topography and that the key process is the relative position of the water table to the soil layer. We model the consequences of the surface and subsurface flow dynamics on transit and residence times by tracing water parcels in the subsurface (via groundwater flow and subsurface stormflow). We deduce both the transient transit time distribution arriving in the river and the transient residence time distribution of groundwater stored in the catchment. We explore the relevance of this modeling framework by comparing its prediction abilities to natural observations of discharge and dissolved silicate concentrations (DSi). By comparing the model to the DSi data, we also determine the informational content of the DSi observations along the following questions: does seasonal DSi variability in rivers inform different surface and subsurface flow paths and transit times? Can DSi be used as a tracer of the mean transit times in streams and how this information should be related to the repartition between the old groundwater storage and the flux going to the stream? Can we infer the processes generating the variability of transient transit times and the influence of the catchment structure?

We set up and test this framework on a series of six watersheds in a crystalline region (Brittany, France) where aquifers are mainly located in the regolith layer within some meters to tens of meters of the surface. We estimate that the DSi weathering rate is of the order of $0.3 \text{ mg L}^{-1} \text{ yr}^{-1}$ for these catchments in agreement with previously estimated weathering rates in similar geological contexts [Burns *et al.*, 2003; Marçais *et al.*, 2018; Rademacher *et al.*, 2001]. For five of the six watersheds, the surface-subsurface model reproduces closely the observed DSi seasonal variations, showing in turn that the nonlinear dynamic of saturation of the aquifer and

the induced repartition between surface and subsurface flows control the mean transit time in the catchment.

2 Sites and data

We present the Brittany catchments (France) studied, the discharge time series in streams, the precipitation and evapotranspiration data and the spatialized topographic data. All these catchments are characterized by an oceanic climate with a strong climatic variability amongst them due to their topography and to the Brittany climatic variability (from west to the east, precipitations decrease by a factor of 2). This climatic seasonal forcing leads to contrasted water quality in streams with a strong seasonal variability.

2.1 Catchments studied

Six coastal catchments are studied, located in Brittany, France (Figure 1). They are of intermediate size, with a range of areas from 36 km² for the Ris catchment to 190 km² for the Dossen catchment. In terms of climate, the 6 catchments are in the far western part of Brittany characterized by an oceanic climate with rainfall averaging 1183 mm/yr. Still, differences in topography lead to some variations in rainfall and net precipitation content (precipitation minus evapotranspiration). Net precipitation contents vary from 413 mm/yr for the Guillec Catchment to 659 mm/yr for the Douffine Catchment (Table 1). We first describe their geological settings and then their topographical properties.

<i>Catchment</i>	<i>P</i> [mm/yr]	<i>ET</i> [mm/yr]	<i>P-ET</i> [mm/yr]	<i>Q</i> [mm/yr]	<i>Area</i> [km ²]	<i>Topography</i> (min- mean- max) [m]	<i>Dominant lithology</i>
<i>Douffine</i>	1322	663	659	760	160	18 - 157 - 373	<i>Sedimentary schists, sandstones and limestones</i>
<i>Dourduff</i>	1148	649	500	400	68	15 - 95 - 186	<i>Granite</i>
<i>Dossen</i>	1226	639	587	513	190	11 - 153 - 365	<i>Granite and schists</i>
<i>Guillec</i>	1009	596	413	521	72	7 - 72 - 125	<i>Granite</i>
<i>Penzé</i>	1220	627	593	659	143	14 - 149 - 379	<i>Granite and schists</i>
<i>Ris</i>	1173	665	508	561	36	5 - 85 - 232	<i>Granite</i>

Table 1: Data on the water budget (P is the precipitation ET , the real evapotranspiration and Q the outflow measured at the outlet of the catchment), on the typical topography range and on the geology for the six watersheds of Brittany investigated.

2.1.1 Geological context

Except for the Douffine catchment, all catchments are located on crystalline basements but differ in terms of dominating materials (crystalline schist, granite or mixture of both, see Table 1). The Douffine catchment geology is more complex, primarily constituted of a clastic sedimentary bedrock (schists, sandstone) and of some chemical sedimentary rocks (limestone).

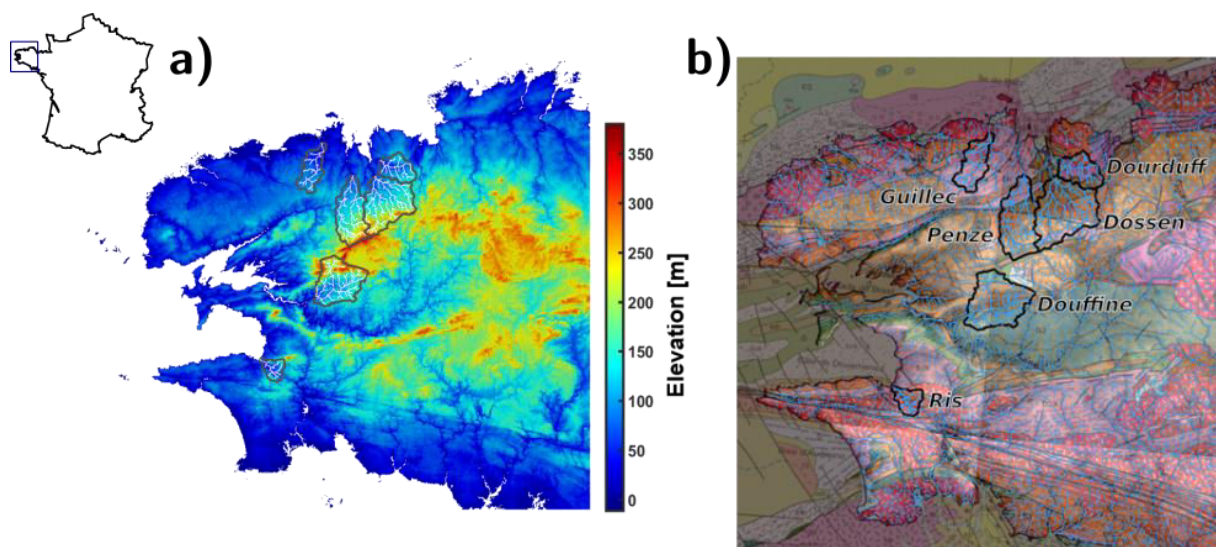


Figure 1: Site locations in Brittany (part of France emphasized in the sketch in the top left corner). a) Locations of the sites on a topographic map of Brittany (obtained with the SRTM30 data [Farr et al., 2007]). b) Locations of the sites on the geological map of Brittany (Data from BRGM, French geological survey [BRGM et al., 1996]).

2.1.2 Topographical properties

Topographical data are retrieved from the freely accessible data coming from the SRTM initiative [Farr *et al.*, 2007]. They now provide DEM data at a 30 m resolution. All topographical map and topographical analyses are performed with the matlab topotoolbox package [Schwanghart and Kuhn, 2010; Schwanghart and Scherler, 2014].

Among these catchments, the average topography varies from ca 75 m for the very coastal catchment to ca 150 m for the other catchments further away from the sea (Figure 1a and Table 1). The average slope varies from 2% for the Guillec catchment to 6% for the Douffine catchment. Overall, these catchments differ mainly in the distribution of their elevation as a function of the distance to the stream (Figure 2). These catchments can be classified in two different types, the Guillec and the Dourduff catchment characterized by gentle slopes especially close to the stream whereas the Ris, the Douffine, the Penze and the Dossen catchment display steeper slopes. Steeper catchments might promote more subsurface stormflow when gentle catchments might promote groundwater flow.

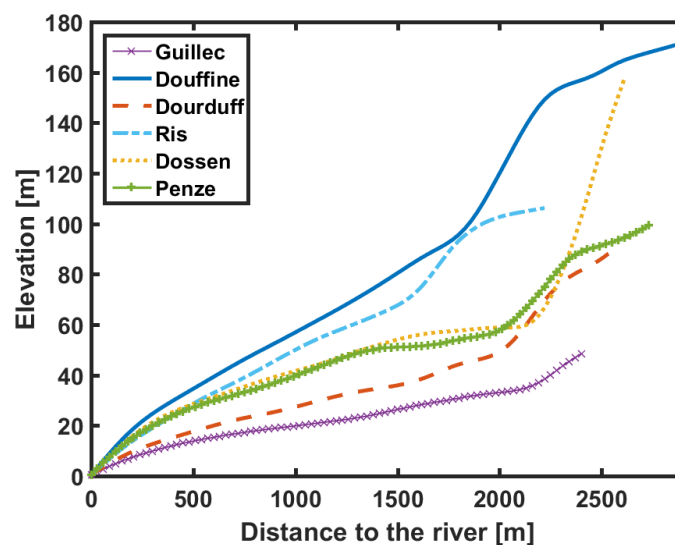


Figure 2: Mean elevation relative to the river (set at 0 m for each catchment) as a function of the distance to the river. Elevation is averaged at the scale of the watershed. This gives an indication of the average slope distribution depending on the distance to the stream of the watershed. Small slopes close to the river will likely promote subsurface stormflow due to the saturation of the soil layer from the groundwater.

2.2 Flow and DSi data

For each watershed, we have discharge time series at gauging stations of this catchment. Net precipitations time series come from a model developed by the French meteorological institute.

Finally, we also have a 14 years DSi solute time series recorded in the rivers at the outlet of these catchments coming from citizen science.

2.2.1 Discharge data

Discharge data come from the national hydrologic station monitoring network (<http://www.hydro.eaufrance.fr/>). For each catchment, hydrometric station provides validated, daily discharge data are available for the time period 1998-2012. These data come from gauging stations draining the same river as the water quality data sampled (section 2.2.2). Nevertheless, when gauging stations did not correspond to the exact water quality sampling stations locations, discharge is translated to the water quality sampling station by applying a ratio of corresponding drainage area [Abbott *et al.*, 2018]. These discharge daily time series are then averaged to obtain monthly discharge time series, Q_{obs} , representative of the seasonal fluctuation occurring in this catchment. Figure 3 and Figure 4 show the typical discharge seasonal variations recorded for two of the catchments studied: the Ris and the Dossen catchment.

2.2.2 Dissolved Silica

DSi data come from a citizen science initiative and is a 14 years time series weekly sampled at different catchments [Abbott *et al.*, 2018]. DSi was quantified as H_4SiO_4 (mg L^{-1}) and quality of these data was assessed in a previous study [Abbott *et al.*, 2018]. These weekly time series are finally averaged at the month time scale to get representative time series (Figure 3). DSi time series display consistent seasonal variations with maximum DSi concentrations reached at low flows in the late dry season, while minimal DSi concentrations occur at high flows during the wet season.

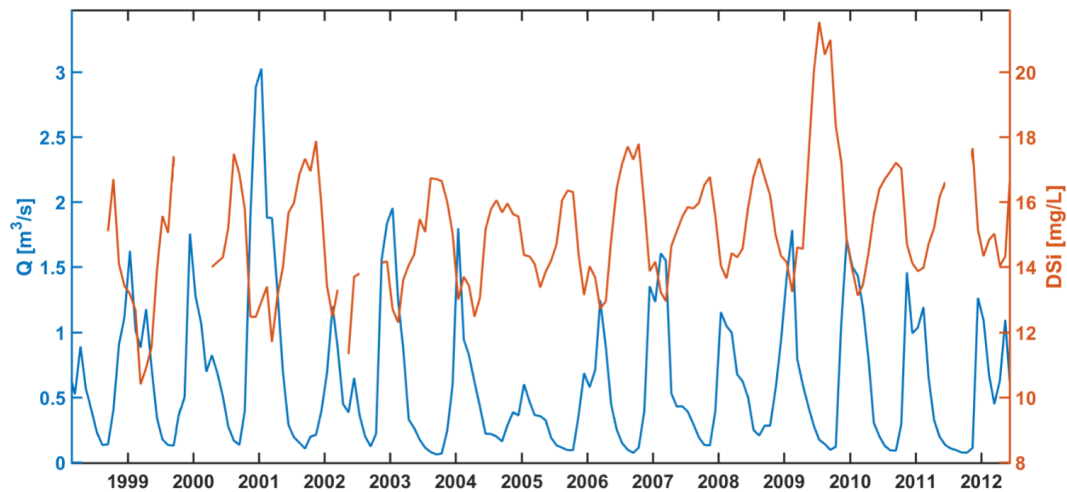


Figure 3: Discharge and DSi recorded time series in the Ris catchment. Note how the high DSi concentrations correspond to the end of the dry season when the catchment discharge is at its lowest flow.

2.2.3 Rainfall and Evapotranspiration

Rainfall and evapotranspiration chronicles are derived from the SURFEX program, a Meteo France model assimilating rainfall, temperature and wind data to produce unified national scale daily time series data on rainfall and real evapotranspiration at the grid scale of 8x8 km [Barbu *et al.*, 2014; Boone *et al.*, 2017; Faroux *et al.*, 2013; Quintana-Seguí *et al.*, 2008a; Quintana-Seguí *et al.*, 2008b]. We consolidate these grid scales data at the catchment scale by averaging the daily time series of the different 64 km² grids covering the catchment proportionally to their relative area of the catchment. Additionally, the daily time series are averaged at the monthly time scale to filter out the daily fluctuations, which are beyond the accuracy of the developed flow models. Typical modeled net precipitation forcing as well as measured discharge at the outlet are showed in Figure 4.

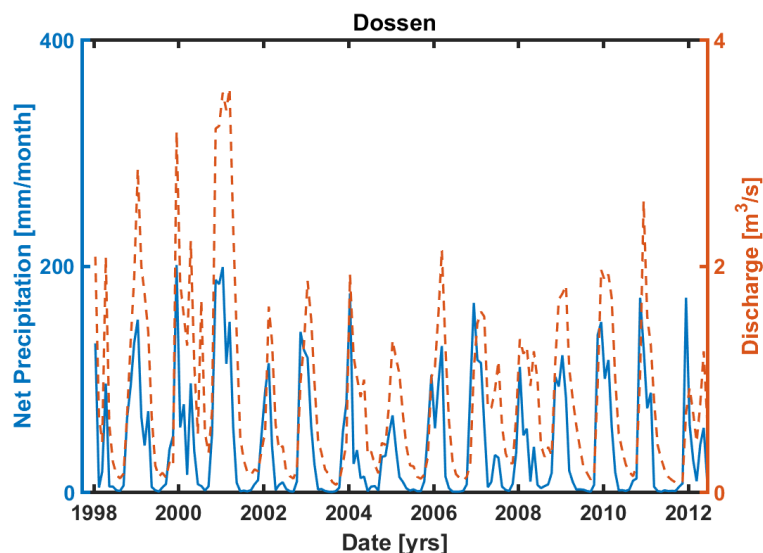


Figure 4: Monthly net precipitation modeled with SURFEX and monthly discharge observed in the Dossen catchment.

3 Models and Methods

We hypothesize that a simple framework describing the catchment as an equivalent hillslope describing the succession of volume stored as a function of the distance to the stream could convey the filter effect of the groundwater volume. We consider the generation of temporary subsurface stormflow by modeling the dynamical interactions between the water table and the soil layer driven by the wetness of the catchment and controlled by its topography. Therefore, the model developed aims at catching the seasonal fluctuation observed in both discharge and water quality described in the previous section (Figure 5). First, we detail the extraction of the equivalent hillslope from the topographic data. These equivalent hillslopes indeed represent the topographic effect aggregated at the catchment scale. We then briefly describe the modeling strategy to solve flux and transport on this equivalent hillslope representation. Finally, we detail the calibration strategy.

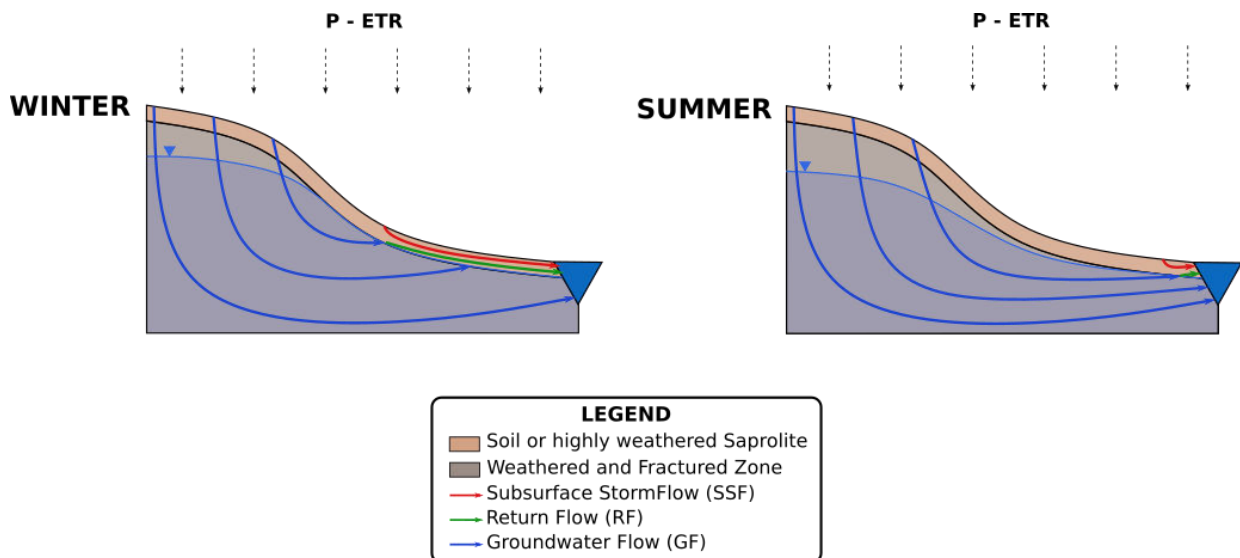


Figure 5: Sketch of the bottom-up runoff process driving water quality between winter and summer in temperate oceanic climates such as Brittany (France). Bottom-up runoff process refer to the generation of subsurface stormflow constituted of seepage flow (also called return flow, green arrow) and/or direct infiltration onto saturated areas (red arrow), both induced by the interception of the water table with the soil/bedrock interface [McDonnell, 2013].

3.1 Definition of equivalent hillslope models

We delineate the drainage area of the catchments from the outlet location using the DEM (SRTM, 30 m) and the D8 algorithm implemented in the topotoolbox matlab package [Farr *et al.*, 2007; Schwanghart and Kuhn, 2010; Schwanghart and Scherler, 2014]. Because of the absence of detailed flow and DSI observations within the catchments, we choose to rely on a representation of the catchment based on an equivalent hillslope characterized by its equivalent structure, which is described by its plan shape and its profile curvature [Loritz *et al.*, 2017; Reggiani and Schellekens, 2003; Troch *et al.*, 2003]. This equivalent hillslope representation is obtained by aggregating the cells of the DEM in a 1D representation according to their distance to the river in the DEM (Figure 6a). It implicitly assumes that the groundwater catchment is identical to the hydrological catchment, i.e. that every groundwater flow paths goes from their recharge point to the closest adjacent streams. This assumption is supported by previous investigations in catchments of limited aquifer depth like in Brittany at least for the flow paths of intermediate ages (<100 years) [Kolbe *et al.*, 2016]. Topographically-driven regional flow cells [Toth, 1963] will not be included as marginal for the crystalline basement of the type of Brittany for century-old flow cells.

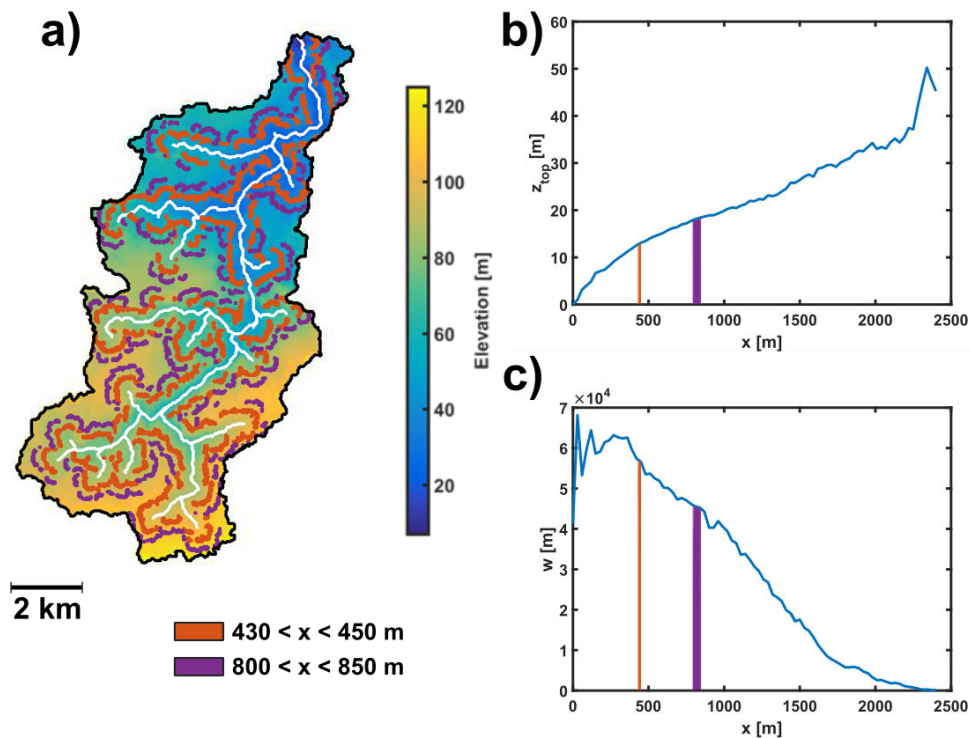


Figure 6: (a) 2D representation of the topography of the Guillec catchment. (b) Elevation function of the equivalent hillslope characterizing the assumed average depth of the aquifer (since the aquifer bottom is assumed to be flat) at a distance x from the stream. (c) Width function of the equivalent hillslope characterizing the partial area distribution of the catchment as a function of the distance x from the stream. To illustrate the aggregating strategy, we highlighted the elevation and the width of the equivalent hillslope in red and purple for two different distances to the stream (corresponding to ca 440 m and 825m). Corresponding DEM cells are highlighted in the same color.

Following these approximations, catchments are eventually described by the three functions of the width of the catchment $w(x)$, the bedrock slope $i(x)$, and the aquifer depth $d(x)$ according to the distance to the river x . Without any detailed characterization of the weathered profiles and as Brittany is characterized by relatively low slopes ($<15\%$), we consider that aquifers have a flat bottom i.e. that the function $i(x)$ is uniformly zero. Width and soil depth functions are derived from the DEM analysis. Figure 6b and c show these functions for the Guillec catchment as an illustrative example. Even though the eventual catchment model is a 1D equivalent hillslope, spatial as temporal data can still be used along the hillslope and in the river with an efficient process-based model. This is specifically important in this type of settings where the processes controlling the transit times are controlled by the saturation profile of the hillslope from the river.

3.2 Groundwater and subsurface stormflow model

Groundwater and subsurface stormflow are obtained by solving the Boussinesq equation in the equivalent 1D hillslopes defined in the previous section. We use a model developed to simulate transient river flow at the catchment outlet through a dynamical partitioning of net precipitations into subsurface stormflow and groundwater flow [Marçais *et al.*, 2017]. Partitioning is based on the dynamical interaction of the water table with the soil layer. Groundwater flow is modeled by a classic Boussinesq approximation while subsurface stormflow in the soil layer is routed to the river by a gravity-driven flow linearly increasing with the slope of the soil/bedrock interface. We assume that this soil/bedrock interface is parallel to the land surface. As the water table of the aquifer intersects the soil layer, subsurface stormflow starts to occur. It can consist both of return flow and direct infiltration onto the saturated soil/bedrock interface, as generally observed in humid and topographically-moderated catchments [Dunne, 1983; McDonnell, 2013]. These subsurface stormflow are fast compared to the groundwater circulation with typical timescales on the order of some hours to some days [Hopp and McDonnell, 2009; Nyberg *et al.*, 1999; Tromp-van Meerveld and McDonnell, 2006b]. Groundwater flow and subsurface stormflow reaching the river at time t constitute the modeled discharge $Q_{mod}(t)$. In this partially integrated representation (integration transversally to the steepest slopes of the catchment), the model solves for the 1D velocity field both in the aquifer and in the soil compartment to the river. The velocity in the soil compartment corresponds to the routing speed of the stormwater kinematic wave. The velocity in the aquifer is much slower due to the limited hydraulic conductivities and to the important quantities of groundwater stored.

3.3 A flux-weighted particle tracking scheme to model transport

A flux-weighted particle tracking scheme has been developed to simulate the transport in the catchment with a Lagrangian description [Marçais *et al.*, in prep.]. Particles are injected at each time steps, proportionally to the net precipitation content and to the partial area represented by the mesh discretization. It simulates the transient advective hydrological flow paths occurring in the aquifer through groundwater flow paths as well as in the soil layer when subsurface stormflow paths occur. Vertical stratification of flow paths is introduced to avoid flow path intersections and respect the constitutive zero velocity normal to the flow path. This enables to represent the vertical spatial distribution of the particles residence times inside the aquifer and to simulate return flow with the youngest particles present at the water table [Marçais *et al.*, in

prep.]. Dispersive effect in the subsurface are integrated on the flow paths assuming a longitudinal dispersivity, which depends linearly on the particle traveled distance [Gelhar *et al.*, 1992; Kirchner *et al.*, 2001]. The solution of the transport problem issues process-based spatially and temporally resolved residence time distributions at each location of the equivalent hillslope and transit time distributions in the stream.

3.3.1 Transit time and residence time distributions descriptors

From this mechanistic model, we can derive the transient transit time distributions $p_Q(\tau, t)$ (respectively residence time distributions $p_S(\tau, t)$) of the transit time τ , present in the river outflow $Q(t)$ (respectively stored in the catchment) at each time t . We can also extract different time-variable hydrological descriptors of these transient distributions.

The mean transit time μ_Q is defined as the first moment of the transient transit time distribution [McGuire and McDonnell, 2006]. The mean transit time at time t is defined by:

$$\mu_Q(t) = \int_0^{+\infty} \tau p_Q(t, \tau) d\tau. \quad (1)$$

The mean residence time μ_S is similarly defined by replacing the transit time distribution in the expression by its residence time distribution counterpart:

$$\mu_S(t) = \int_0^{+\infty} \tau p_S(t, \tau) d\tau. \quad (2)$$

The young streamwater proportion P_{3m} is obtained as a fraction of transit times smaller than 3 months [Kirchner, 2016] and derives from the following expression of the cumulative of the transient transit time distributions:

$$P_{3m}(t) = \int_0^{t_0=3months} p_Q(t, \tau) d\tau. \quad (3)$$

which represents the proportion (between 0 and 1) of streamwater less than 3 months old [Kirchner, 2016]. The time-variable storage selection functions $\omega_Q(\tau, t)$ for the outflow Q is derived from the transient transit time distributions and residence time distributions through the equation [Rinaldo *et al.*, 2015]:

$$\omega_Q(\tau, t) = \frac{p_Q(\tau, t)}{p_S(\tau, t)}, \quad (4)$$

332 Finally, with an adapted change of variable, the storage selection function can be expressed as
 333 a function of the aquifer storage S , ordered from the youngest to the oldest ages:

$$S(\tau, t) = \int_0^\tau p_S(u, t) du, \quad (5)$$

334 Defined according to S , the storage selection function is the probability distribution that the
 335 proportion of each stored water of a given age contributes to the streamflow. Overall, $\omega_Q(\tau, t)$
 336 gives the preference for the catchment to release younger and older water [Harman, 2015].

337 3.3.2 Solute transport models

338 DSi concentrations in streams are derived from the transient transit time distributions assuming
 339 that silica dissolution follows a zero-order weathering reaction:

$$C_{DSi}^{prod}(\tau) = \alpha\tau + C_{DSi}^0, \quad (6)$$

340 where τ is the transit time, α is the weathering rate constant and C_{DSi}^0 the initial DSi
 341 concentration in the infiltrated water to the top of the saturated zone [Marçais et al., 2018].
 342 Convolved with the transient transit time distributions, the DSi concentration accounts for the
 343 effect of hydrological mixing coming from the advective dispersive transport at the catchment
 344 scale. We therefore got the following equation to describe the DSi concentrations river time
 345 series $C_{DSi}^{mod}(t, \alpha, C_{DSi}^0)$:

$$C_{DSi}^{mod}(t, \alpha, C_{DSi}^0) = \int_0^{+\infty} C_{DSi}^{prod}(\tau, \alpha, C_{DSi}^0) p_Q(t, \tau) d\tau. \quad (7)$$

346 3.4 Model calibration strategy

347 To assess the relevance of the presented flow processes to model the residence and transit times,
 348 we compare the model presented in the previous sub-sections to the data of the six studied
 349 catchments. Comparison is performed in a classical calibration framework with the success of
 350 the calibration giving the potential degree of relevance of the proposed processes. Equivalent

bedrock hydraulic conductivity is calibrated by river discharge values, silicate weathering rates and initial concentrations are calibrated by DSi values. Other parameters including porosity and dispersivity are fixed to their observed values in similar conditions. With such a limited number of parameters for long chronicles of discharge and DSi concentrations, the model to data agreement can be assessed.

3.4.1 Flux calibration

The hydraulic conductivity of the model is calibrated with the monthly climatic forcing time series (P-ETR) and the monthly averaged discharge. The goodness of fit is evaluated with a Nash-Sutcliffe model efficiency coefficient [Nash and Sutcliffe, 1970]:

$$NSE = 1 - \frac{\sum_{k=1}^{N_t} (Q_{mod}(t_k) - Q_{obs}(t_k))^2}{\sum_{k=1}^{N_t} (Q_{obs}(t_k) - \overline{Q_{obs}})^2} \quad (8)$$

where N_t is the number of time steps on the time period considered, Q_{obs} is the observed discharge time series and Q_{mod} the simulated one. As the calibration requires to determine the optimal value of a single parameter, the calibration strategy chosen consists in systematically sampling the hydraulic conductivity in the range chosen ($[2.8 \cdot 10^{-8} - 2.8 \cdot 10^{-3}]$ m/s) with some refine sampling to determine more accurately the optimal value. Porosity was assigned to 20% as the average value reported for the weathered crystalline rocks of Brittany [Ayraud *et al.*, 2008; Kolbe *et al.*, 2016; Roques *et al.*, 2014].

3.4.2 Transport calibration

Once the hydraulic conductivity has been calibrated on discharge, we determine the consequences of the flow pattern on solute transport. Transit time distributions $p_Q(t, \tau)$ and transient residence time distributions $p_S(t, \tau)$ for each modeled catchment are derived on the basis of the transit time distributions on the tracked flow lines. To reach a representative sampling of the velocity field, particle tracker is run on a 333 years period in steady state for initiation prior to the first date of sampling. We set this duration so that the particular estimated discharge is equal to the discharge estimated with the flux method at the end of the steady state simulation. This ensures that the injected particles have sampled the overall water catchment volume.

DSi time series are computed from the transit time distribution through equation (6) with different weathering parameter sets (α, C_{DSi}^0) . Optimal weathering parameters set

379 $(\alpha_{opt}, C_{DSi_{opt}}^0)$ are determined by equating the simulated and observed temporal average
 380 concentrations ($\bar{C}$) and coefficient of variations of the concentrations ($CV(C)$) of the DSi time
 381 series:

$$\begin{cases} \overline{C_{DSi}^{mod}(t, \alpha_{opt}, C_{DSi_{opt}}^0)} = \overline{C_{DSi}^{obs}(t)} \\ CV(C_{DSi}^{mod}(t, \alpha_{opt}, C_{DSi_{opt}}^0)) = CV(C_{DSi}^{obs}(t)) \end{cases} \quad (9)$$

382 4 Results and discussion

383 We assess the relevance of the hydraulic and chemical assumptions presented in the previous
 384 section by the capacity of the calibrated flow and transport models to follow the discharge and
 385 DSi chronicles. We also derive and analyze the transient transit time distributions for each of
 386 the catchments.

387 4.1 Flow calibration

388 River discharge chronicles obtained with hydraulic conductivities ranging from $2.8 \cdot 10^{-8}$ to
 389 $2.8 \cdot 10^{-3}$ m/s have been systematically compared to the observations according to one minus the
 390 Nash Sutcliffe Efficiency defined in equation (8) (Figure 7). Best data to model agreement is
 391 obtained for the lowest 1-NSE value ranging from 0.1 to 0.3 for the six studied catchments. The
 392 corresponding NSE values between 0.7 and 0.9 (Table 2) demonstrate a close agreement
 393 between the data and the optimal model. As a matter of comparison, perfect agreement
 394 corresponds to NSE=1 whereas a negative NSE occurs when the time series equal to the mean
 395 value is a better predictor than the modeled time series. The sharp variations of the 1-NSE
 396 function around their minimum for 5 of the 6 catchments show well-defined optimal hydraulic
 397 conductivities. Optimal hydraulic conductivities are found in the range of $3.3 \cdot 10^{-6}$ to
 398 $3.3 \cdot 10^{-5}$ m/s, which compare well with typical values previously reported in similar weathered
 399 rocks [Ayraud *et al.*, 2008; Clement *et al.*, 2003; Grimaldi *et al.*, 2009; Kolbe *et al.*, 2016; Le
 400 Borgne *et al.*, 2004; Martin *et al.*, 2006]. Corresponding average transmissivities are reported
 401 in Table 2.

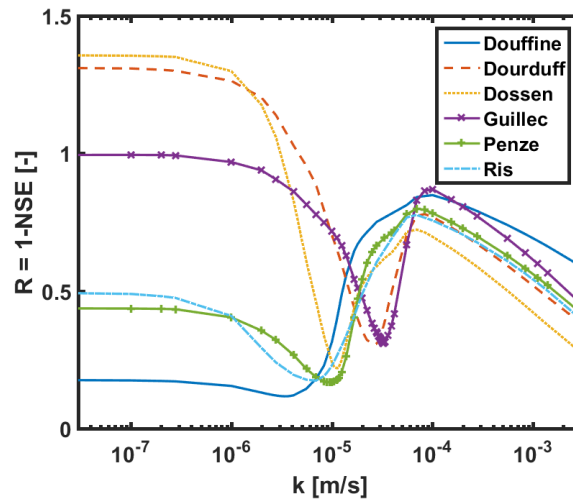


Figure 7: Relative model to data agreement on river discharges as measured by the 1-NSE factor defined by equation (8) for the six studied catchments. Minimum R values correspond to the closest model to data agreement. Note the broad range of tested hydraulic conductivities covering 5 orders of magnitude.

The good agreement between observed and modeled discharges is also shown by the discharge chronicles for the Guillec catchment (Figure 8). Overall, the variations between the wet and the dry season in the observed discharge are well represented demonstrating the precise influx estimate of the net precipitation forcing. Overall, there is only at low flows for dry years that the model is not able to catch the recession. This is because the transmissivity in Boussinesq equations does not decrease fast enough close to the stream.

<i>Catchment</i>	<i>k [m s⁻¹]</i>	<i>T [m² s⁻¹]</i>	<i>NSE [-]</i>
<i>Douffine</i>	<i>3.33 10⁻⁶</i>	<i>1.26 10⁻⁴</i>	<i>0.87</i>
<i>Dourduff</i>	<i>2.64 10⁻⁵</i>	<i>5.26 10⁻⁴</i>	<i>0.80</i>
<i>Dossen</i>	<i>1.14 10⁻⁵</i>	<i>3.26 10⁻⁴</i>	<i>0.82</i>
<i>Guillec</i>	<i>3.28 10⁻⁵</i>	<i>5.47 10⁻⁴</i>	<i>0.7</i>
<i>Penze</i>	<i>9.44 10⁻⁶</i>	<i>2.58 10⁻⁴</i>	<i>0.88</i>
<i>Ris</i>	<i>6.94 10⁻⁶</i>	<i>2.18 10⁻⁴</i>	<i>0.87</i>

Table 2: Calibrated hydraulic conductivity on river discharges for each of the studied catchments. Transmissivity is taken here as the spatially and temporally averaged transmissivity. NSE values quantify the model-to-data agreement.

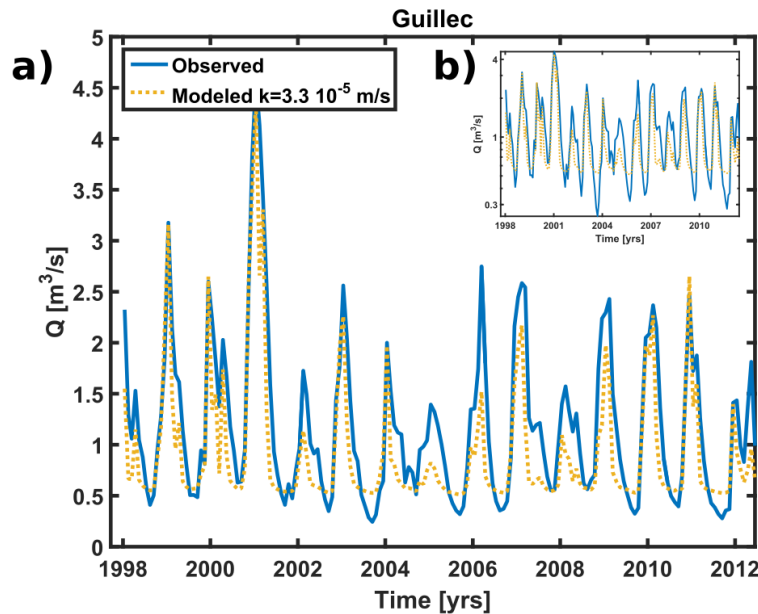


Figure 8: Comparison of the discharge simulations with the optimal hydraulic conductivity value to the discharge data for the Guillec catchment (NSE=0.7) with a) linear and b) logarithmic scales for the discharge axis.

4.2 Transport calibration

Following the methodology described in section 3.4, the parameters of the weathering law (equation (6) and (7)) are calibrated by the observed DS_i concentrations independently for the six studied sites. Overall, excepted the Douffine catchment, the estimation lead to weathering rate between 0.2 and 0.45 mg/L/yr. This is partially in agreement with previously published weathering rates estimated in aquifers [Marçais *et al.*, 2018]. Indeed, these weathering rates were on the order of 0.2 mg/L/yr. Other studies on the same type of crystalline basement where the typical weathered mineral is plagioclase, conclude on weathering rate between 0.15 and 1.11 mg/L/yr which is in agreement with these estimated weathering rates [Bohlke and Denver, 1995; Burns *et al.*, 2003; Denver *et al.*, 2010; Rademacher *et al.*, 2001; Tesoriero *et al.*, 2005].

<i>Catchment</i>	α (mg/L/yr)	$[DSi]_0$ (mg/L)
<i>Douffine</i>	<i>0.05</i>	<i>4.4</i>
<i>Dourduff</i>	<i>0.36</i>	<i>9.3</i>
<i>Dossen</i>	<i>0.34</i>	<i>7.5</i>
<i>Guillem</i>	<i>0.45</i>	<i>9.3</i>
<i>Penze</i>	<i>0.16</i>	<i>9.2</i>
<i>Ris</i>	<i>0.22</i>	<i>10.4</i>

Table 3: Calibration results for the six different catchments studied.

Finally, we compared numerical time series of mean transit times with sampled time series of DSi concentration for each catchment (Figure 9). We found that this optimized model was able to catch much of the seasonal variability of the DSi concentration time series.

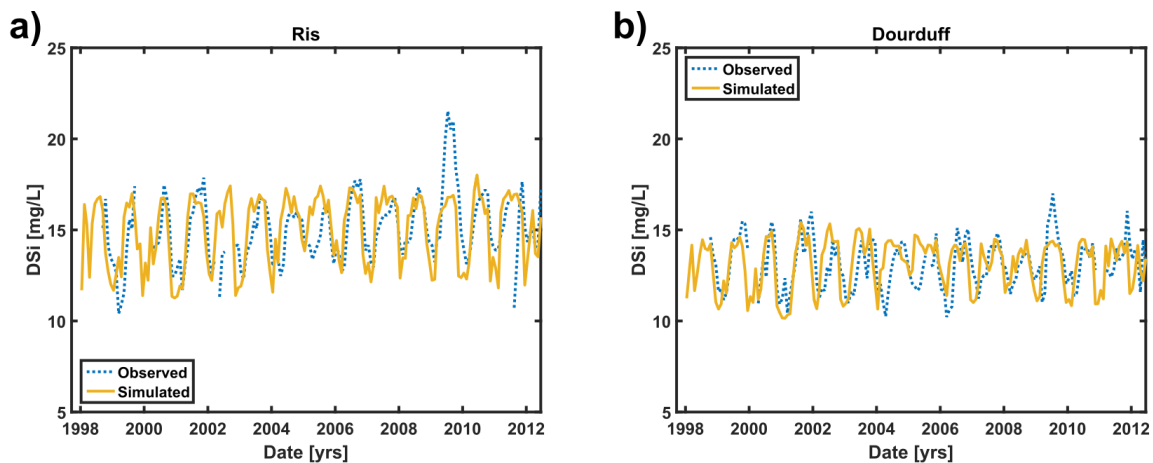


Figure 9: Observed DSi time series versus the simulated DSi time series after the optimization carried on the two weathering law parameters (α and $[DSi]_0$). Note how the models catch the seasonal variations in DSi even if it is not able to predict the maxima recorded in the 2009 dry season.

4.3 Transit time distributions

We derive the temporal evolution of the transit time distribution with the numerical methods defined in section 3.3. Transit time distributions should be understood as the translation in terms of times of the temporally and spatially evolving flows. Their temporal fluctuations are first displayed and secondly synthesized as the mean transit time and young streamwater fraction [Kirchner, 2016; McGuire and McDonnell, 2006].

4.3.1 Temporally evolving Transit Time Distributions

The transit time distribution is displayed monthly on a “one year” period between September 2007 and August 2008 in the Dossen catchment (Figure 10) with strong seasonal variations. Young water proportion is highest in winter (December 2007 to April 2008) following the occurrence of subsurface stormflow. Indeed, in the wet season, saturation is high, the water table goes up to the soil layer leading to the presence of return flow and direct infiltration onto saturated soil/bedrock interface. At the end of the dry season, in October 2007, the water table is significantly below the soil layer, evaporation dominates over infiltration for fewer precipitations (Figure 4), and the remaining infiltration percolates through the soil layer with longer circulation paths and times. At the other end of the distribution, waters older than 20 years are always present in the groundwater mix to the streamwater as expected for these deeper flow paths less influenced by seasonal variations. In between these two extremes, the distribution is variable reflecting the sensitivity of the transit times to the multiple variations of the infiltration, induced changes of flows and sudden subsurface stormflow sequences in the soil layer along the hillslope.

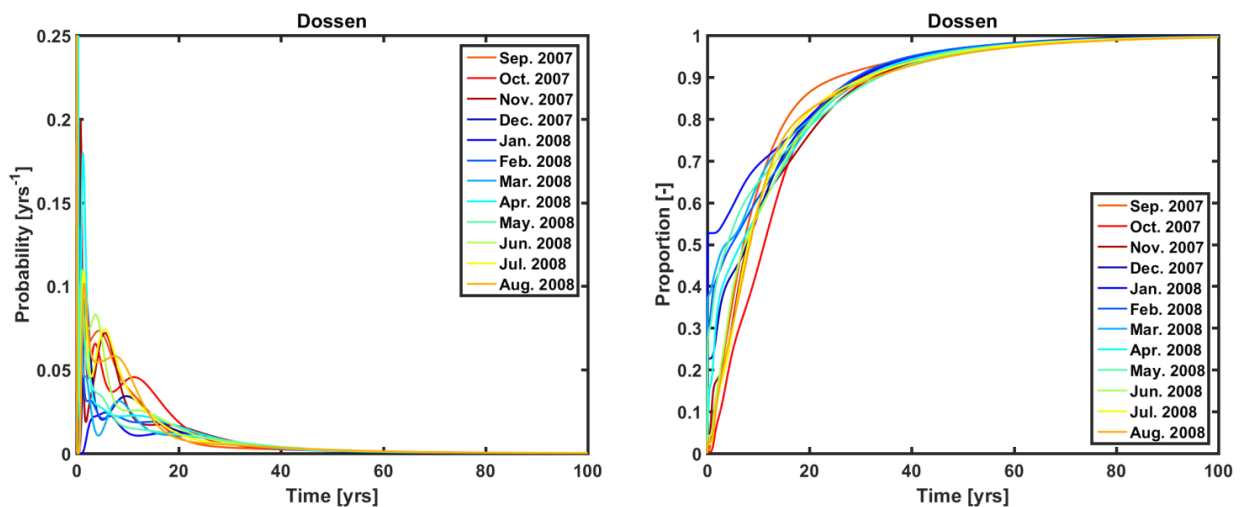


Figure 10: Transient Time Distributions modeled at the outflow of the Dossen catchment: a) probability density function b) cumulative density function. Note how the proportion of young streamwater (less than 3 months old) significantly increases in the wet season.

For a more quantitative analysis of the relative contribution of the younger and older waters, we use the young water age fraction (proportion of water younger than 3 months) and the mean transit time more influenced by the proportion of older waters.

4.3.2 Mean transit time and young streamflow proportion

Reflecting the analysis of the distributions, the mean transit time and young streamwater proportion for the Dourduff catchment on the period 1998-2012 have opposite variations (Figure 11). Large proportions of young streamwaters (ca. 50%-60%) with low mean transit times of 3 to 5 years in wet seasons alternate with vanishing young streamwaters and at least twice larger mean transit times in dry seasons.

Beyond the seasonal pattern, interannual variabilities highlight the drier and wetter years as well as their effect on transit times. The wet winter of 2001 displays the highest young streamwater proportion (ca 77%) and the smallest mean transit time at 2 years. Comparatively, the dry winters of 1998 or 2005 lead to ca 48% and 35% of young streamwater proportion and mean transit times up to 6 to 9 years showing high variabilities in winter. Variabilities in the dry seasons are more limited with proportion of young waters getting systematically down to zero and mean transit times varying between 13 and 17 years. Variability in summer is logically more limited because of the buffering effect of the deeper flow paths.

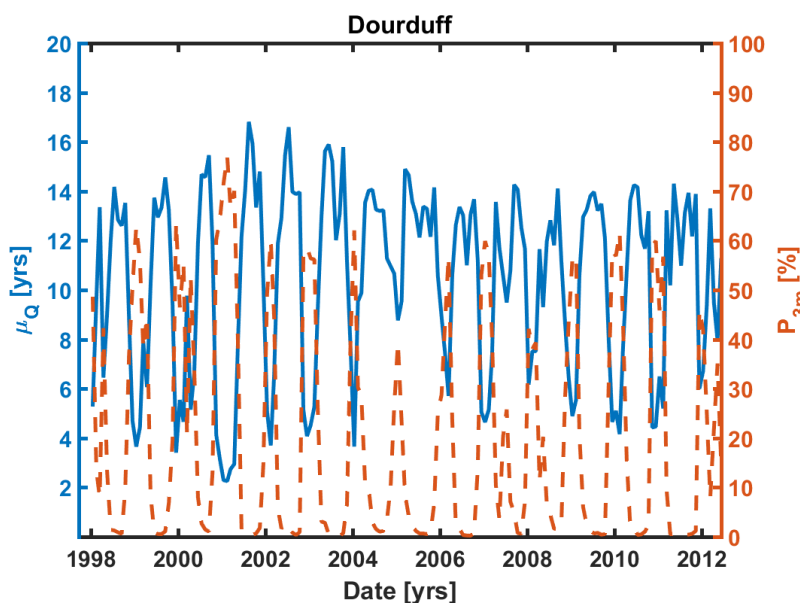


Figure 11: mean transit time (in blue, left y-axis) and young streamwater proportion evolution during the period considered. Notice how the seasonal variations in the climatic forcing lead to anticorrelated evolution of mean transit times and young streamwater proportion.

Other catchments display similar seasonal pattern although the exact proportion of young streamwater and of the mean transit time can significantly differ between the catchments. Statistics about these indicators are summarized in Table 4. Overall, the average mean transit time of all these Brittany catchments are about 16 years and the young streamwater proportion is in average equal to 24%. This average young streamwater proportion is in agreement with

previously published results [Jasechko et al., 2016] but the model provides significant information on the seasonal variability of this proportion.

<i>Catchments</i>	$\overline{\mu_Q}$	$\min \mu_Q$	$\max \mu_Q$	$CV(\mu_Q)$	$\overline{P_{3m}}$	$\min P_{3m}$	$\max P_{3m}$	$CV(P_{3m})$
<i>Douffine</i>	27	4.4	55	0.65	37	0.0	73	0.71
<i>Dourduff</i>	10	2.2	17	0.36	20	0.0	77	1.1
<i>Dossen</i>	14	3.8	21	0.30	11	0.0	64	1.5
<i>Guillec</i>	10	1.7	19	0.39	26	1.0	85	0.97
<i>Penze</i>	17	3.0	32	0.48	26	0	71	0.99
<i>Ris</i>	21	3.8	34	0.41	24	0	69	0.94
<i>Average</i>	16	3	30	0.43	24	0	73	1.0

Table 4: Statistics summarizing the temporally evolving characteristics of the transient transit time distributions, namely the mean transit time μ_Q and the young streamwater proportion P_{3m} . $\bar{A}$ stands for the temporal average of the quantity while $CV(A)$ is the temporal coefficient of variation of the quantity A (ratio of the standard deviation upon the average). The last line averages all these statistics about the descriptors of these temporally evolving transit time distributions to give a typical estimate of the behavior of the Brittany catchments.

4.4 Residence time distributions

The residence time distributions within the aquifer reconstructed following the procedure described in section 3.3 shows in fact little apparent variations between the two extremely wet and dry seasons over the 1998-2012 period. The wettest, respectively driest, event is identified as the time step with the biggest, respectively lowest, discharge, which correspond to January 2001 (respectively September 2003). Most of the deeper part of the saturated zone is little modified between these extreme events. Only the thin upper layer of young groundwater (0-1 years) is more significantly modified. The strong variations of the transit time distributions cannot be explained by corresponding evolutions of the residence time distributions in the groundwater system. They are more likely coming from irregular transfers from the groundwater to the streamwater systems, when subsurface stormflow occurs, which corresponds to the selection of the groundwater transferred to the stream water in the terminology of the Storage Selection function [Harman, 2015; Rinaldo et al., 2015; van der Velde et al., 2012].

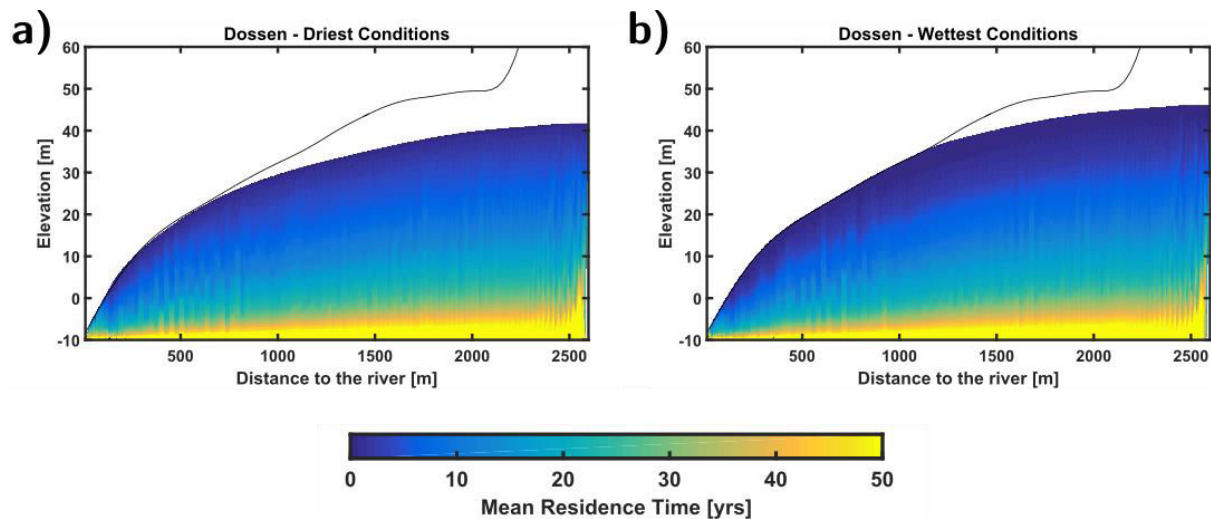


Figure 12: Spatialized mean residence time in the aquifer in the a) the driest and b) wettest conditions encountered of the 1998-2012 period. Black line materializes the soil/bedrock interface.

4.5 Storage Selection Functions from a process-based perspective

Storage selection functions are derived following the methodology given in section 3.3.1 for the driest and wettest conditions presented before. They are displayed as a function of the adimensional storage (Figure 13). As expected, they strongly differ with dominant outlet of young waters in the wettest condition. 70% of the outlet water to the stream are given the youngest 5% of the stored waters. In the driest conditions, water transferred to the streams are dominated by the older compartments with uniform proportions between the 20% and 100% older waters. Overall, in the dry season, the catchment has a slight preference for releasing older water stored, as illustrated when comparing the cumulative of the storage selection function for the dry season and the cumulative of the storage selection function representative of a perfectly mixed catchment (materialized by the x-y black line in Figure 13). This analysis confirms that large temporal differences in transit times are strongly linked to the evolving preference of the watershed to release younger or older groundwater into the streams with a detailed characterization given by the storage selection function. Comparison with the previous analysis of the residence time distribution additionally shows that these variations do not dominantly come from the limited influence of flows within the saturated zone. They should rather be linked to the saturation process of the aquifer and to the outflow in the soil layer. The strong differences in the storage selection function and in the transit time distributions are linked to the threshold effect of the full saturation of the aquifer and its consecutive outflow in the soil layer with a rapid transfer to the stream network.

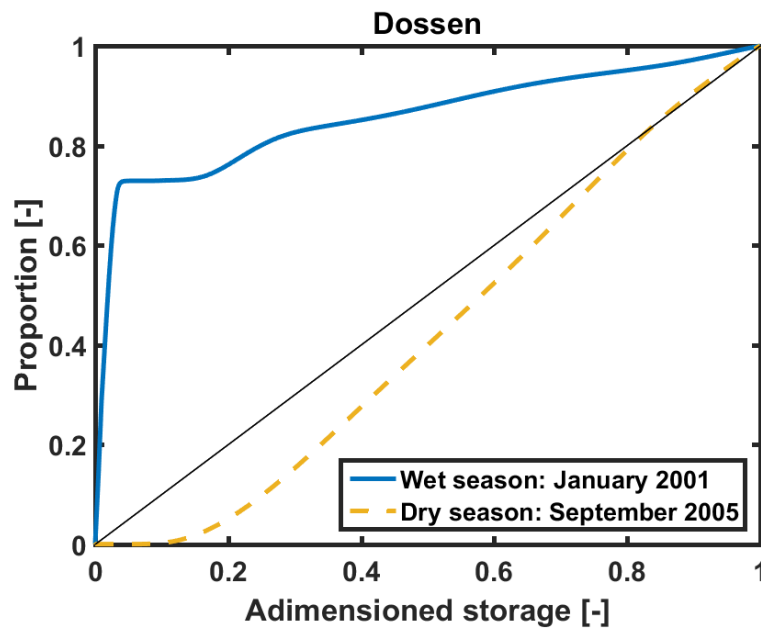


Figure 13: Cumulative of the storage selection functions displayed for the same wettest and driest conditions of Figure 12. The x-y line represents the cumulative of the storage selection function for a random selection process, characteristic of a perfectly mixed catchment.

5 Conclusion and perspectives

We developed a physically based model able to represent the dynamical interaction between the water table and the soil / bedrock layer. This interaction enables to represent perennial groundwater flow as well as temporary subsurface stormflow. Coupled with an advective dispersive particle tracking scheme, the model simulates transient discharge and time-varying transit time distributions in the river as well as transient residence time distributions of the groundwater stored in the catchment. We calibrated these models on a 14 years discharge and DSi time series sampled at the month time scale for six different Brittany catchments. We were able to model discharge with NSE ranging from 0.7 to 0.9 and to simulate the typical DSi seasonal variations with optimized hydraulic conductivities between $3.3 \cdot 10^{-6}$ m/s and $3.3 \cdot 10^{-5}$ m/s and optimized weathering rates between 0.16 and 0.45 mg/L/yr. Both values agree with previously estimated values in similar geological context [Grimaldi et al., 2009; Le Borgne et al., 2004; Marçais et al., 2018; Martin et al., 2004; Rademacher et al., 2001].

We learned that water quality data reflects the temporal variability of transit times inside the catchment and that these water quality data are primarily driven by the proportion of young water in the streamwater in average equal to 25% which is in agreement with previously published estimates [Jasechko et al., 2016]. However, we learned this young streamwater

proportion varies significantly according to the season from 0% to 73%, in average for the different catchments. This variability of the young streamwater proportion can be explained by the seasonal variability of subsurface stormflow processes which reflect the preference for the catchment to release preferentially the young groundwater stored rather than the oldest ones depending on the climatic and moisture (e.g. quantity of groundwater stored) conditions. In winter, the process of interception between the water table and the soil bedrock interface prevent infiltration to the aquifer and promotes the apparition of subsurface stormflow. This enhances connectivity at the watershed scale and induces rapid response to precipitations as well as fast subsurface stormflow paths towards the river. On the contrary, in summer, the water table is deeper and the aquifer, constituted of old flow paths, feed the stream to sustain low flows. This creates a major shift in the mean transit times and in the young streamwater proportion in the river in the dry season compared to the wet season. This enhances the seasonal variation in mean transit times responsible for the typical patterns observed in water quality data in rivers.

These subsurface stormflow processes are both controlled by the net precipitation intensity but also by the wetness of the catchment through the amount of water stored in the aquifer. It is indeed the presence of the seeping areas which promote the occurrence of significative subsurface stormflow events. Overall, this process seems to be widespread in very different catchments across the world [Gabrielli *et al.*, 2018; Yang *et al.*, 2018]. Deciphering these physical processes through discharge and water quality data opens new perspective to advance towards the characterization of reactivity at the catchment scale, through the integration of reactive solute species such as nitrates.

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835

3.3 Bilan

Nous avons étudié dans ce chapitre la variabilité saisonnière des concentrations en silice dans les cours d'eau de plusieurs bassins versants bretons. Il apparaît que, pour l'intégralité de ces bassins versants hormis la Douffine (qui est sur une géologie composite, partiellement cristalline), le maximum de concentrations en silice est atteint à l'étiage, à la fin de la saison sèche tandis que les minima de concentrations en silice est atteint aux hautes eaux, à la fin de la saison hivernale. Nous avons relié cette variation de qualité de l'eau avec la variabilité temporelle des distributions de temps de transit en rivière. En effet, cette variabilité temporelle des distributions de temps de transit en rivière n'est en fait que le reflet de la variabilité saisonnière des chemins empruntés par l'eau. En hiver, quand la nappe est haute, l'aquifère intersecte les horizons les plus perméables du sol et les sature engendrant un ruissellement dû au suintement de la nappe dans ces horizons perméables et à l'infiltration qui tombe sur du sol en grande partie saturé. Ce ruissellement étant rapide, il est moins concentré en silice que les écoulements de l'aquifère. L'interaction de la nappe avec les horizons les plus perméables du sous-sol apparaît donc un processus capable d'avoir un rôle clef dans la formation de la qualité de l'eau en rivière.

Ce modèle une fois calibré nous permet d'avoir une première quantification de la variabilité des écoulements à l'échelle du bassin versant. Il apparaît bien que ce sont les circulations d'eaux jeunes qui sont les plus variables temporellement tandis que les circulations d'eaux âgées sont plus stables dans le temps et les moins sensibles aux variations climatiques. Ces circulations alimentent la rivière en étiage. L'eau stockée dans les aquifères a un âge moyen important (de l'ordre de la dizaine d'année) qui varie peu au cours du temps tandis que l'eau s'écoulant en rivière a un temps de transit très variable, de l'ordre de quelques années en hiver (2-3 ans) à la décennie également en été.

Cette explicitation des temps de transit dans le bassin versant ouvre la voie à plusieurs perspectives. Tout d'abord, si ce processus d'interception de la nappe avec les horizons les plus perméables est important pour appréhender la qualité de l'eau en rivière, il apparaît essentiel de comprendre par quelles contraintes (topographiques, climatiques, géologiques) il est contrôlé. Plus généralement, il est intéressant d'étudier comment la distribution des temps de transit est conditionnée par ces différents contrôles. Enfin, cette transcription des écoulements souterrains en temps de transit ouvre la voie à différentes méthodes pour décrire la réactivité (par exemple des éléments nitrates) à l'échelle du bassin versant. Nous évoquons donc l'ensemble de ces perspectives dans la partie suivante.

Partie IV Discussions et perspectives

Dans cette partie, nous donnons quelques perspectives qui pourraient être envisagées à la suite de ce travail de thèse. Nous avons dans les précédentes parties détaillé différentes stratégies d'utilisation de données (semi-explicites ou explicites) pour inférer les temps de transit et les temps de résidence, en vue d'une prédiction de la qualité de l'eau à l'échelle de la Bretagne. Si le terrain d'étude de cette thèse est la Bretagne, ces stratégies sont cependant génériques puisqu'elles ont permis le déploiement d'outils de modélisation adaptables à de nombreux contextes climatiques. Le choix de ces stratégies dépend des données disponibles et des prédictions à réaliser ainsi que du degré de compréhension qu'on veut tirer du domaine d'étude.

Idéalement, la donnée dont on voudrait disposer à l'échelle mondiale (ou pour commencer à l'échelle de la Bretagne...) pour pouvoir prédire le devenir de la qualité de l'eau est une empreinte multi-traceurs (e.g. débit, conductivité électrique, nitrate, silice, phosphore, CFCs) dans les rivières, distribuée sur le territoire à des échelles différentes (du versant de tête aux grands bassins versants) et acquises en continu (du moins à haute fréquence) qu'on caractériserait à l'aide d'une connaissance fine de la géologie (structure et minéralogie), des forçages climatiques (pluie, évapotranspiration réelle) ainsi que de la géomorphologie via les données de topographie haute résolution. Avec ces données et des puissances de calcul importantes, nous serions capables de construire un cadre de modélisation cohérent qui prend en compte 1. la structure du bassin versant ; 2. les flux qui la traversent ; 3. le transport conservatif associé ; et 4. la réactivité des différents solutés transportés. Bien entendu, disposer d'un tel gisement de données ne serait-ce qu'à l'échelle d'une région est illusoire. De plus, les puissances de calcul, si elles progressent considérablement, demeurent limitées. Cette stratégie fine de modélisation ne peut se penser qu'à une échelle agrégée et de manière dégradée comme nous avons tenté de le montrer dans la Partie III après avoir estimé le potentiel informatif des différentes données (Partie II).

Cependant, pour aller au bout d'une logique parcimonieuse et adaptable, nous pouvons imaginer des stratégies pour lier plus directement les données de structure et de forçages à la qualité de l'eau des rivières bretonnes. Pour cette raison, nous esquissons dans cette partie des pistes pour mieux prendre en compte les données spatialisées (données de topographie) pour une meilleure compréhension des interactions entre flux souterrains et flux de subsurface (Partie IV Chapitre 1) et, *in fine*, une meilleure compréhension des distributions de temps de résidence et de transit (Partie IV Chapitre 2). Nous détaillons également des stratégies de modélisation, à l'échelle du bassin versant, des écoulements d'eaux (Partie IV Chapitre 3) ou de la réactivité qui leur est associés (Partie IV Chapitre 4). Ces travaux préparatoires ne se sont pas encore confrontés à des données de terrain, à même de leur apporter sinon une validation au moins une preuve de cohérence [Oreskes *et al.*, 1994].

Chapitre 1 Comprendre les déterminants géomorphologiques du ruissellement à l'échelle du versant

Dans cette partie, nous envisageons d'évaluer le potentiel de certains indicateurs topographiques et géomorphologiques pour prédire la proportion de ruissellements contribuant au débit total à l'échelle d'un versant. Nous évaluons ce potentiel d'abord à l'aide de simulations issues du modèle à bases physiques détaillé en Partie III (Partie III Chapitre 1). Ce travail a été initié lors d'une mobilité internationale de trois mois à l'université d'Arizona durant ma thèse. J'ai alors pu mener une collaboration avec Hoshin Gupta et Peter Troch sur ce sujet. Ce travail a fait l'objet de nombreuses discussions avec Philippe Steer et Louise Jeandet lors de mon retour à l'OSUR. Il a été présenté lors d'un poster à l'AGU 2016 à San Francisco (Figure 25 , développé ci-après tout au long du chapitre).

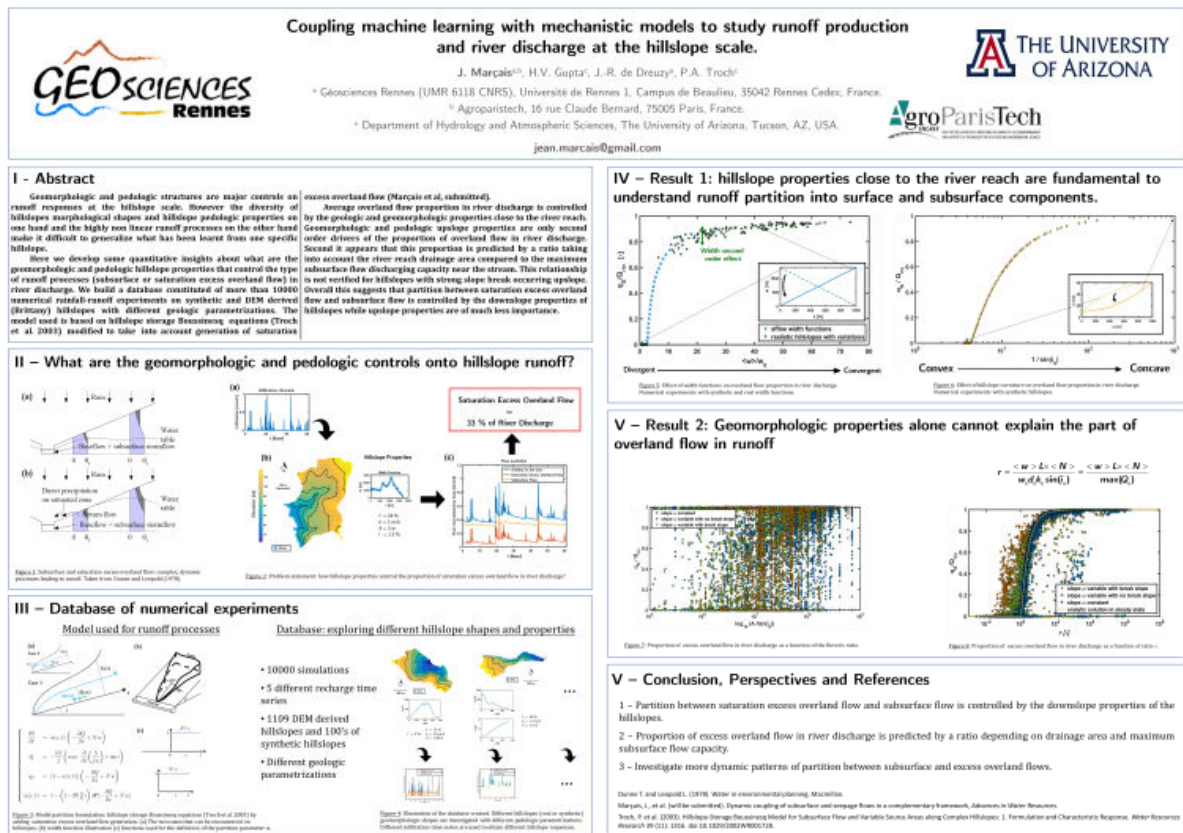


Figure 25: Poster présenté à l'AGU 2016.

1.1 Position du problème : prédire l'importance des écoulements rapides sur le débit en rivière

Les déterminants géomorphologiques sont d'une importance majeure pour comprendre et prédire les réponses des versants aux précipitations [de Lavenne et al., 2015; Devauchelle et al., 2012; Rodríguez-Iturbe and Valdés, 1979; Schmittner and Giresse, 1996]. La connaissance de tels déterminants est également d'une attractivité majeure pour les hydrologues qui sont constamment à la recherche de paramètres aisément calculables pour caractériser la réponse de versant ou de bassin versant sur des domaines d'étude non jaugés à des échelles régionales [Hrachowitz et al., 2013b]. La question qui se

pose est donc de savoir si des données spatialisées issues par exemple d'analyse de MNT (modèle numérique de terrain) peuvent fournir des capacités de prédiction sur des phénomènes hydrologiques de ruissellements ?

Sans nul doute, la plus connue des approches s'inscrivant dans cette dynamique, est celle initiée par Keith Beven avec le modèle TopModel [Beven and Kirkby, 1979]. TopModel, s'inspire de prérequis physiques réalistes pour postuler que la topographie est un descripteur majeur de l'écoulement à l'échelle des versants [Quinn et al., 1991; Quinn et al., 1995]. Ce modèle s'appuie sur des quantités comme l'index topographique pour prédire la saturation en un endroit donné du versant. Cet index topographique λ se définit comme :

$$\lambda = \ln \left(\frac{A}{\tan \theta} \right), \quad (6)$$

où A est l'aire contributive drainée en amont du point considéré et θ , la pente locale. Toute une littérature s'est attachée à améliorer cet index topographique, prenant en compte d'autres contrôles (autre que la topographie) comme le climat ou les caractéristiques du sol [Merot et al., 2003]. La détermination de seuil à partir duquel l'index topographique prédit une existence de zones saturées a ainsi été analysé sur un grand nombre de site [Liang and Chan, 2017; Sørensen et al., 2006].

Cependant, la diversité des formes géomorphologiques des versants, l'hétérogénéité de leurs propriétés souterraines (porosité, perméabilité, degré de fracturation,...), la complexité des chroniques d'infiltrations combinées au fait que les processus de ruissellements sont hautement non linéaires (avec particulièrement des effets de seuil) rendent difficiles la transposition des connaissances acquises sur un versant spécifique et bien instrumenté à d'autres versants, voire à des prédictions du ruissellement à des échelles régionales.

1.2 Méthodes : un laboratoire numérique permettant des expériences de synthèse basées sur un modèles physique pour réduire la complexité du réel

Une première approche pour analyser cette question peut être d'analyser des expériences numériques basées sur un modèle physique (le modèle développé dans la Partie II Chapitre 1). En effet, la réalisation de modèles physiques est une première étape pour démêler les effets cités plus hauts. Cette approche, qui considère les modèles comme un laboratoire virtuel [Thomas et al., 2016], permet de s'affranchir partiellement de l'hétérogénéité du milieu souterrain en considérant des problèmes plus simples. Dans cette partie, nous envisageons de tirer parti des expériences numériques réalisées précédemment (expériences réalisées pour tester la robustesse du modèle de versant basé sur les équations de Boussinesq et prenant en compte l'interaction de la nappe avec la topographie) pour analyser les déterminants du processus de ruissellements ainsi que la probabilité d'occurrence de zones humides en un endroit donné. Ces expériences numériques constituent en effet une base de données de plus de 10000 expériences pluies/débits réalisés à partir de versants extraits d'une analyse de la topographie bretonne (avec un MNT LiDAR à 5m).

Dans un second temps, les quantités physiques inférées par cette analyse de données synthétiques issues d'expériences numériques pourraient être comparées à des zones où les zones humides ont été précisément cartographiées, la connaissance du partitionnement des flux entre écoulements de ruissellements et écoulements de nappe étant encore plus mal contrainte.

Nous avons donc développé un cadre d'analyse des simulations issues de modélisation à base physique pour déterminer un prédicteur de la quantité de flux transitant par les flux de ruissellements pour un versant donné (Figure 26). Une simulation est constituée d'un versant (décrit par son profil de pente et de fonction « largeur », caractéristique de l'étendue du versant perpendiculairement à la direction d'écoulement), de propriétés hydrauliques données (porosité et perméabilité), et d'une chronique d'infiltration donnée. Ce cadre d'analyse quantifie pour chaque simulation la proportion de ruissellement de surface générée dans la simulation par rapport au débit total en rivière.

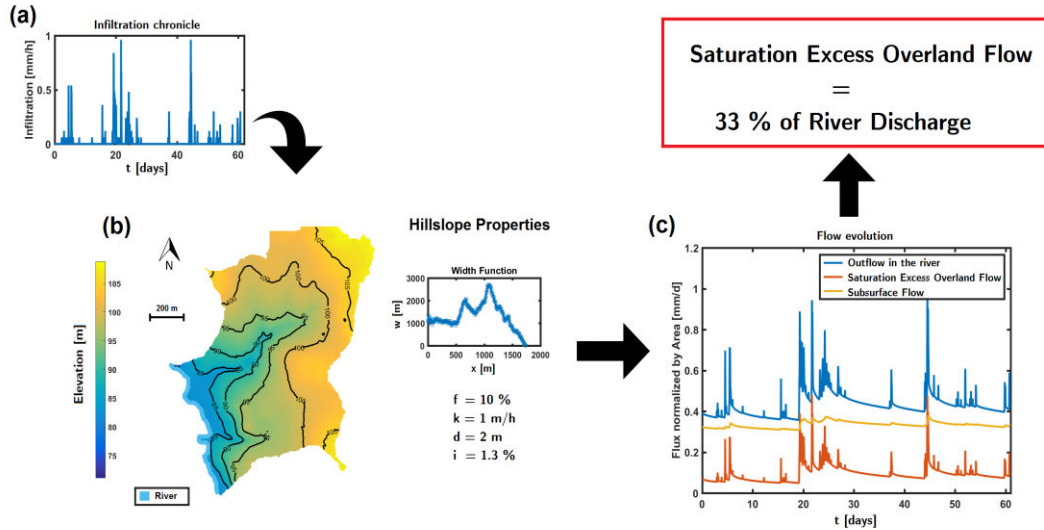


Figure 26: Illustration du cadre de modélisation qui permet de quantifier la proportion moyenne de ruissellement pour une simulation sur un versant, un set de paramètres hydrauliques et une chronique d'infiltration donnée.

1.3 Résultats préliminaires : l'importance des propriétés de la zone riparienne

Une analyse de sensibilité du modèle démontre que la pente est d'une importance critique (Figure 27), tout comme la prise en compte de l'aire drainée par un bras de rivière (Figure 28). Plus on privilégie un versant concave, plus la faible pente proche de la rivière aura tendance à générer des flux de ruissellement. De la même manière, plus le versant aura une forme convergente proche de la rivière, plus le ruissellement sera important. Ces deux caractéristiques montrent bien la pertinence de l'index topographique de Beven qui s'appuie sur la pente locale et l'aire drainée.

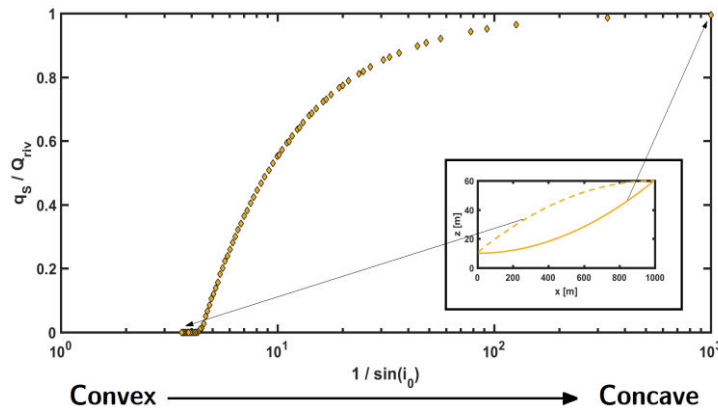


Figure 27: Effet de la fonction pente du versant sur le ruissellement de surface : en abscisse, l'inverse de la pente du versant au niveau de son contact avec la rivière, en ordonnée la proportion (variant entre 0 et 1) du ruissellement sur le débit total

estimé en rivière. En insert, illustration des profils de pente choisis pour les deux cas les plus extrêmes en fonction de la distance à la rivière. On le voit, le versant le plus convexe présente des pentes fortes proches de la rivière empêchant le ruissellement tandis que le versant concave, du fait de sa pente quasi-nulle proche de la rivière génère un ruissellement très important.

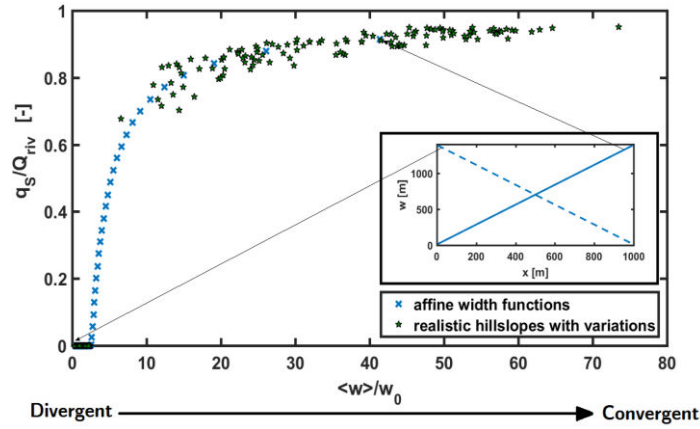


Figure 28: Effet de la forme de la fonction largeur du versant sur le ruissellement de surface : en abscisse, le rapport entre la largeur moyenne du versant et sa largeur au niveau de son contact avec la rivière, en ordonnée la proportion (variant entre 0 et 1) du ruissellement sur le débit total estimé en rivière. En insert, illustration des fonctions de largeur choisies pour les deux cas les plus extrêmes (largeur du versant en fonction de la distance à la rivière). Le versant divergeant, présentant une largeur importante de rivière drainant l'aquifère, empêche le ruissellement tandis que le versant convergent, de par sa forme « d'entonnoir », génère un ruissellement très important. La prise en compte de fonctions largeurs plus réalistes typiquement rencontrées sur des versants réels jouent un rôle de deuxième ordre pour la prédiction de la proportion de ruissellement en régime permanent.

Cependant, si on applique directement l'index topographique de Beven pour prédire cette proportion de flux de ruissellement sur le flux total, l'index se révèle être un pauvre prédicteur (Figure 29). En effet, les propriétés hydrauliques du versant tout comme les propriétés de la chronique d'infiltration sont essentielles à prendre en compte pour prédire les proportions de ruissellements. Pour cette raison, l'utilisation d'un prédicteur couplant ces différents contrôles :

$$r = \frac{A \langle N \rangle}{\max Q_0} = \frac{\langle w \rangle L \langle N \rangle}{w_0 d_0 k_0 \sin i_0}, \quad (7)$$

où A est l'aire drainée du versant (pouvant aussi se mettre sous la forme $A = \langle w \rangle L$ où $\langle w \rangle$ est la largeur moyenne du versant et L sa longueur longitudinale, de la ligne de partages des eaux à la rivière), $\langle N \rangle$ est la moyenne de l'infiltration sur la période considérée, w_0 est la largeur de la portion de rivière drainant le versant, d_0 est la hauteur de l'aquifère à son contact avec la rivière, i_0 est la pente du versant au niveau de la rivière et k_0 est la perméabilité au niveau de la rivière, est bien plus adapté pour rendre compte du partitionnement du flux (Figure 30). On peut noter que ce prédicteur couple en fait les prédicteurs appelés index climato-topographique [Merot et al., 2003] et l'index pédo-topographique [Ambroise et al., 1996; Hjerdt et al., 2004]. Cet index met l'accent, de par sa paramétrisation, sur les propriétés proches de la rivière, ce qui serait intéressant à tester sur des versants avec des topographies ripariennes contrastées. Cependant, les versants à pentes variables, dans lesquels les profils de pente présentent des inflexions voire des inversions de pente, sont susceptibles de générer des proportions de flux de ruissellement supérieures à ce qui est prédit par notre index. Cette connaissance pourrait vraisemblablement être rationalisée en prenant un descripteur qui intègre l'effet en amont du versant.

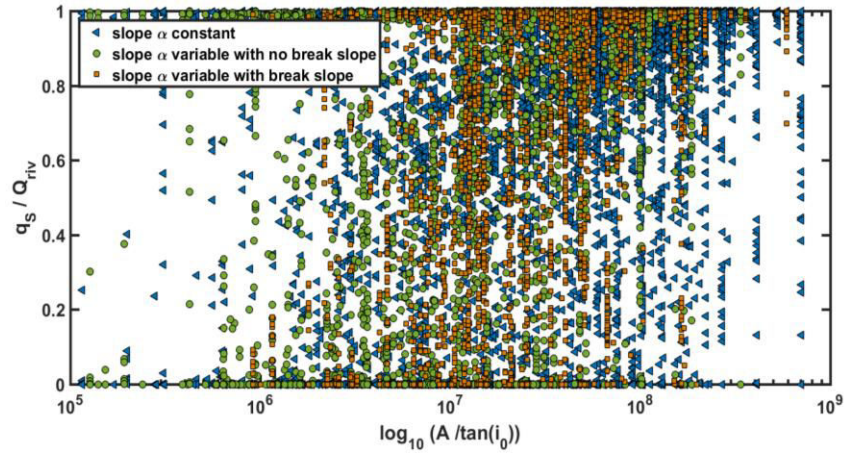


Figure 29: Utilisation de l'index topographique comme prédicteur du ruissellement à l'échelle du versant [Beven and Kirkby, 1979; Quinn et al., 1995].

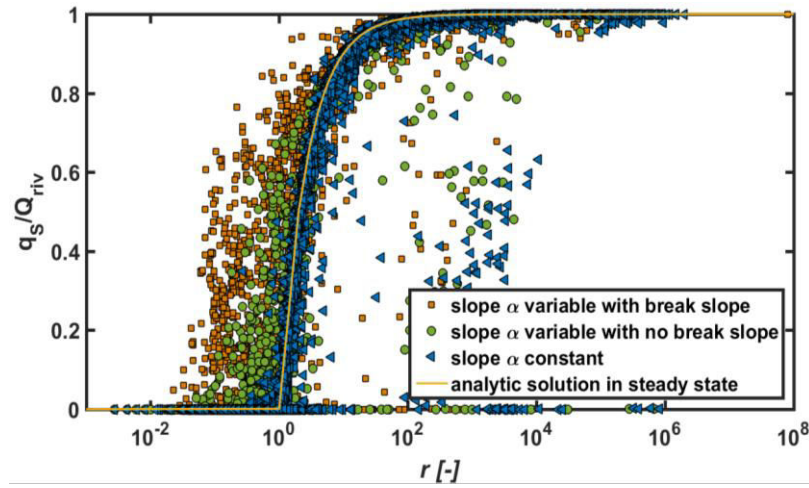


Figure 30: Utilisation d'un index climato-topographique avec prise en compte des propriétés pédologiques du sol comme prédicteur du ruissellement à l'échelle d'un versant. Les versants avec des pentes variables (et en particulier ceux présentant une rupture de pente) présentent une proportion de ruissellement supérieure à celle prédite par le ratio r . Les points se trouvant sous la courbe jaune et présentant de facto une part de ruissellement moindre que ce qui est prédit par le paramètre r sont des simulations qui n'ont pas été démarrées à partir d'un état établi en régime permanent (début de simulation sur un versant vide par exemple).

1.4 Perspectives : comment enrichir cette analyse et la tester sur des cas « réels »?

Le descripteur r vu à la section précédente n'a pas été utilisé pour prédire la quantité d'aire de zones humides existant sur le versant mais uniquement pour prédire le partitionnement de flux de ruissellement versus flux souterrain. Il serait intéressant d'étudier si on peut construire un descripteur de la proportion d'aire du versant susceptible de se transformer en zone humide. On peut suspecter qu'un tel descripteur se baserait sur la forme du ratio r et prendrait aussi en compte la forme du versant au niveau de la rivière pour savoir sur quelle longueur et sur quelle aire, une telle zone saturée peut remonter vers l'amont du versant. Disposer d'un tel descripteur permettrait alors de tester cette approche sur des cas réels où l'on dispose de données cartographiant les zones humides.

D'autre part, diverses analyses seraient nécessaires pour estimer la robustesse de ce prédicteur. En particulier, il faudrait évaluer jusqu'à quel niveau le descripteur r qui traduit un régime permanent est fiable pour décrire un état transitoire. Bien que les expériences numériques utilisées précédemment aient

été réalisés en état transitoire, il semble que ce régime soit plutôt quasi-statique puisque ne s'éloignant pas beaucoup de l'état d'équilibre. En particulier, pour certaines simulations n'ayant pas atteint l'état d'équilibre, le coefficient r se révèle logiquement être un pauvre prédicteur de la proportion du ruissellement (Figure 30). Un test de ce prédicteur sur des chroniques temporelles bien plus marquées (avec une alternance saisonnière par exemple) pourrait nous amener à trouver ses limites en terme de fenêtres temporelles sur lequel il peut être utilisé pour la prédiction.

Chapitre 2 Recherche des descripteurs géomorphologiques des distributions de temps de transit

Dans la partie précédente, nous avons cherché un nombre physique adimensionné à même de donner une indication de la proportion de ruissellement dans l'écoulement total à l'échelle d'un versant. Pour continuer sur cette méthodologie, nous nous intéressons maintenant à comprendre les déterminants des formes des versants sur la distribution des temps de transit en rivière. Ce travail a fait l'objet d'une présentation orale lors de la conférence HydroEco 2017 qui s'est tenue à Birmingham.

2.1 Position du problème : est-il possible de prédire la forme de la distribution des temps de transit à partir de la topographie du versant ?

On peut en effet se demander comment la structure géologique ainsi que la topographie du versant conditionne la forme de la distribution des temps de transit ainsi que ses paramètres (e.g. temps moyen, variance, proportion sur la cumulée) [Hrachowitz *et al.*, 2013a]. Cette question assez théorique (prédire la forme de la distribution à partir de la connaissance structurale du versant) a en fait un grand nombre d'implications très pratiques. En effet, si ce lien entre structure du versant et forme de la distribution était avéré on pourrait alors imaginer prédire directement cette distribution de temps de transit à partir de données spatialisées de topographie ou de géologie [Hrachowitz *et al.*, 2009; Tetzlaff *et al.*, 2009a; Tetzlaff *et al.*, 2009b]. La distribution des temps de transit étant fondamentale à contraindre pour le transport de solutés, les implications que cela peut avoir sur des bassins versants non jaugés en terme de transport sont nombreuses [de Lavenne *et al.*, 2015; Hrachowitz *et al.*, 2013b; Soulsby *et al.*, 2010]. Nous pouvons donc formuler les questions suivantes : Quel est l'effet de la structure du versant sur la distribution des temps de transit ? Peut-on prédire à partir de la connaissance des compartiments structuraux (sols, structures géologiques d'altération) ou des compartiments fonctionnels du versant (par exemple, la zone riparienne, la partie de l'aquifère active hydrologiquement) les propriétés de la distribution des temps de transit ? ou plus prospectivement encore : Peut-on prédire la qualité de l'eau dans les rivières bretonnes à partir de données spatialisées (carte géologique, topographie SRTM et caractérisation des quantités d'intrants épanchue par bassin versant) ?

Pour aborder cette question nous avons regardé la distribution de temps de transit sur quatre versants synthétiques dont la forme est résumée dans la Figure 31. En particulier, nous déterminons l'impact de la pente de l'aquifère et de la forme de la zone riparienne sur la forme de la distribution de temps de transit en régime permanent. Pour avoir une distribution de temps de transit comparable entre le versant 1 et le versant 2, nous avons fortement augmenté la porosité du versant 2 (égale à 40%) relativement à celle du versant 1 (égale à 10%) pour que le temps moyen qui dépend du volume total de l'aquifère (voir partie Partie II.3.1) soit égal dans les deux cas.

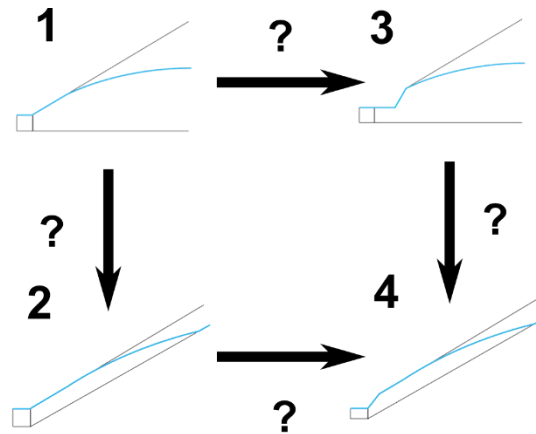


Figure 31: Base de test pour étudier l'effet de la pente de l'aquifère et des propriétés topographiques de la zone riparienne sur les distributions de temps de transit. Chacun des versants sont référencés comme suit : (1) « Flat bedrock aquifer », (2) « Slope bedrock aquifer », (3) « Flat bedrock aquifer with a slope break » et (4) « Slope bedrock with slope break ».

2.2 Résultats préliminaires : la distribution des volumes sur le versant est un facteur de contrôle clef de la distribution des temps de transit

En comparant les distributions de temps de transit obtenues pour les versants 1 et 2, on voit premièrement qu'elles possèdent quasiment le même temps moyen, égal à 18 ans environ, en accord avec notre paramétrisation de la porosité pour que ces deux versants aient le même volume stocké dans l'aquifère. Cependant si on étudie la répartition de la distribution sur les eaux jeunes, on voit que ces deux distributions présentent des différences très marquées selon qu'on regarde le versant « à fond plat » ou le versant « penté » (Figure 32). En particulier, si on prend comme descripteur la proportion d'eaux jeunes (i.e. de moins de 3 mois) contenues dans cette distribution, on voit que celle-ci est bien plus importante dans le cas du bassin versant à fond plat (Figure 32) et que cette variation varie du simple au double (Tableau 2, première et troisième colonne).

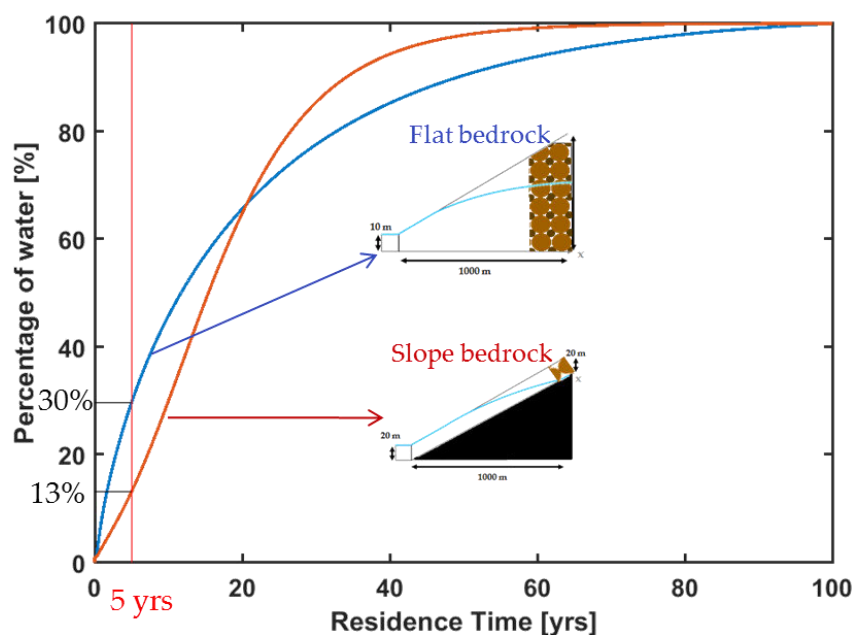


Figure 32: Cumulée de la distribution des temps de transit pour un aquifère penté et un aquifère à fond plat. Les porosités ont été adaptées pour que les distributions de chaque versant aient les mêmes temps moyens.

	Flat bedrock	Flat bedrock slope Break	Slope bedrock	Slope bedrock slope break
Young water (%)	30	62	13	23
Riparian water (%)	5	2	25	14

Tableau 2: Effet de la forme de l'aquifère (penté ou non) et de la topographie du versant au voisinage de la rivière, dans la zone riparienne sur la distribution des temps de transit (proportion d'eaux jeunes, i.e. de moins de trois mois). Sur la seconde ligne, l'impact de tels changements de pente et de topographie sur la répartition des volumes, facteur déterminant pour la vitesse des écoulements (l'eau riparienne représente le pourcentage du volume de l'aquifère situé à moins de 100m de la rivière).

Cette observation est vraisemblablement à mettre en relation avec la distribution des volumes (i.e. leur répartition) à l'échelle du versant (Figure 33). En effet, de la même manière que le temps moyen de la distribution des temps de transit est relié au volume global stocké dans le versant, on peut faire l'hypothèse que la proportion d'eaux jeunes est liée aux volumes stockés dans la zone riparienne, i.e. proche de la rivière. Des volumes importants proche de la rivière allongent le temps de transit, et diminuent d'autant la proportion de temps courts (eaux jeunes). Même si *comparaison n'est pas raison*, cette explication semble confirmée par la représentation de la cumulée de la distribution des volumes du versant par rapport à la distance à la rivière et par les estimations quantitatives données dans le Tableau 2. La distribution des temps de résidence semble contrôlée par la répartition du volume souterrain le long du versant. Une analyse plus approfondie nécessiterait de tracer la localisation de l'infiltration en fonction du temps de transit, ce qui pourrait être fait avec la même méthode particulière utilisée pour réaliser les simulations. Les particules avec des temps de transit de moins de trois mois seraient analysées en premier.

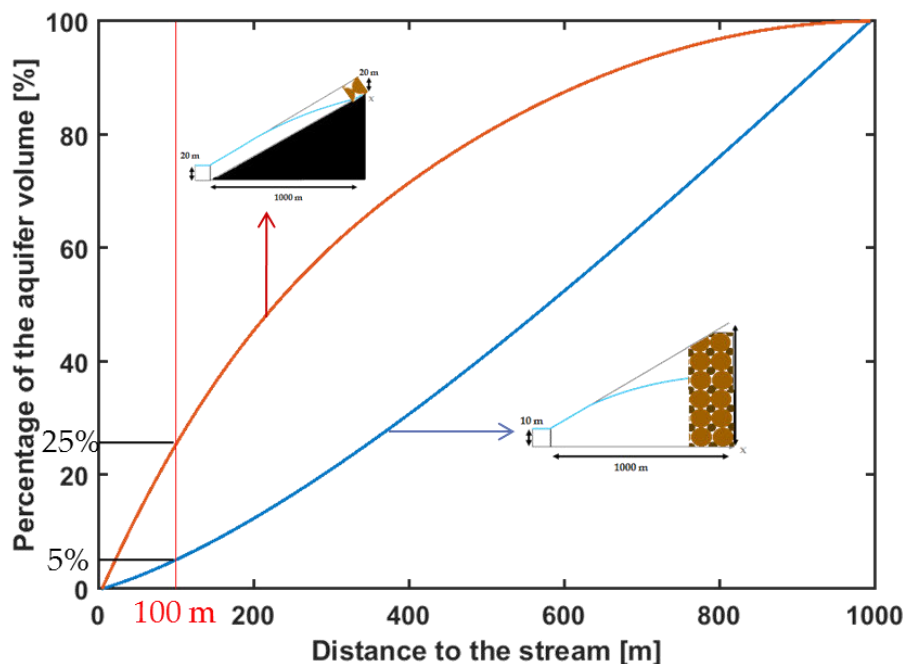


Figure 33: Cumulée de la distribution de répartition des volumes sur le versant représentée en fonction de la distance du stock d'eau considéré à la rivière.

De plus, l'étude de l'effet de la topographie dans la zone riparienne amène à des conclusions similaires sur l'importance de la répartition des volumes pour prédire la forme de la distribution des temps de transit (Figure 34). Cet effet est d'autant plus important qu'il génère en plus des ruissellements de surface quand la nappe intersecte la topographie. Ces ruissellements sont d'autant plus importants que

la topographie proche de la rivière est plate comme montrée sur le cas du versant à fond plat avec « abrasion » de la topographie proche de la rivière. Ces formes de topographies ripariennes sont souvent observées dans la réalité (Figure 35) [Anderson et al., 2007; Jencso et al., 2009; McGlynn and McDonnell, 2003].

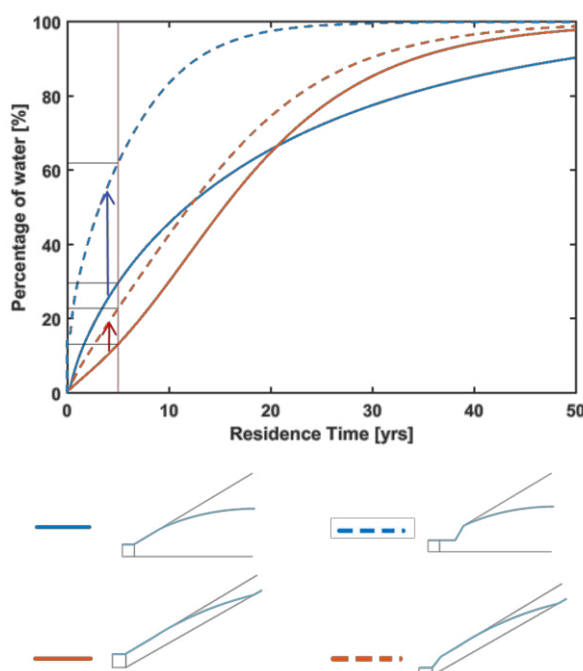


Figure 34: Effet de second ordre : la structure topographique proche de la rivière, en zone riparienne, peut augmenter la proportion d'eaux jeunes si cette topographie contraint les volumes stockables dans l'aquifère à proximité de la rivière. Cette « abrasion » de la topographie facilite de surcroît le ruissellement proche de la rivière.

2.3 Discussion : comment tester cela sur des cas réels ?

Pour donner à ce travail une coloration plus concrète, il faudrait disposer d'un estimateur fiable et bon marché de la proportion d'eaux jeunes dans les eaux s'écoulant en rivière et échantillonner ce traceur dans un grand nombre de tête de versants aux profils topographiques contrastés. L'idée étant qu'en regardant un grand nombre de versant, on pourra compenser l'unicité de chaque tête de versant par une représentativité accrue due au nombre de cas d'études [Gupta et al., 2014]. Pour estimer la proportion d'eaux jeunes, on ne dispose que des données isotopiques ($\delta^{18}\text{O}$ ou $\delta^2\text{H}$) qui nécessite d'avoir réalisé un suivi haute fréquence (*a minima* hebdomadaire) et ce, pendant plusieurs années [Kirchner, 2016; McGuire and McDonnell, 2006; Soulsby et al., 2000]. Ce suivi est coûteux et demande un investissement long terme dans des stratégies d'échantillonnage. Il n'est donc pas adapté à cette étude qui nécessiterait d'étudier un grand nombre de têtes de versants. Avec ces contraintes, il semble que des traceurs idéaux pourraient être des mesures de concentrations en éléments hydrochimiques classiquement mesurés en rivière [Beyer et al., 2016]. En effet, une telle étude ne nécessiterait pas des traceurs extrêmement précis, l'idée étant d'évaluer relativement plus que d'estimer précisément la proportion d'eaux jeunes pour différentes têtes de versants. Pour le choix des têtes de versants, il semble que les zones montagneuses soient un terrain expérimental de choix du fait du fort signal topographique. Une analyse des têtes de versants à l'échelle nationale à l'aide de données topographiques plus précises que les données SRTM pourraient être un bon départ. En effet, les données SRTM n'ont au mieux qu'une précision de 30m, ce qui limite leur utilisation pour l'étude de la topographie à une échelle fine typiquement une distance inférieure à 100m des rivières.

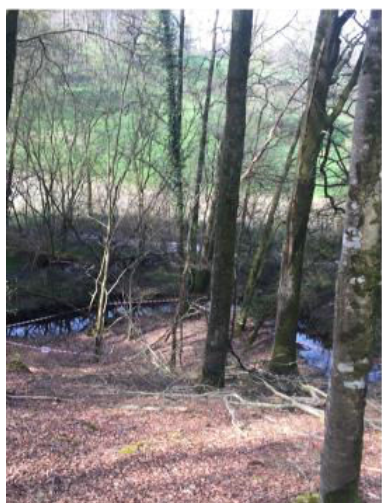


Figure 35: Photographies représentant la zone riparienne sur la Zone Atelier Armorique (Long Term Ecological Research - LTER) de Pleine Fougères. Cette zone présente souvent un décroché topographique caractéristique. Photographies personnelles de Benjamin W. Abbott.

Chapitre 3 Modélisation des aquifères libres de proche subsurface à l'échelle régionale

Ces perspectives sont issues de réflexions relatives au projet *AquiFR* qui vise à disposer de modèles hydrogéologiques à l'échelle nationale. À terme ces modèles permettront de mieux prendre en compte l'impact des réservoirs hydrogéologiques sur le changement climatique ainsi que de faire des scénarios sur l'impact du changement climatique sur les stocks et les dynamiques de ces aquifères. Pour la Bretagne, la particularité des systèmes cristallins bretons a nécessité le développement d'approches de modélisation dédiées. Ce projet fait l'objet d'un travail de thèse mené par Quentin Courtois à Géosciences Rennes (2018-2020), auquel j'ai contribué en proposant des approches de modélisation parcimonieuses adaptées aux attendus du projet *AquiFR*. J'ai proposé notamment d'étendre les approches de versants précédemment à l'échelle de bassins versants de plusieurs dizaines à centaines de km².

3.1 Position du problème : disposer d'un système de modélisation sur le territoire cristallin breton

Les interactions entre l'atmosphère et les systèmes aquatiques continentaux demeurent très mal connues [Hartmann *et al.*, 2017; Maxwell *et al.*, 2007; Maxwell *et al.*, 2010]. Une question qui se pose en particulier est de savoir comment intégrer les grands réservoirs d'eau douce continentales que sont les aquifères dans les projections sur le climat qui servent de base aux recommandations du GIEC. En effet, actuellement, ce couplage n'est pas pris en compte, ce qui pose des problèmes d'évaluation du rôle qu'aura ce stock dans le changement climatique en cours. Deuxièmement, l'impact du changement climatique sur les réserves d'eau stockées dans ces aquifères est relativement mal connu bien que plusieurs études aient maintenant été publiées [Anyah *et al.*, 2008; Etchevers *et al.*, 2002; Maxwell and Kollet, 2008; Quintana-Seguí *et al.*, 2010]. Or ces réservoirs ont un rôle essentiel pour les écosystèmes et les communautés humaines du fait de leur rôle critique en période sèche (soutien des étiages, approvisionnement en eau potable, existence d'arbres étant capables d'utiliser les réserves en eaux des aquifères grâce à des systèmes racinaires dédiés, etc.).

Dans ce contexte, le projet *AquiFR* vise à modéliser les différents systèmes aquifères français à l'échelle régionale. Cette modélisation permettra le suivi et la prédiction de la ressource en eau souterraine en France. Différents systèmes aquifères français présentent ainsi déjà leur propre système de modélisation comme, par exemple, le bassin parisien ou le bassin aquitain [Habets *et al.*, 2015; Ledoux *et al.*, 2007; Roux *et al.*, 2016; Thiéry, 2013]. Cependant, d'autres parties du territoire français ne disposent pas de tels modèles. C'est le cas de la Bretagne qui, du fait de sa géologie cristalline et de sa topographie fragmentée, présente un grand nombre de bassins versants de l'ordre de quelques centaines de km². Sa géologie fracturée conduit ainsi à un système hydrogéologique très hétérogène. Pour cette raison, cette région nécessite des approches de modélisation dédiées.

3.2 Approches de modélisation : à base de versants élémentaires représentatifs

Nous avons vu au chapitre 3 de la partie II que les écoulements dans le bassin versant de Pleines Fougères étaient majoritairement locaux de l'ordre de quelques centaines de mètres et majoritairement contrôlés par la topographie [Kolbe *et al.*, 2016]. En particulier, ces écoulements sont typiquement compris entre la crête de versant (« *water divide* ») et la rivière la plus proche. Ces écoulements ont ainsi lieu dans la zone altérée et sont drainés par la rivière [Molenat *et al.*, 2008; Rempe and Dietrich, 2014; Wyns *et al.*, 2004]. Si des écoulements régionaux existent bien à l'échelle de la Bretagne [Aquilina *et*

al., 2015; Goderniaux et al., 2013], ils ne comptent pas pour une proportion importante en terme de flux participant activement au cycle de l'eau [Gleeson et al., 2015; Jasechko et al., 2016; Kolbe et al., 2016]. Par ailleurs, on peut se demander si ces écoulements régionaux sont eux aussi contrôlés par la topographie comme cela est classiquement supposé pour les milieux sédimentaires homogènes [Toth, 1963]. Il apparaît plus probable que ces écoulements soient contrôlés par la géologie du fait de fracturation selon des directions et des localisations préférentielles [Le Borgne et al., 2006; Leray et al., 2013; Roques et al., 2014b; Touchard, 1999].

Pour ces raisons, une stratégie de modélisation visant à approcher les ressources souterraines participant activement au cycle de l'eau et sensibles au changement climatique peut-être de développer des modèles à l'échelle du versant, en faisant l'hypothèse que le bassin versant hydrogéologique correspond au bassin hydrologique. Le versant est alors considéré en quelque sorte comme le bassin versant élémentaire représentatif dans un esprit similaire à la définition des volumes élémentaires représentatifs [de Marsily, 1986; Reggiani and Schellekens, 2003; Reggiani et al., 1998]. Le bassin versant est donc segmenté en versants sur lesquels la modélisation de l'écoulement est réalisée. Chacun de ces versants est lié à un segment de rivière qui est son exutoire (Figure 36). Sur chacun de ces versants, on peut alors appliquer le modèle développé dans la partie III (Partie IIIChapitre 1 et Partie IIIChapitre 2) pour résoudre les équations de flux et de transport présentées précédemment.

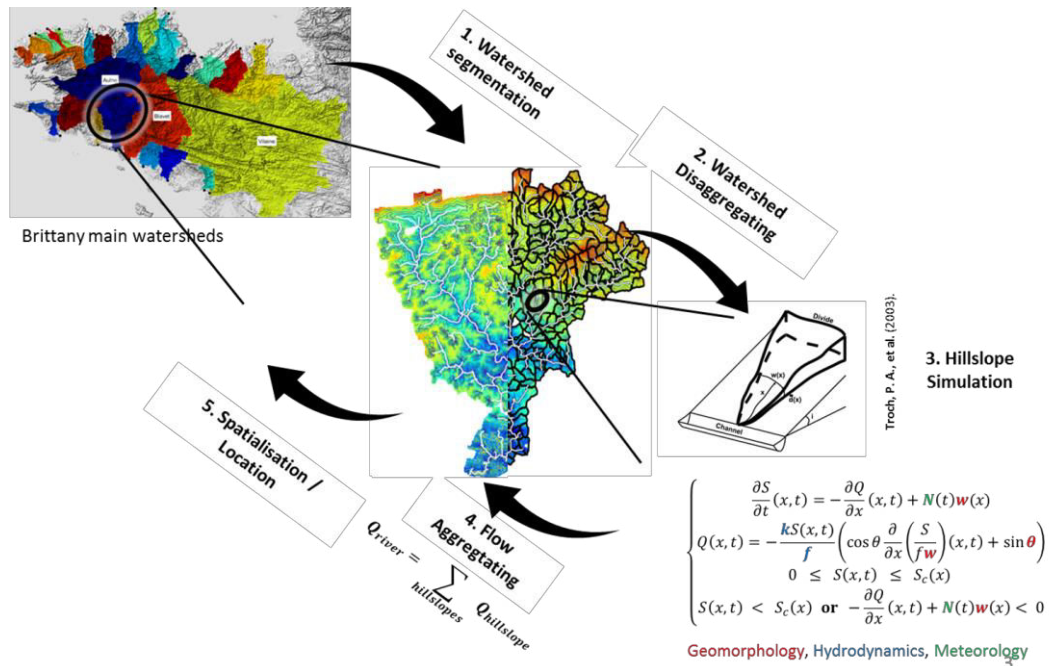


Figure 36: Stratégie de modélisation des écoulements à l'échelle de la Bretagne. Découpage d'un bassin versant en multiples versants sur lesquels on résout l'écoulement en aquifère avec prise en compte du ruissellement. D'après [Courtois et al., 2018].

3.3 Identification des propriétés hydrauliques des versants à l'échelle régionale

La question qui suit est de savoir comment inférer les paramètres hydrauliques du versant à partir de données réelles, typiquement des chroniques de débit en rivière et à quelle résolution il est possible de parvenir. En effet, le nombre de stations de jaugeage en Bretagne est très limité et ne permettra vraisemblablement pas d'inférer l'ensemble des paramètres de ce modèle semi distribué (Figure 37). Même si ce type de modèle présente un moins grand nombre de paramètres que les modèles 2D ou 3D, l'information disponible dans les données de stations de jaugeage ne permettra de lever l'équifinalité

qui se présentera quand des modèles compétitifs, présentant des paramétrisations différentes, mèneront à des prédictions de qualité équivalente [Beven, 2006]. Une solution pourrait être de classer les versants en fonction de leur caractéristique (topographique, géologique) de manière à encore réduire la paramétrisation nécessaire. Des travaux récents ont ainsi montré que l'information contenue dans les données topographiques pour prédire le débit pouvaient se réduire à un nombre restreint de versants emblématiques illustrant la diversité des formes rencontrés sur l'ensemble du bassin versant [Loritz *et al.*, 2018]. On peut aussi imaginer réduire l'équifinalité via la prise en compte de contraintes multiples, issues de l'expertise, pour diminuer l'espace de paramètres disponibles dans ces versants. Ceci pourrait être réalisé, par exemple, en prenant en compte les données de cartes géologiques, de données sur l'épaisseur altérée et fracturée des roches cristallines du bassin versant considéré [Kelleher *et al.*, 2017]. De plus, l'analyse des récessions dans les données de débit pourraient permettre de faire la distinction entre les écoulements de ruissellements, rapides et les écoulements de nappe, plus lents. Cette distinction est essentielle pour aborder les questions de transport (Partie III Chapitre 3).

La deuxième question est de savoir comment inférer les processus de transport et de réactivité à l'échelle du versant. En effet, si les stations de jaugeage de débit sont éparses à l'échelle du territoire breton (Figure 37), les données de qualité d'eau le sont tout autant avec des prélèvements de fréquences mensuelles ne permettant pas de restituer la variabilité de ces chroniques. D'autre part, le processus de mélange induit une perte d'information qui empêche de remonter à une paramétrisation précise des processus de transport [Kirchner, 2016]. Ici les données de puits pourraient aider à la mise à l'échelle (« *upscaling* ») du transport à l'échelle du versant. Bien sûr, cet « *upscaling* » ne peut s'envisager que 1. sur les versants où un puits est disponible. 2. à l'aide de méthode « *d'upscaling* » visant à reconstituer par des priors l'information perdue [Choi *et al.*, 2013; Ebrahimi and Or, 2016; Kollet *et al.*, 2010]. Ces priors peuvent venir d'une expertise apportée par la communauté [Kelleher *et al.*, 2017]. L'*upscaling* peut se faire en séparant le versant en différents compartiments horizontaux (zones ripariennes, zones de transition, plateaux) aussi bien que des compartiments verticaux (sol, aquifère) [Pinay *et al.*, 2015; Savenije, 2010]. Plus généralement, l'inférence du fonctionnement du réacteur biogéochimique d'un bassin versant demande d'appliquer une théorie de la réactivité développée à cette échelle. Enfin, cette stratégie de modélisation est destinée à intégrer un grand nombre de traceurs suivis dans les observatoires de la zone critique. C'est ce que nous allons voir dans la partie suivante.



Figure 37: Carte des stations de jaugeage (débit) en Bretagne. Données DREAL Bretagne.

Chapitre 4 Une approche de la réactivité pour intégrer de nouveaux traceurs, révélateurs du fonctionnement de la zone critique

Cette perspective est le fruit d'une réflexion sur les possibilités entrevues suite au développement de nouvelles méthodes de suivi et de caractérisation des écosystèmes environnementaux. En France, ces outils ont été particulièrement développés par le programme CRITEX ; ce sont le monitoring intensif des petits bassins versants de têtes (projet RiverLab sur le site de l'Orgeval, maintenant aussi déployé sur la bassin versant de Naizin et du Strengbach), ainsi que les outils de suivi en continu des gaz dissous (outil Mass-Inlet-Mass Spectrometer-MIMS développé durant la thèse d'Eliot Chatton [Chatton *et al.*, 2017]). Cette perspective est très large et s'inscrit également dans la thèse d'Eliot Chatton, de Tamara Kolbe et de Camille Vautier et, plus généralement, a fait l'objet de nombreuses discussions avec la communauté zone critique. Cette perspective sera l'objet de mon travail de recherche lors de mon prochain postdoctorat à l'IPGP sous la direction de Lou Derry. L'objectif de ce chapitre est donc de mieux comprendre le fonctionnement du réacteur biogéochimique qu'est le bassin versant en déchiffrant l'importance relative des processus d'écoulements, de transport et de réactivité à l'aide du suivi d'un certain nombre d'éléments chimiques, traceurs du fonctionnement du bassin versant. Nous avons dans cette thèse proposé une stratégie originale visant à modéliser les écoulements et le transport à l'échelle du versant. Il reste donc à développer une théorie de la réactivité plus accomplie que celle esquissée jusqu'ici et applicable à l'échelle du versant. Cette compréhension du fonctionnement de la zone critique vise dans un second temps à extrapoler les résultats obtenus à plus grande échelle et sur des sites moins instrumentés.

4.1 Position du problème : vers une description mécaniste de la réactivité à l'échelle du versant

Si nous avons développé dans les différentes parties de cette thèse une description mécaniste des écoulements et du transport conservatif à l'échelle du bassin versant, de manière mécaniste et parcimonieuse, nous n'avons qu'effleuré la manière dont la réactivité pouvait être décrite de manière physique à l'échelle du bassin versant. Disposer d'une telle « théorie de la réactivité » à l'échelle du versant est essentiel pour plusieurs raisons. Tout d'abord, la plupart des solutés mesurés en rivière, par exemple dans le projet RiverLab (K^+ , Na^+ , Ca^{2+} , NO_3^- , DOC – carbone organique dissous, ...) ne peuvent pas être considérés comme des traceurs inertes. Bien au contraire, l'information que recèlent ces solutés est justement liée à leur réactivité, aux interactions eaux/roches, à leur origine localisée dans certaines couches. Par exemple, pour les éléments Ca^{2+} et SO_4^{2-} , dans le bassin versant de l'Orgeval, ces éléments sont liés aux couches sédimentaires contenant du gypse [Billy *et al.*, 2011; Mégnien, 1979].

Ces traceurs peuvent aussi être le reflet des activités anthropiques (par exemple agricoles, pour les nitrates NO_3^-) ainsi que des processus biogéochimiques tel que la dénitrification [Bohlke, 2002]. La description de la réactivité à une échelle de quelques km^2 est donc essentielle à la compréhension du réacteur biogéochimique qu'est le bassin versant [Grathwohl *et al.*, 2013]. Cette compréhension se redouble d'enjeux de politiques publiques par exemple pour la prédiction des teneurs en nitrates suite aux réductions d'intrants imposées par la législation européenne [Directive, 1991]. La question est donc de savoir quelle est la complexité adaptée à la description de la réactivité des différents solutés à l'échelle du versant ou des petits bassins versants ?

4.2 Une nouvelle approche des bassins versants comme des réacteurs compartimentés

Nous avons vu dans la Partie III que le formalisme que nous avons développé pour modéliser le transport dans le bassin versant était à la fois basé sur le temps de circulation des parcelles d'eau (i.e. les particules dans la méthode numérique lagrangienne) mais comportait aussi une description *a minima* de la spatialisation de ces trajectoires : connaissance des compartiments dans lesquels ces parcelles d'eau circulent (i.e. sol et aquifère), stratification des trajectoires à l'intérieur de l'aquifère, connaissance des zones saturées potentiellement anoxiques. Cette description de la spatialisation permet de prendre en compte les conditions physico-chimiques dominantes des compartiments hydrologiques et des structures lithologiques majeures. La réactivité peut être représentée explicitement puisque les trajectoires sont résolues spatialement en 3D (voir Partie III Chapitre 2). Pour aborder la question de la résolution nécessaire pour intégrer une réactivité à l'échelle du versant, nous proposons plusieurs formalismes de complexité croissante en recherchant une représentation de la réactivité grande échelle à la fois pertinente et applicable.

4.2.1 Les temps de transit et de résidence comme proxys de la réactivité

Pour modéliser le transport réactif relatif à des réactions hétérogènes (typiquement des réactions eaux / minéraux) ayant lieu dans le milieu souterrain, nous avons jusqu'ici privilégié une application de la réactivité qui dépende du temps de transit parcouru en milieu souterrain. Cette conceptualisation est classique en chimie et en théorie des réservoirs, puisque l'avancement d'une réaction dépend du temps que les différentes espèces chimiques ont passé en contact [Appelo and Postma, 1994; Frei and Peiffer, 2016; Ginn, 1999; Levenspiel, 1999; Oldham et al., 2013]. On définit ainsi un ordre de réaction. Pour une espèce chimique A, l'évolution de sa concentration le long d'une ligne de flux (« *flow path* ») pour une certaine catégorie de réactions de dégradation ou de sorption par :

$$\frac{dC^A}{d\tau} = \pm k C^{A\beta}, \quad (8)$$

où τ est le temps de transit durant lequel la réaction s'effectue, β définit l'ordre de la réaction et k est la constante de réaction qui traduit la vitesse de réaction en fonction, entre autres, des conditions de température, de surface de contact fluide/solide, de porosité et de la composition minéralogique des milieux rencontrés [Gabet et al., 2006; Lasaga, 1984]. Le signe dans l'équation de réaction dépend de la situation de l'espèce A, réactif ou produit. Des solutions analytiques existent, par exemple pour $\beta = 0, 0.5, 1$ ou 2 [Serrano, 2001; 2003]. En particulier, pour $\beta = 1$, la réaction est dite de premier ordre. Elle est classiquement utilisée pour la dégradation des nitrates en milieu souterrain [Tesoriero and Puckett, 2011]. On a ainsi un taux de dégradation:

$$r_{NO_3^-}(\tau) = \exp\left(-\frac{\tau}{\tau_{NO_3^-}^{app}}\right), \quad (9)$$

où r est en fait un moins la réactivité (r traduit la proportion de nitrates restant en solution) et $\tau_{NO_3^-}^{app} = \frac{1}{k}$ est le temps apparent de dénitrification. Cette hypothèse de réactivité, qui suppose qu'elle ne dépend que du temps parcouru dans le milieu souterrain, est valide pour les pollutions diffuses [Botter et al., 2010; Gianluca et al., 2005; Rinaldo et al., 2006a; b]. Le temps apparent est souvent bien plus important que celui mesuré en laboratoire pour évaluer le potentiel de dénitrification puisqu'il prend également en compte la probabilité que les nitrates rencontrent des donneurs d'électrons d'origine organique ou

minérale (e.g. carbone organique dissous, pyrite) [McClain *et al.*, 2003; Oldham *et al.*, 2013; Zarnetske *et al.*, 2012]. Cette distinction amène naturellement à considérer le concept de hotspots, qui permettrait, une fois le temps apparent de dénitrification connu, de remonter à une proportion moyenne de distribution des hotspots où se fait réellement la réactivité en milieu souterrain [Li *et al.*, 2007; McClain *et al.*, 2003]. Cette différence entre temps apparent de réaction et temps mesuré en laboratoire se retrouve également dans les études sur l'altération de roches du fait des limites physiques à l'altération des minéraux comme la chenalisation des écoulements et la structure des minéraux qui limite l'accès aux surfaces minérales réactives d'une part, et les contraintes thermodynamiques qui diminuent fortement l'altération lorsque la concentration en solution s'approche de l'équilibre d'autre part [Maher, 2010; Velbel, 1993; White and Brantley, 2003].

A partir de l'équation (9), la concentration que ce soit dans un puits ou à l'exutoire du milieu souterrain vers la rivière ou une zone humide peut être intégrée et aboutir au produit de convolution suivant avec τ le temps de résidence ou le temps de transit :

$$C_{out}^A(t) = \int_0^{+\infty} C_{in}^A(t - \tau) r(\tau) p(t, \tau) d\tau. \quad (10)$$

Cette formulation repose sur l'hypothèse implicite d'une réactivité uniforme à travers un taux de réaction qui ne dépend finalement que du temps de résidence ou du temps de transit quelle que soit la structure des circulations. Cette hypothèse peut mener à une sous-estimation ou à une surestimation de la résilience des aquifères aux pollutions aux nitrates comme nous allons le voir dans la partie suivante [Kolbe *et al.*, in rev.]. Il s'avère donc nécessaire de décrire la réactivité non seulement en fonction du temps de transit mais aussi en fonction de la structure des circulations vis-à-vis des différentes conditions chimiques et structures géologiques rencontrées.

4.2.2 Le temps d'exposition comme descripteur supplémentaire de la réactivité

L'objectif des concepts d'exposition est de limiter le temps de réaction par rapport aux temps de transferts aux seules périodes où les contaminants ou réactifs étudiés sont dans des conditions propices à la réaction (e.g. proximité de minéraux réactifs) [Ginn, 1999]. Avec les modèles développés ici, l'exposition peut être explicitée comme la localisation de la réaction dans certaines couches du domaine souterrain plus ou moins profondes ou superficielles par exemple [Kolbe *et al.*, in rev.]. Dans le cas où la réactivité est majoritairement autotrophe avec un réducteur minéral localisé en dessous de la zone de battement de nappe (où il a pu être progressivement lessivé), on introduit un temps nécessaire pour que la réactivité commence, ce temps étant le délai nécessaire aux écoulements souterrains pour arriver à la profondeur de la couche réactive (ce qui peut être le cas, dans le cas d'une réaction d'oxydo-réduction avec la pyrite). Dans le cas où la réactivité est majoritairement hétérotrophe avec un réducteur organique venant de la surface, on introduit un temps maximum au-delà duquel la réaction ne pourra plus avoir lieu lorsque la source de carbone aura été complètement consommée (Figure 38).

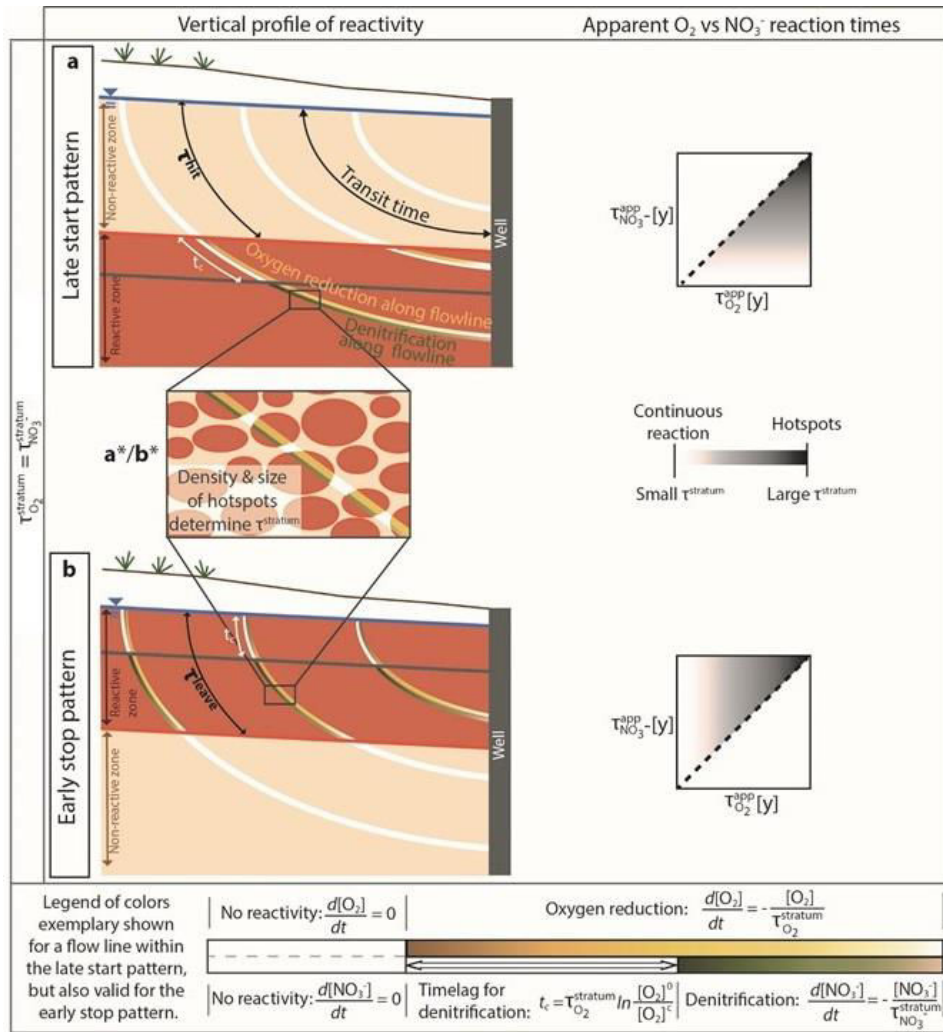


Figure 38: Figure représentant les deux concepts de réactivité stratifiée soit avec une réactivité ayant lieu à partir d'une certaine profondeur (late start pattern), soit s'arrêtant à partir d'une certaine profondeur early stop pattern). La densité de hotspots contrôle également le temps caractéristique de réaction. Plus cette densité est faible, plus la réaction est lente. D'après Kolbe et al. [in rev.].

Cette dernière description reste uniquement basée sur le temps de résidence auquel on ajoute des facteurs correctifs d'exposition. Elle ne pourra peut-être pas s'appliquer à l'ensemble du bassin versant comme elle a été appliqué avec succès à l'échelle d'un aquifère cristallin [Kolbe et al., in rev.]. En effet, à l'échelle du bassin versant, il semble qu'il faille, *a minima*, distinguer la réactivité ayant lieu dans les grands compartiments du bassin versant. Cette compartimentation biogéochimique pourrait s'appuyer sur le sol, la zone non saturée, la zone riparienne, l'aquifère superficielle, l'aquifère plus profond et même plus précisément certaines unités géologiques [Pinay et al., 2015]. La distinction entre aquifère superficielle et aquifère profond peut se faire sur une connaissance de la géologie du milieu souterrain (connaissances des zones altérées en milieu cristallin, connaissances des différentes strates de roches en milieu sédimentaire) [Rempe and Dietrich, 2014]. Plus généralement, la compartimentation de la réactivité doit se faire en fonction des structures géologiques et des compartiments hydrologiques (Figure 39).

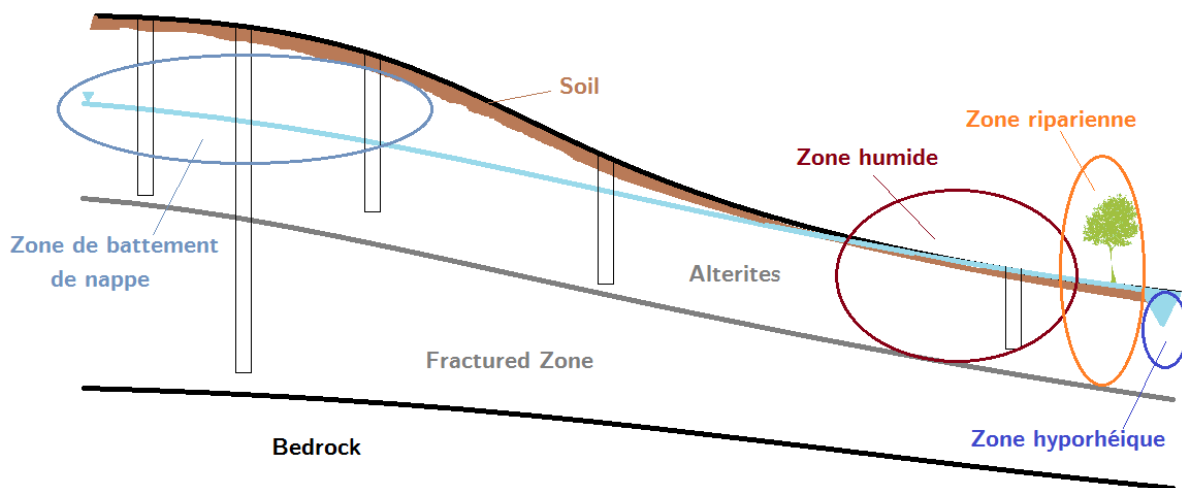


Figure 39: Vision simplifiée d'un versant en grands compartiments structurels liés à la géologie (séparé par des traits horizontaux) et liés à l'hydrologie (entourés sur le schéma). Les compartiments structurels sont structurés verticalement, du fait de la géologie et de l'organisation verticale de la zone critique tandis que les compartiments hydrologiques suivent une organisation latérale (en fonction de la distance à la rivière). L'illustration est prise ici pour les milieux de socle cristallin et peut être étendue aux conditions géologiques où la stratification est dominante..

Une telle description de la réactivité doit prendre en compte : 1. Le temps de transit ou le temps de résidence passé dans les différents compartiments (temps d'exposition). 2. Une réactivité différenciée en fonction du compartiment souterrain. En effet, le sol et l'aquifère n'ont pas la même densité de hotspots 3. Une réactivité qui peut varier en fonction des conditions rencontrées dans ces différents compartiments. Par exemple, lorsque le sol subit des cycles de saturation, il peut localement présenter des profils anoxiques, qui sont connus pour faciliter la réactivité du fait de la présence simultanée de surfaces oxiques et anoxiques facilitant les réactions de nitrification / dénitrification [Ebrahimi and Or, 2015].

Dès lors, on ne peut plus supposer que la réactivité dépende seulement du temps passé dans le bassin versant. La réactivité d'un compartiment donné peut alors s'écrire $r(t, \tau, \mathbf{x}, S(\mathbf{x}, t))$, où t représente le temps auquel on veut évaluer la réactivité, τ est le temps de transit passé dans ce compartiment, $\mathbf{x}$ est le vecteur décrivant la position de la particule d'eau suivie et $S(\mathbf{x}, t)$ caractérise par exemple l'état de saturation du compartiment à cet instant. Cette description spatialisée pose cependant un certain nombre de questions ouvertes parmi lesquelles la caractérisation de la distribution des temps de transit de l'eau dans chacun de ces compartiments sachant que les écoulements souterrains peuvent être constitués de lignes de flux traversant différents compartiments au cours de leur séjour dans le bassin versant. Ceci ne peut pas être approché avec une unique distribution de temps de transit. Il conviendrait donc de considérer une convolution des temps de transit (équation (10)) améliorée et conditionnée par la nature et la structure des différents compartiments.

4.3 Comment informer la réactivité ? Exemple de données en nitrate sur des bassins versants bretons

Pour informer la réactivité d'un élément donné, la mesure des variations de sa concentration dans une rivière drainant un bassin versant semble essentielle pour contraindre notre compréhension des processus associés à cette réactivité à l'échelle du versant. En effet, ces chroniques temporelles sont comme des prises de vue faites à intervalle régulier de l'état du bassin versant dans des conditions climatiques, hydrologiques (et donc biogéochimiques) distinctes. Elle permet donc non seulement

d'avoir une vision temporelle de l'évolution des concentrations en soluté dans un bassin versant mais surtout d'envisager de progresser dans une connaissance spatiale du bassin versant et de ces compartiments souterrains qui sont inaccessibles à la mesure. Pour aborder cet objectif, il convient d'avoir un système de modélisation qui nous permette de remonter à une connaissance spatialisée via des mesures temporelles. C'est ce que nous avons développé dans la Partie III.

Par exemple, pour les nitrates dans différents bassins versants bretons présentés en Partie III (Partie III Chapitre 3), on dispose également du suivi hebdomadaire de la concentration en nitrates sur une période de 12 ans (Figure 40). Ce suivi se caractérise par différentes caractéristiques : 1. les teneurs en nitrates observées dans ces bassins versants varient fortement d'un bassin versant à l'autre, 2. ces concentrations ont une tendance globale (long terme) à la diminution, spécialement dans les bassins versants présentant des concentrations en nitrate élevées (Guillec, Penzé), 3. ces concentrations présentent des fluctuations saisonnières contrastées avec un certain nombre de bassins versants présentant des maxima de nitrates en hiver (comme la Douffine) et d'autres présentant des maxima de nitrates en été (comme le Guillec). Ces trois observations sur les chroniques de nitrate en Bretagne nous permettent de formuler un certain nombre d'hypothèses à tester en vue de contraindre la réactivité de ces nitrates dans le bassin versant et d'en tirer une prédiction sur l'évolution future de ces concentrations.

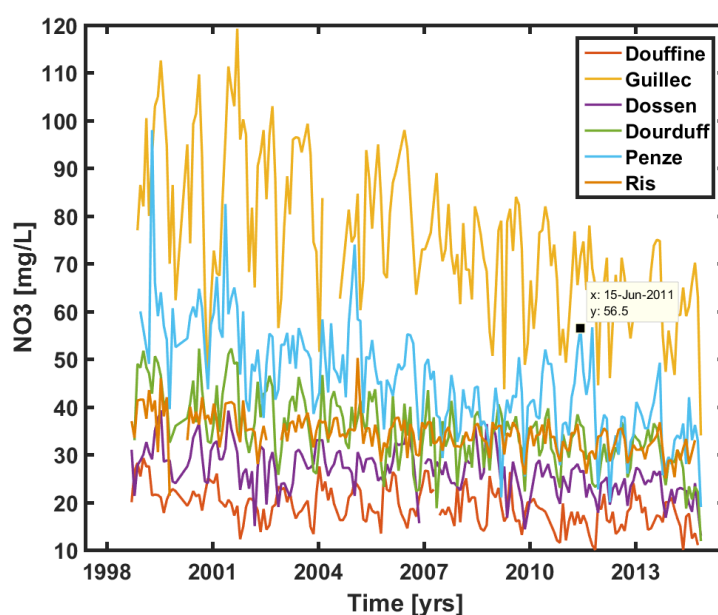


Figure 40: Suivi de l'évolution des concentrations en nitrates dans différents bassins versants côtiers bretons. Données Ecoflux [Abbott et al., 2018].

Comme on dispose de modèle de transport calés grâce aux données en silice (voir Partie III Chapitre 3), qui nous renseigne sur l'évolution temporelle des distributions des temps de transit $p_Q(t, \tau)$, on peut donc évaluer différentes représentations de la réactivité pour essayer de comprendre les « patterns » observés dans ces variations, détaillés au paragraphe précédent. Par exemple, on peut faire l'hypothèse que la réactivité a lieu dans les sols et dans les aquifères de deux façons.

D'une part, on peut supposer que la réactivité a lieu dans les sols quand du ruissellement de subsurface est généré. En effet, ce ruissellement a pour effet de faciliter la connectivité du versant et donc de mettre en contact les nitrates dissous dans ce ruissellement de subsurface avec des donneurs d'électrons (carbone organique dissous principalement). La présence de ruissellement de subsurface a également pour effet de contribuer à créer des zones oxygènes / anoxiques qui peuvent favoriser la présence

symbiotique de bactéries nitrifiantes / dénitrifiantes nécessaires pour une dénitrification complète et rapide [Ebrahimi and Or, 2015; Ebrahimi and Or, 2016; Parkin, 1987; Sexstone et al., 1985]. Ces épisodes de ruissellement hivernaux sont donc des « *hot moments* » pour la dénitrification dans le sol [McClain et al., 2003]. On fait donc l'hypothèse que durant ces épisodes humides, le flux de nitrates transitant dans le ruissellement de subsurface peut être dénitrifié comme suit :

$$\begin{cases} r(t, \tau < 1 \text{ month}) = \exp\left(-\tau/\tau_{soil}^{NO_3^-}\right) \\ r(t, \tau \geq 1 \text{ month}) = 1 \end{cases}$$

où on rappelle que le taux de réaction est égal à 1- r . $\tau_{soil}^{NO_3^-}$ est le temps caractéristique pour dénitrifier l'eau dans le sol quand la connectivité est réalisée. Le fait de considérer uniquement les temps de transit inférieur à un mois traduit justement le fait que la dénitrification n'a lieu que lors des « *hot moments* » de connectivité, quand du ruissellement de subsurface assure la connectivité (qui, du fait des perméabilités du sol à saturation, retourne en rivière en un mois maximum, cf. Partie III Chapitre 2 ou Chapitre 3).

Pour la réactivité dans l'aquifère, on suppose par contre que les nitrates sont dénitrifiés lorsqu'ils rencontrent une zone réductrice avec présence de pyrite (FeS₂) [Pauwels et al., 1998; Tesoriero et al., 2000], ce qui se traduit mathématiquement :

$$\begin{cases} r(t, \tau < \tau_{hit}) = 1 \\ r(t, \tau \geq \tau_{hit}) = \exp(-(\tau - \tau_{hit})/\tau_{app}^{NO_3^-}) \end{cases}$$

où τ_{hit} représente le temps caractéristique nécessaire pour atteindre cette zone réductrice et $\tau_{app}^{NO_3^-}$, le temps caractéristique pour dénitrifier l'eau une fois atteinte cette couche réductrice [Kolbe et al., in rev.]. Cette zone réductrice dans l'aquifère peut être vue comme un « *hot spot* » de réactivité [McClain et al., 2003]. Pour réduire, la paramétrisation (3 paramètres pour la réactivité en nitrates), on pourrait par exemple fixer $\tau_{app}^{NO_3^-} = 5$ ans, en cohérence avec des études précédemment publiées [Kolbe et al., in rev.; Tesoriero and Puckett, 2011]. Finalement, l'optimisation se réduirait à déterminer les paramètres $\tau_{soil}^{NO_3^-}$ et τ_{hit} optimaux qui permettraient de rendre compte de 1. la tendance globale à la diminution des concentrations en nitrate ainsi que 2. de leur variation saisonnière avec une explication des différences observées en bassins versants.

La tendance globale à la diminution permettrait de valider le temps de transit de l'eau puisque cette diminution est supposée être liée à la diminution en intrants effectuée dans les années 90 et renseignerait également sur la quantité totale de nitrates dénitrifiés. Les variations saisonnières permettraient de déterminer l'importance relative de chacun des compartiments (sols et aquifères) sur la dénitrification. En effet, les variations hydrologiques saisonnières permettent d'échantillonner préférentiellement l'un ou l'autre de ces compartiments en saison sèche et en saison humide. La modélisation choisie permettrait également de tirer des informations quantitatives sur les moments où la dénitrification est la plus active. Enfin, cette modélisation permettrait de réaliser des scénarios d'évolution des teneurs en nitrates dans les cours d'eau suivant les politiques publiques mises en place ou les réductions d'intrants décidée. Ces scénarios issus de modélisation pourraient ouvrir la voie à une évaluation quantitative du bienfondé des différentes mesures mises en place pour réduire les pollutions diffuses en vue d'éradiquer les phénomènes d'eutrophisation ainsi que des alternatives économiquement acceptables.

Il est à noter que, comme l'élément nitrate (contrairement à la silice), n'est pas produit à l'intérieur du versant mais provient des intrants agricoles, il convient d'avoir une information sur l'historique

spécialisée des intrants appliqués. On dispose ainsi pour ces différents bassins versants de chroniques de forçage agricole, modélisant l'évolution des surplus azotés sur ces différents bassins versants (Figure 41) [Poisvert *et al.*, 2017]. Ces surplus azotés présentent un maximum au début des années 90 suivi d'une diminution importante suite à la mise en place de la directive nitrates dans les pays de l'Union européenne parue en 1991 [Directive, 1991]. Ces chroniques traduisent le forçage en $\text{kgNO}_3/\text{ha}/\text{an}$.

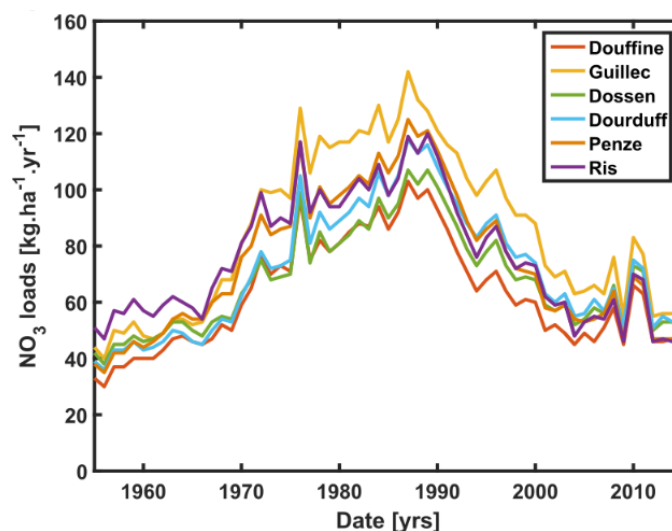


Figure 41: Surplus en nitrates en $\text{kg}/\text{ha}/\text{an}$ sur différents bassins versants bretons présentés dans la Partie III Chapitre 3. D'après Poisvert *et al.* [2017]

4.4 Identification des compartiments d'intérêts, recherche d'une inférence ciblée à l'aide de traceurs spécifiques et intérêt de la haute fréquence pour le suivi de la qualité de l'eau en rivière

Finalement, au travers de cet exemple visant à développer des modèles de réactivité pour les nitrates, nous avons esquissé une méthode pour évaluer quels sont les compartiments responsables de la dénitrification en rivières et comment ils sont sollicités au cours du temps. Cet exemple prospectif tend à démontrer le potentiel de cette approche mécaniste pour quantifier et prédire le transport et la réactivité des solutés que ce soit pour des applications de compréhension du système « zone critique » comme pour des applications destinées aux gestionnaires. En effet, une fois confrontées aux données, on peut envisager de quantifier la dégradation totale de nitrates à l'échelle du bassin versant, la localisation de la réactivité dans les bassins versants et de prédire l'évolution long terme de ces concentrations.

Pour comprendre le fonctionnement de ce réacteur biogéochimique qu'est le bassin versant, l'intégration de nombreux traceurs renseignant sur différents processus (processus d'écoulements, de transport ou de réactivité) et sur différentes structures de la zone critique (structures géologiques par exemple) est essentiel. En effet, une compréhension fine des différents processus et de leur « enchevêtrement » à l'échelle du bassin versant nécessite de développer une utilisation multi-traceur où, idéalement, chaque espèce chimique renseignerait sur un processus. Par exemple, certaines mesures isotopiques permettent de renseigner très finement sur un processus et ouvre des perspectives pour répondre des questions bien précises comme par exemple: quelle est l'importance relative des flux d'eau provenant de la zone altérée sur ceux provenant de la zone fracturée et d'où proviennent les éléments issus de l'altération en rivières (sols, aquifères) [Derry *et al.*, 2005; Kurtz *et al.*, 2002] ? Quelle est le processus de dénitrification dominant (autotrophe ou hétérotrophe) dans un bassin versant donné [Hosono *et al.*, 2014] ? Cette utilisation multi-traceurs peut se résumer en un schéma traduisant la manière dont des mesures temporelles multi-traceurs et en continu peuvent aider à la caractérisation spatiale de différents

processus ainsi que de leur utilisation pour faire de la prédiction sur l'évolution long terme du bassin versant suite aux forçages anthropiques (Figure 42).

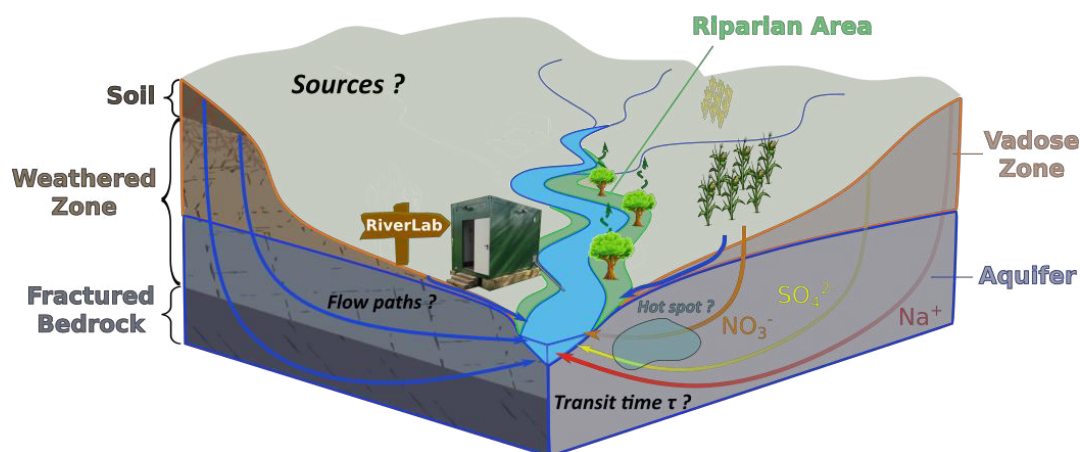


Figure 42: La mesure haute fréquence acquise en rivière pour différents solutés permettra de mieux contraindre les structures géologiques, les grands compartiments hydrologiques ainsi que les processus d'écoulements, de transport et de réactivité à l'échelle du versant. En effet, cette mesure haute fréquence est comme de multiples prises de vue du bassin versant sous des conditions et des historiques climatiques toujours différents.

De plus, l'utilisation de données hautes fréquences permettra de développer la logique de l'inférence de la structure du bassin versant à partir de chroniques temporelles. En effet, ce que nous avons décrit sur les chroniques saisonnières de nitrates se trouve démultiplié quand on dispose de chroniques de mesure de qualité d'eau en rivière à une fréquence infra horaire [Flourey *et al.*, 2017]. En effet, cela ouvre la voie à l'identification d'une structuration des écoulements, du transport et de la réactivité plus précise, du fait du plus grand nombre d'événements échantillonnés et de leur diversité. Par exemple, avec ce type de mesures, on dispose à la fois de crues hivernales et de crues estivales qui échantillonnent différemment la zone critique et sont le reflet de différents processus dominants. Les possibilités offertes doivent aussi être mises en regard des défis que posent une telle assimilation de données. Pour répondre à ce défi, on peut ainsi envisager d'utiliser des signaux qui compressent la donnée acquise à partir d'un a priori hydrologique [Weijs *et al.*, 2013a; Weijs *et al.*, 2013b]. Pour réaliser cela des outils issus de la théorie de l'information sont disponibles [Gupta and Nearing, 2014; Nearing and Gupta, 2015; Nearing *et al.*, 2016]. On peut également envisager d'obtenir des signatures hydrologiques de ces données hautes fréquences qui seront à interpréter par des modèles mécanistes parcimonieux à bases physiques [Hrachowitz *et al.*, 2014; McMillan *et al.*, 2017]. Dans cet ordre d'idées, les diagrammes C/Q sont vraisemblablement les signatures hydrologiques les plus utilisées à l'heure actuelle par la communauté des hydrologues s'intéressant à la qualité de l'eau [Aguirre *et al.*, 2017; Moatar *et al.*, 2017; Musolff *et al.*, 2017]. La possibilité de modéliser ces signatures avec les modèles développés précédemment (Figure 43, voir Partie III pour le modèle) permettent d'envisager de nombreuses perspectives pour comprendre de manière synthétique la variation de la qualité de l'eau à haute fréquences dans les bassins versants.

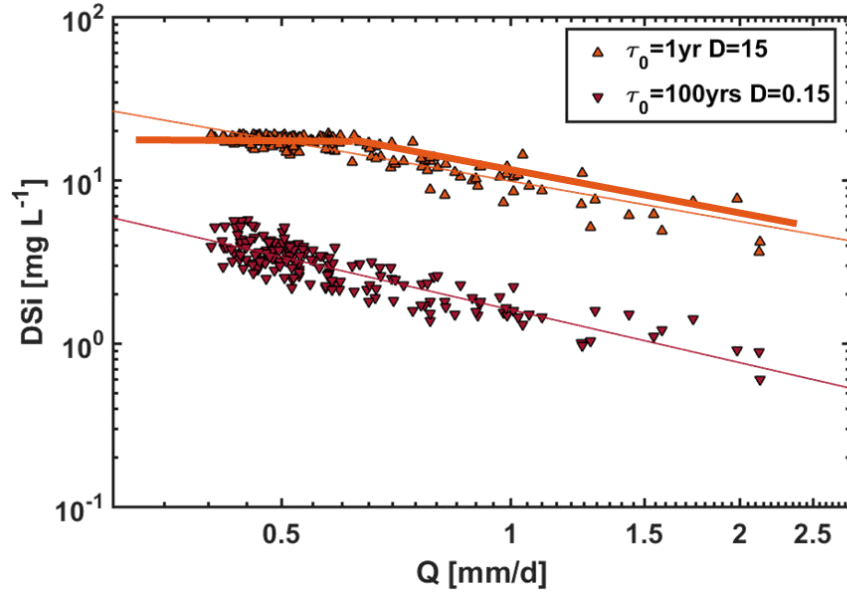


Figure 43: Données numériques représentant la concentration en silice en fonction du débit en rivières. Ces relations C/Q numériques ont été modélisées à l'aide du modèle présenté en Partie III suivant différentes hypothèses de réactivité pour la silice (loi cinétique de premier ordre avec différents temps caractéristiques d'altération τ_0). D représente le nombre de Damköhler, nombre sans dimension représentant le ratio du temps de transit caractéristique sur le temps caractéristique de réaction [Maher and Druhan, 2014; Oldham et al., 2013]. Noter comment la vitesse de réaction d'altération contrôle le caractère chémostatique de la relation DSi/Q , spécialement pour les débits faibles puisqu'ils sont majoritairement alimentés par des circulations souterraines âgées.

Chapitre 5 Vers une meilleure intégration des données et des modèles à base physique

5.1 Introduction

Pour finir cette partie de discussion et perspectives, nous esquissons une prospective sur le potentiel du développement de nouvelles méthodes en intelligence artificielle pour progresser dans la voie de la découverte scientifique appliquée à l'hydrologie. Le grand nombre de données acquises sur les milieux environnementaux rendent de plus en plus difficile l'intégration des données aux modèles mécanistes telle qu'elle était pratiquée jusqu'alors. La méthode du problème inverse [*Certes and de Marsily*, 1991; *Zimmerman et al.*, 1998], paradigme classique en hydrogéologie, se heurte aux grands nombres de données hétérogènes produites. Cette méthode demande en effet de représenter explicitement l'ensemble des processus menant à l'observation des données à intégrer pour être en mesure de les intégrer au modèle. Cette représentation explicite de nombreux processus peut faire croître le nombre de paramètres du modèle plus rapidement que la donnée assimilable. Ceci pose de nombreux problèmes pratiques. Par exemple, les modèles mécanistes classiquement développés ne sont pas, une fois calibrés, actualisés lorsque de nouvelles données sont disponibles, du fait du coût que cela représente. De plus, pour intégrer deux types de données différentes (géophysiques et géochimiques par exemple), ce sont souvent deux modèles concurrents qui sont développés. Cela rend impossible la confrontation de données de différentes origines alors qu'il semble que ce soit justement de données hétérogènes permettant d'informer un processus donné de manière la plus transversale possible, qui nous permettra de progresser dans une compréhension toujours plus fine d'un phénomène observé.

Plus fondamentalement, il semble qu'il convienne de s'interroger sur l'information contenue dans les données disponibles pour comprendre un phénomène donné [*Gupta and Nearing*, 2014; *Nearing and Gupta*, 2015]. On peut ainsi voir le travail du scientifique face aux données comme celui d'une synthèse à réaliser, synthèse qui permette de compresser les informations diverses contenues dans les données en vue de mettre en lumière un processus spécifique. Dans cette optique, et dans une évolution avec toujours plus de données, nous pensons cependant que les modèles explicites ont encore toute leur place. En effet, pour l'hydrologie, même si le nombre de données disponibles croît de manière importante, il demeure faible face à l'hétérogénéité du milieu souterrain et à la complexité des processus de transferts. Cette hétérogénéité couplée au fait que ce milieu demeure majoritairement inaccessible à la mesure directe (hormis les quelques forages dont on dispose) rendent nécessaire de tester des a priori forts via des modèles mécanistes. Cependant, de nouvelles stratégies d'articulation modèles / données pourraient être testées, stratégies qui tirent parti des progrès récents réalisés en intelligence artificielle [*LeCun et al.*, 2015; *Silver et al.*, 2016]. Par exemple, nous envisagerions ainsi de tester des modèles d'intelligence artificielle couplant données réelles et données synthétiques issues de modélisation mécanistes. C'est cette prospective que nous détaillons dans les parties suivantes.

5.2 Abstract

Interest in Artificial Intelligence has recently been renewed by successes of deep learning methods on several computational benchmarks. Deep learning may even display more general capacities in automatic category classification, abstract identification, hierarchical modeling and adaptation. As these properties are of fundamental and practical interests for hydrological sciences, we prospectively discuss their potential for calibration, model structure evaluation and uncertainty quantification. We argue that deep learning might not modify our approaches but provides additional abilities to cope with the growing amount of data and models provided by rapid progresses in sensing, communication and computation means.

5.3 Article: Prospective Interest of Deep Learning for Hydrological Inference

Prospective Interest of Deep Learning for Hydrological Inference

by Jean Marçais^{1,2,3} and Jean-Raynald de Dreuzy³

Introduction

Decision making relative to groundwater resources requires the characterization, modeling, and prediction of complex and dynamical systems with many degrees of freedom. Nonetheless, these systems have large-scale structure that emerges from hierarchical properties based on conservation principles applied to fundamental physical quantities (e.g., mass, momentum and energy). Difficulties arise as hydrologic systems are inherently heterogeneous and sometimes chaotic. This is not specific to hydrology, but it is generic to natural or man-made complex systems. Two approaches have been proposed to handle these complex systems. Whether they are called model-driven or data-driven, explicit or implicit, they differ widely by methodology. In the explicit model-driven approach, processes are physically modeled at each characteristic scale and progressively scaled up. Patterns, equivalent properties, and effective laws emerge progressively through upscaling. This has been performed extensively in stochastic hydrology to derive equivalent permeability and in percolation theory to identify universal scaling laws (Stauffer and Aharony 1992). Large-scale observations are integrated by adapting the model parameters through the classic, but generally ill-posed, inverse problem (Zimmerman et al. 1998). In the implicit data-driven approach, minimal assumptions are made on the structure of the models developed (Hastie et al. 2003; Montgomery 2006). Rather, this approach relies on generic data-driven analysis based on statistics and artificial intelligence. Among numerous

methods, supervised-learning algorithms and, especially, artificial neural networks became popular in the 1990s in hydrology. One well-cited example is their use for prediction and understanding of rainfall runoff processes (Hsu et al. 1995, 2002).

Implicit data-driven methods have been less active for the past decade (a period called the Artificial Intelligence Winter). But, there is renewed interest in machine-learning methods due to the recent successes of deep neural networks in several Artificial Intelligence benchmarks including the first-time computer win at the game of Go (Silver et al. 2016). In general, deep network successes have been attributed to their ability to provide efficient high-dimensional interpolators that cope with multiple scales and heterogeneous information (LeCun et al. 2015; Mallat 2016). This suggests a natural opportunity for the use of deep networks for hydrological sciences. We discuss these possibilities with particular focus on their complementary and combined use with well-established model-driven approaches.

Generalization, Classification, and Hierarchical Combination Abilities in Deep Learning

Deep learning is a new class of machine-learning algorithms that recognizes high-level abstractions in data. They are called deep because they are made up of some tens of hierarchically arranged layers, compared with classic neural networks that had only very few. Abstraction is achieved through the processing of the data by the internal layers to automatically identify patterns of increasing complexity. We review three essential properties for their potential interest in hydrological sciences.

Deep learning can be used for calibration. Classic neural networks have been shown to be universal estimators (Hornik et al. 1989). Deep learning can significantly improve their efficiency and accuracy (Bengio and Delalleau 2011; Mhaskar and Poggio 2016).

Deep learning can find robust invariants from large, high-dimensional datasets, leading to improved

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Article impact statement: Deep learning may assist hydrological inference through its increased capacities to interpolate, classify, and hierarchically model databases.

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interpolation and generalization (Hinton and Salakhutdinov 2006). For example, a deep convolutional generative adversarial network (Goodfellow et al. 2014) was able to generate new bedroom images having all the same elements (bed, lamp, bedside table, etc.) as the bedroom pictures used for training (Radford et al. 2015).

Deep learning successes might indicate fundamental capacities to replicate multiscale modeling of physical principles. Generalization properties of deep convolutional networks have been related to the locality and upscaling principles of wavelets (Mallat 2016). The multilayer convolutive structure of deep networks is well adapted to let hierarchical patterns emerge through the combination of small-scale elements. Potential consistency with physical processes may be further linked to the compositional nature of some physical processes, which might be derived from advanced combinations of symmetry, locality, and compositional principles (Lin and Tegmark 2016). As an illustration, deep networks have prospectively been used to infer quantum energy of complex molecules, reaching state of the art quality of evaluation alternatively derived from Schrödinger equations (Hirn et al. 2016). This inherent upscaling opens new opportunities to apply deep learning to real physical systems (Baldi et al. 2014; Denil et al. 2016).

Deep Learning Prospects for Hydrological Inference

Among the different interests of deep learning for hydrology, the first is its potential contribution to calibration, following the use of artificial neural networks in the 1990s. Deep networks are especially designed for handling large datasets. They might be considered for prediction issues (Figure 1, blue arrows), provided that the following conditions are met. Hydrological data are highly diverse and would require some extensive preprocessing to produce uniform training sets for deep networks. Basic prerequisite of deep learning methods should also be checked in terms of the density and nature of the training information. Nevertheless, deep neural networks have already been used for predicting precipitation from satellite clouds images and reduce significantly the bias compared with traditional neural networks (Tao et al. 2016).

Second, deep networks may contribute to the initial choice of the structure of a physical model, which strongly conditions eventual predictions. For geological storage of high-level nuclear wastes, this issue has been handled by requesting independent models (models ensemble) from different research groups (Zimmerman et al. 1998; Bodin et al. 2012). Such benchmarks are, however, possible only for highly sensitive applications with significant costs. On the other hand, modeling as well as computational capacities have critically progressed to the point such that it is feasible to simulate a broad range of model configurations (Kumar 2015). Models also become more faithful to the point where synthetic catchments, synthetic aquifers,

and virtual observatories no longer seem out of reach (Thomas et al. 2016; Yu et al. 2016). The limiting factor increasingly comes from the exploration and analysis of the resulting simulations (Hermans 2017). Deep networks might contribute to more systematic interpretation through interpolation and category classification. They could be considered for interpolating explicit models as has been done in surrogate modeling (Figure 1, green arrows) (Razavi et al. 2012; Asher et al. 2015). They could also be trained on extensive databases of model realizations that support uncertainty analyses (de Pasquale 2017). The advantage of deep networks over other interpolators is their ability to cope with many simulations while inherently complying with different levels of organization of the hydrological systems (Sposito 1998). Practically, this will require careful consideration of methods to execute many models, manage errors, systematize formatting of inputs and outputs, and ensure easy access to simulation results.

Using deep networks as a possible high-dimensional interpolator is motivated by some reduction in computational costs through the use of existing simulations. But, current interest is also directed to model reduction, category classification, and uncertainty quantification through the constitution of extensive databases of simulations (Figure 1, green arrows) (Clark et al. 2015). Model reduction is an active field of research in applied mathematics and computational science (Schilders 2008) designed to retain only the key structural parameters of the models for the phenomena or predictions of interest (Castelletti et al. 2012). While the first target would be to refine our understanding of hydrological processes, several other issues could be handled. For example, the ability to identify model classes would help to address the question of the model structural adequacy beyond the identification of optimal parametrization (Gupta et al. 2012; Guthke 2017). It might also contribute to identify classes of acceptable models at the core of null-space identification (Gallagher and Doherty 2007), equifinality analysis (Beven 2006), and, more generally, uncertainty quantification. Even more prospectively, we might investigate its potentialities in proposing alternative model structural assumptions, especially for investigating the likelihood of diverse hydrological scenarios of critical importance for stakeholders (Ferre 2017; Marshall 2017) and in assisting the design of hydrological experiments (Kikuchi et al. 2015) (Figure 1). Deep networks might be used to assess expert knowledge in a more systematic way (Seibert and McDonnell 2002; Hrachowitz et al. 2014). The real strength of deep networks, and implicit data-driven models in general, is that emergent system properties can be identified that cannot be uncovered by explicit models that are imposed on an analysis (Figure 1, orange arrows). This may automatically adapt our models to conform to natural processes and to the data available (Kirchner 2006; Troch et al. 2009), while exploring model space more completely.

Despite the potential contributions of deep learning, we do not suggest that they should replace classic

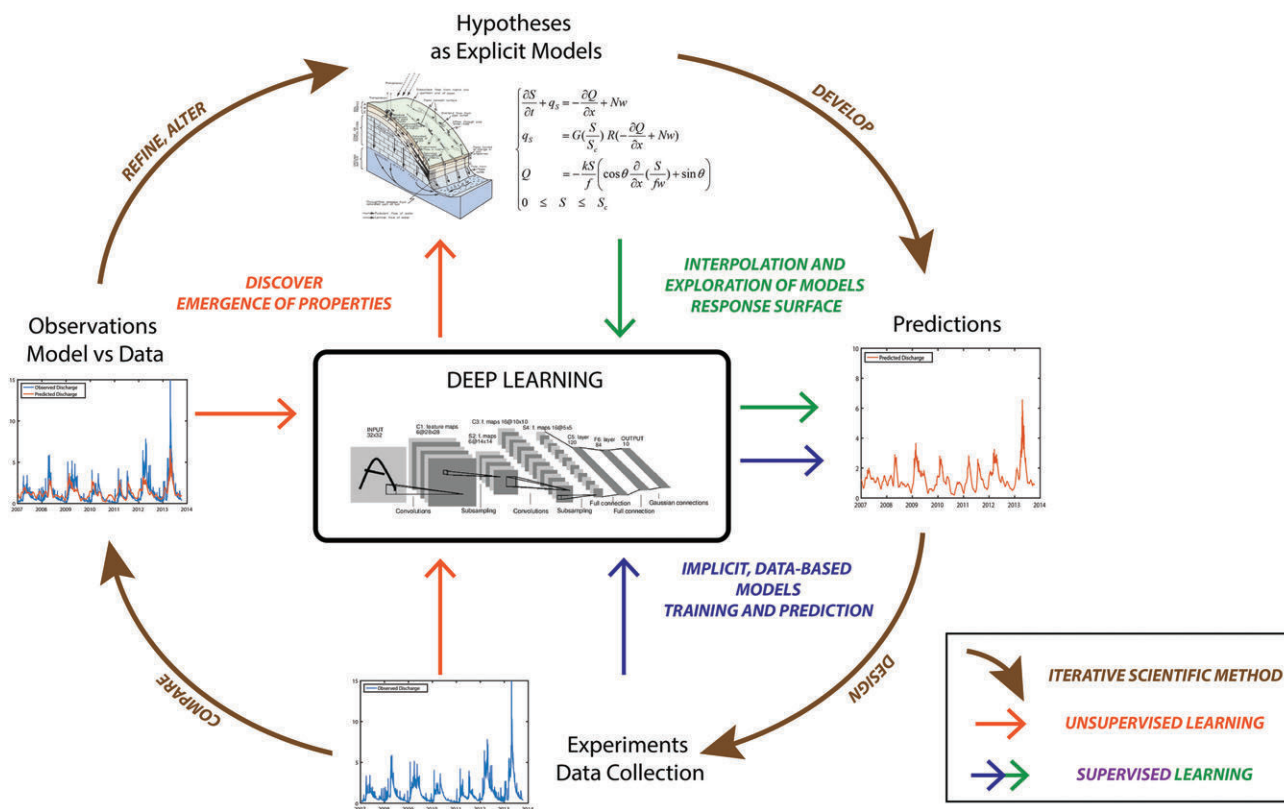


Figure 1. Deep learning seen as a complementary tool to assist iterative hydrological inference. Brown arrows show the classic methodology for understanding processes (here rainfall/runoff processes) by confronting hypotheses (explicit, process-based models) formulated as predictions to experiments and data. Deep learning could be used as implicit, data-based models trained (calibrated) on real datasets to perform predictions (blue arrows). It could provide a tool to explore and interpolate model simulations, or even model ensembles (green arrows). More prospectively, it might be applied to discover patterns in data, find trends in synthetic versus real data misfits to assist hydrologists in formulating testable hypotheses (orange arrows). This last possibility is seen as an unsupervised learning task as opposed to supervised learning for the other ones with real or synthetic datasets. (Hillslope illustration adapted from Kirkby 1979. Deep learning architecture illustration adapted from LeCun et al. 1998.)

approaches in hydrology. Rather, they are attractive as a complementary tool having, at least conceptually, some properties highly relevant to hydrological systems like their built-in hierarchical combination. This could similarly benefit ongoing automated model-building efforts that also require some definition of the range of model structures to consider and the ways in which they should be combined (Clark et al. 2015). In addition to these enhanced capacities, deep networks will find particular use in integrating larger datasets and explicit model results produced by rapid technological progress in automated and remote sensing. In this sense, we see deep learning as a loose coupling between growing data-driven and model-driven approaches (Figure 1). It is not designed as an effective calibration technique applied on explicit physical models (Certes and de Marsily 1991; Doherty 2003), but rather as an implicit data-driven approach to correct errors from explicit physical based models (Szidarovszky et al. 2007; Demissie et al. 2009; Gusyev et al. 2013). Prospective testing and interactions are needed with the deep learning community to understand how information content between synthetic models and field data should be balanced in the training sequence (Nearing and Gupta 2015).

A Roadmap to Investigate the Relevance of Deep Learning to Hydrology

We propose three steps toward integrating deep learning into hydrologic science: testing on data; testing on benchmarks; and collaboration with the wider deep learning community.

Testing on hydrological numerical data will require the collection and organization of systematic and well-organized databases. Availability of such database has been one of the main reasons for the success of deep learning techniques (Krizhevsky et al. 2012). This could include measured data, but should also rely heavily on synthetic datasets. Such synthetic hydrological databases are achievable, for example, by building extensive stochastic simulations performed on heterogeneous media (Pirot 2017). Constitution of systematic and standardized field databases is also under way following the dynamics of critical zone observatories, open international normalization initiatives (Ames et al. 2012) and regulatory incentives.

Testing on hydrological benchmarks can begin with target synthetic benchmarks described above. More

complicated benchmarks can be developed according to their consistency with existing deep learning benchmarks, that is, based on images or succession of images to describe processes (Mathieu et al. 2015). Hydrologic insight will be necessary to ensure that the benchmarks are relevant to important hydrological complexities, especially those related to the multiscale nature of the hydrologic systems.

Cross-disciplinary discussions with the deep learning community will be required to take full advantage of deep learning methods and to introduce hydrology as a topic of interest to that community. Data heterogeneity, in terms of quantities measured and scales, has already been mentioned and is critical to improve our ability to integrate diverse information sources. Hydrology offers an opportunity for the deep learning community to expand their interest beyond controlled and deterministic systems like the double pendulum (Schmidt and Lipson 2009) to natural systems that are characterized by epistemic or aleatory uncertainties. The heterogeneous and sometimes chaotic nature of the hydrologic system makes it difficult to directly transpose existing results obtained on deterministic experiments but is an opportunity to assess deep learning potentialities.

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5.4 Bilan

Dans cet article, nous faisons le constat que 1. le nombre de données environnementales collectées croît de manière sans précédent, 2. la puissance de calcul des ordinateurs continuent de progresser 3. les méthodes développées en intelligence artificielle rencontrent toujours plus de succès. Nous nous interrogeons sur les raisons du succès des nouvelles méthodes d'apprentissage profond [Mallat, 2016] et évaluons si ces propriétés sont intéressantes pour l'inférence en hydrologie. Nous envisageons ensuite de développer des stratégies complémentaires à celles développées dans la communauté pour progresser dans le couplage modèle / données [Goldstein and Coco, 2015; Goldstein Evan and Coco, 2014]. Cette stratégie que nous envisageons ne vise pas à se substituer aux autres stratégies développées [Castelletti et al., 2012; Ratto et al., 2012] mais bien à tester de nouvelles approches couplant intelligence artificielle et hydrologie comme cela a été réalisé dans d'autres disciplines [Hirn et al., 2016]. Ces méthodes d'intelligence artificielle pourraient être envisagées comme des outils de rapprochement entre modèles, données et prédictions dans un esprit de fermeture (« *closure condition* ») régulièrement rencontré pour formaliser les problèmes de changement d'échelle, l'objectif étant de réaliser des prédictions avec un maximum de vraisemblance par rapport aux données tout en respectant un certain nombre de conditions physiques. Cette perspective ouvrirait la voie à une collaboration fructueuse entre la communauté de l'intelligence artificielle et la communauté des hydrologues.

Partie V Conclusions générales

« *Ces eaux-ci sont à la fois ivres et pures ; on n'en voit pas le commencement, ni la fin. [...] Si je me laissais aller, j'en ferais volontiers l'attelage scintillant du Temps.* »

Philippe Jaccottet, *Après beaucoup d'années*,
« Eaux de la Sauve, eaux du Lez », ed. Gallimard
(1994).

Comprendre, quantifier et prédire l'impact des activités humaines sur les écosystèmes aquatiques terrestres est un enjeu majeur pour accompagner les politiques publiques mises en place pour réduire notre empreinte sur les milieux naturels. Du fait de l'inertie de ces milieux naturels, il est difficile de démêler l'impact de politiques précises sur la qualité de l'eau, en rivières par exemple. La modélisation reste donc l'outil de choix pour comprendre l'interrelation entre flux d'eaux, transport d'éléments dissous et réactivité de ces éléments à l'échelle du bassin versant. Ces trois grandes familles de processus sont en effet la clef de la connaissance d'une qualité de l'eau donnée à un moment et un endroit précis du territoire.

Pour intégrer ces diversités de processus, la communauté a changé de paradigme et s'est engagée dans la description du système « zone critique » qui se définit comme étant le système s'étendant de la base des roches non altérées au sommet de la canopée où se rencontrent lithosphère, atmosphère, hydrosphère et biosphère. Cette zone se caractérise donc par les interrelations et les interdisciplinarités qui sont la clef des processus qui ont lieu à l'échelle de quelques kilomètres carrés. Cette zone ne représente qu'un très faible volume du globe terrestre mais est pourtant essentielle à la vie terrestre [Arènes *et al.*, 2018]. C'est cette zone que nous impactons majoritairement en milieu continental via, par exemple, l'urbanisation, l'artificialisation des sols ou l'agriculture intensive.

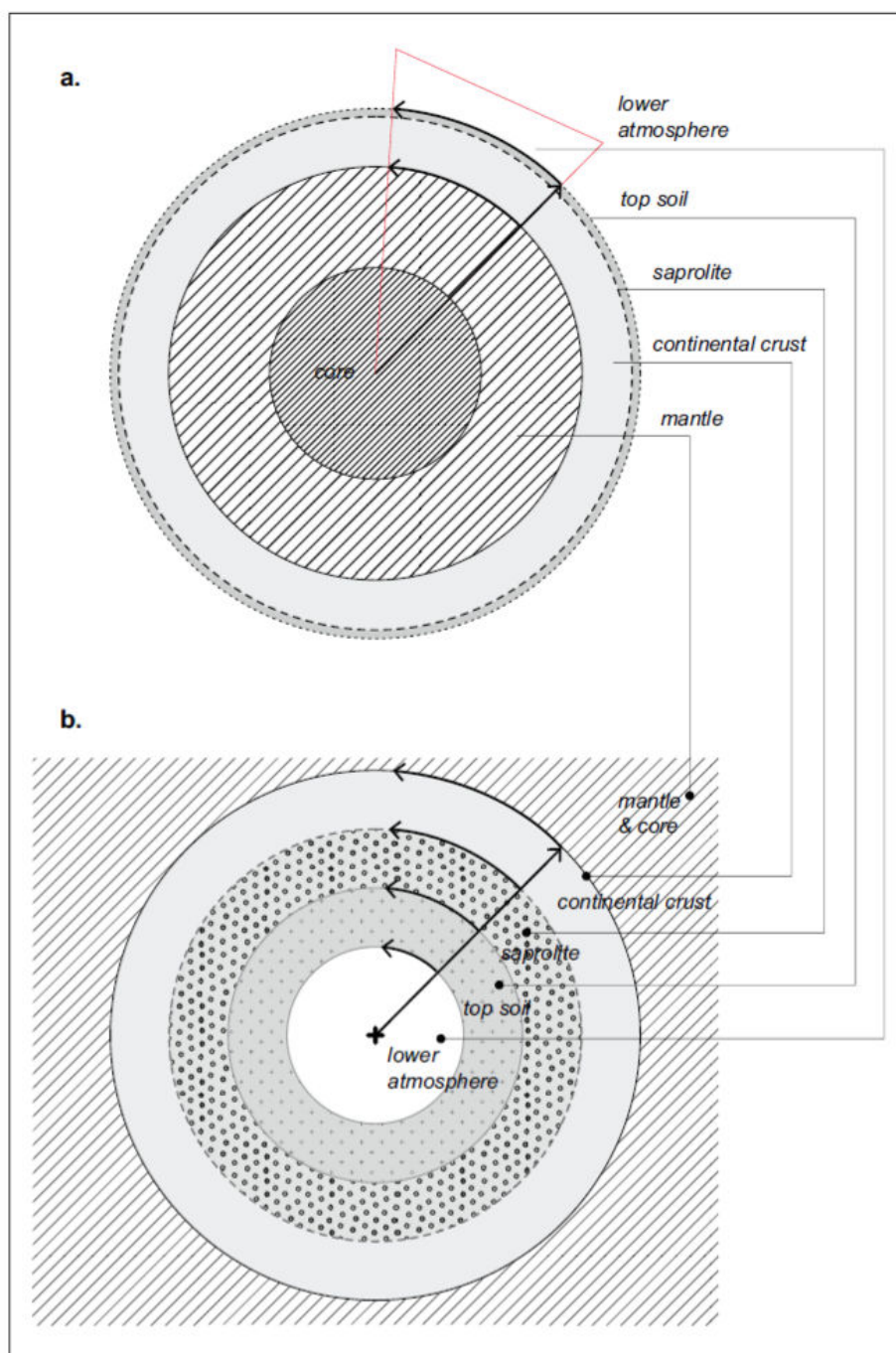


Figure 44: (a) De la représentation traditionnelle de la zone critique à (b) une nouvelle représentation de la zone critique. Cette nouvelle représentation remplace cette zone critique pour l'humanité et la vie en général, au centre de nos représentations conceptuelles par un procédé d'anamorphose. D'après Arènes et al. [2018]

Pour comprendre, quantifier et prédire ces impacts via la modélisation, la communauté travaillant sur ces hydrosystèmes continentaux a investi massivement dans la collecte de données environnementales. Cette collecte de données est spécifique en ce sens qu'elles caractérisent massivement les entrées et les sorties du système « bassin versant » que ce soit à l'aide des systèmes de télédétection ou des mesures de suivi en rivière. Les mesures de télédétection caractérisent en effet par une mesure spatialisée les entrées et les sorties spatialisées du système (pluie, intrants, évapotranspiration, croissance des végétaux) tandis que les mesures de suivi en rivières caractérisent les sorties du bassin versant (débits, concentration de solutés, transport solide). Ces données restent cependant très parcellaires sur le système

« bassin versant » dont bien des processus se jouent en milieu souterrain. On ne dispose en effet que de quelques puits ou de quelques mesures dans la colonne de sol qui renseignent localement sur le fonctionnement du bassin versant in situ.

Dans ce contexte, nous nous sommes engagés dans une démarche de modélisation adaptée à la complexité du milieu naturel qui soit capable d'utiliser ces données hétérogènes qui renseignent indirectement sur le bassin versant. Cet outil de modélisation devait pouvoir intégrer les données d'entrée spatialisées ainsi que les données de sortie majoritairement temporelles. Ce modèle devait rendre compte de la structure du bassin versant, des circulations d'eaux qui s'y déroulent, des transports d'éléments qui y ont lieu ainsi que des réactions chimiques. Pour ces raisons, nous avons fait le choix de développer un modèle à base physique. Cependant, vu le peu d'information sur le compartiment d'intérêt, ce modèle devait rester parcimonieux. Pour cette raison et comme la question nous intéressant étant celle de la réponse du bassin versant aux pollutions diffuses nous nous sommes appuyés sur le concept clef de temps de résidence et temps de transit des eaux pour étudier sous l'angle physique comment les forçages climatiques, topographiques et géologiques dictaient l'évolution des circulations souterraines et la qualité de l'eau qui leur est associés.

Pour avoir une information précise sur ces temps de résidence, l'hydrologie a développé de nombreux traceurs qui renseignent sur les temps des circulations souterraines et plus précisément sur la distribution des temps de transit et de résidence qui caractérisent à la fois les temps des différentes circulations ainsi que le mélange auquel elles sont soumises pour contribuer au flux d'eau ou à son stock en un endroit donné. Nous avons donc d'abord évalué la capacité des traceurs de temps de résidence que sont les CFCs pour prédire les temps de renouvellement des aquifères. En effet, cette prédiction est essentielle à réaliser pour évaluer la vulnérabilité quantitative des ressources en eaux dans les aquifères cristallins ainsi que leur vulnérabilité potentielle aux pollutions diffuses si aucun phénomène d'épuration naturelle (comme la dénitrification) n'a eu lieu. Nous avons ensuite développé l'utilisation de nouveaux traceurs de temps de résidence, traceurs qui soient à même d'être utilisés régionalement, en rivière comme en aquifère en répondant aussi à un impératif de faible coût. Nous avons ainsi utilisé la silice comme un traceur des temps de résidence dans les aquifères cristallins puisque la silice est un marqueur de l'altération des roches par l'eau et donc du temps qu'elles ont passé en contact. Plus généralement, cette utilisation de données géochimiques pourrait être généralisée pour quantifier les temps de résidence et de transit. Nous nous sommes enfin intéressés au potentiel informatif de ces traceurs et à la manière de les intégrer à la démarche de modélisation ainsi qu'à comprendre ce que ces traceurs apportaient en terme de caractérisation temporelle des circulations mais aussi en terme d'extensions spatiales. On a ainsi vu que, pour les aquifères en connexion avec la rivière, la majorité des circulations souterraines étaient locales (quelques centaines de mètres), guidées par la topographie mais étaient pourtant relativement anciennes (supérieures à 30 ans).

Ces constations nous ont amenés à développer un modèle parcimonieux, à base physique capable de modéliser le flux et le transport à l'échelle du versant, à même d'être mis à l'échelle du bassin versant. Cette modélisation repose sur une description des écoulements souterrains à l'aide des équations de Boussinesq qui reposent sur l'hypothèse de Dupuit-Forchheimer avec la prise en compte de la dynamique d'interception des nappes avec les horizons très perméables du sol. Dans le cas de tels interceptions, le ruissellement généré dans le sol, du aux précipitations sur cette zone saturée ainsi qu'aux flux de suintement, est routé en rivière à l'aide d'une équation traduisant un écoulement gravitaire. Deuxièmement, pour décrire la dynamique des temps de transit de ces circulations souterraines, nous avons développé un schéma de suivi particulière qui permet d'avoir accès aux distributions de temps de résidence de l'eau stockée dans le bassin versant ainsi qu'aux distributions de temps de transit de l'eau s'écoulant en rivière. On a pu voir que cette description lagrangienne du

transport conservatif respectait le bilan de masse et nous avons pu étudier l'impact des processus d'écoulements décrits plus haut sur les temps de transit et de résidence. Ce modèle nous a ensuite permis d'étudier des caractéristiques types relevées dans les séries temporelles de qualité de l'eau en rivière (silice) et de les relier aux processus responsables de ces variations. Les caractéristiques de ces chroniques de silice sont en fait leurs variations saisonnières et interannuelles que nous avons interprétées comme étant dû à l'alternance des circulations d'eaux jeunes dues aux processus de ruissellement de proche subsurface. Ce faisant, cette compréhension nous a permis d'en tirer des compréhensions essentielles sur les temps caractéristiques de circulations de l'eau dans les différents compartiments du bassin versant.

C'est cette compréhension qui permet ensuite de développer un cadre mécaniste pour comprendre et prédire l'évolution des concentrations en solutés réactifs comme le nitrate en rivière. Nous avons abordé cette question de la prise en compte des solutés réactifs en faisant une hypothèse de cinétique d'ordre 0 pour décrire l'évolution en silice en rivière. Pour les nitrates l'hypothèse de réactivité doit être plus accomplie et tenir compte des différents compartiments (sols, aquifères) qui contribuent de manière différente aux concentrations en nitrates observées en rivière. C'est ce que nous avons discuté en perspectives. Décrire la réactivité à l'échelle du versant nécessite d'avoir une bonne idée de la manière dont se partitionne les flux de précipitations entre circulations courtes et circulations plus longues. Pour cette raison, nous avons aussi discuté comment différents contrôles (topographiques, géologiques) pouvaient aider à prédire les partitionnements entre écoulements de subsurface et écoulements plus profonds. Dans le même ordre d'idée, nous nous sommes également intéressés à savoir si on pouvait prédire la distribution de temps de transit observée en rivière à l'aide de descripteurs topographiques ou géomorphologiques. Pour cela il apparaît indispensable de connaître la distribution spatiale des volumes d'eaux stockées dans le bassin versant ainsi que la distribution des flux de précipitations si on ne peut pas les supposer uniforme.

Finalement, toutes ces perspectives laissent envisager à terme d'arriver à une stratégie de modélisation qui soit capable de prédire les flux et l'évolution des concentrations en nitrates à l'échelle régionale. Enfin, l'obtention de toujours plus de données et plus précisément l'acquisition de données hautes fréquences, de données isotopiques et enfin de données biologiques permettent d'envisager une progression dans la conception que nous nous faisons de la zone critique. Ces modèles pourraient ainsi être utilisés pour comprendre l'évolution de la concentration d'autres solutés en rivière qui nous permettent d'affiner notre compréhension de la zone critique, à savoir sa structuration géologique, les circulations hydrologiques qui y transitent et la réactivité rencontrée par les solutés. Cette compréhension du cycle des grands éléments (C, N, P, DSi) en milieu continental a de nombreuses applications pratiques, allant de l'évaluation du potentiel des sols et de la végétation à être des puits de carbone, à la quantification de l'héritage en nutriments dans les bassins versants issues d'années d'agriculture intensive en passant par la prédiction du potentiel d'eutrophisation dans les bassins versants suite aux mesures de réduction d'intrants. Cette compréhension est fondamentale à développer si nous voulons nous engager dans une démarche durable de préservation de cette zone critique, critique pour la vie et pour l'humanité, à l'ère de l'anthropocène.

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Titre : Variabilités des temps de résidence de l'eau et du débit dans les rivières et les nappes phréatiques : implications sur la qualité de l'eau

Mots clés : Hydrologie - Zone critique - Eaux continentales - Qualité de l'eau - Datation - Altération - Réactivité

Résumé : Le transport de contaminants, l'altération des roches ainsi que les grands cycles biogéochimiques sont contrôlés par les temps de séjour de l'eau. Ces temps de séjour représentent le temps de transit durant lequel l'eau « voyage » dans un bassin versant. Contraindre ces temps de transit est donc un enjeu essentiel pour quantifier l'impact de l'homme sur la qualité de l'eau en rivières et dans les aquifères et pour évaluer la résilience des écosystèmes aquatiques continentaux. Cependant, les rivières comme les nappes phréatiques sont constituées d'un mélange d'eau de différents âges (une distribution des temps de transit ou des temps de résidence) qui varie avec le temps, en fonction des aléas météorologiques et climatiques, rendant difficile leur caractérisation ainsi que leur prédiction.

Dans cette thèse, nous inférons ces temps de résidence à l'aide de traceurs géochimiques et de modèles guidés par les données. Nous montrons comment cette connaissance permet de quantifier l'altération des roches cristallines. Nous développons ensuite un cadre original de modélisation à base phy-

sique, capable de représenter la variabilité saisonnière et interannuelle des débits et des temps de transit mesurés en rivière. Nous montrons comment le processus de battements de nappes et son interaction avec les couches perméables du sol mène à la génération d'un ruissellement qui explique les fluctuations saisonnières de qualité de l'eau en rivières, traduites par des mesures de silice dissoute.

Enfin, nous esquissons un cadre général de représentation de la réactivité à l'échelle du versant capable de rendre compte des processus biogéochimiques. En effet, représenter la dégradation des éléments réactifs (oxygène, nitrates, carbone) permettra d'évaluer les mesures de réduction d'intrants agricoles, de prédire l'évolution long terme de ces solutés en rivières, et donc leur potentiel d'eutrophisation ainsi que d'évaluer des mesures pour réconcilier agriculture et environnement. Cette réactivité apparaît comme le dernier maillon manquant pour comprendre, mesurer et prédire, les impacts anthropiques sur la zone critique.

Title: Variabilities of transit times, residence times and discharge: implications on water quality in streams and shallow aquifers.

Keywords: Hydrology - Critical zone - Groundwater dating - Travel time - Process-based model - Reactivity

Abstract: Groundwater travel time controls contaminant transport, weathering processes and biogeochemical cycles. Groundwater travel time is a fundamental descriptor characterizing the transit time of water inside the catchment, from precipitation events to the streams. Quantifying these transit times is pivotal to predict the impact of anthropogenic pressure and assess freshwater ecosystems resilience. However, streamwater and groundwater are a mixture of water of different ages (the transit time and the residence time distribution), which vary according to climatic forcings. This makes difficult its characterization and prediction.

Here we infer residence times with geochemical tracers and data-driven models. We show how this can be constrained by silicate weathering at the catchment scale. We then develop

a novel process-based framework, which can model discharge and transit time seasonal and interannual variabilities. We identify water table fluctuations, its interaction with permeable soil layers and the resulting subsurface stormflow generation as a key process for seasonal water quality variations described by dissolved silica measurements.

Finally, we draw a reactivity framework to represent biogeochemical processes. Indeed, evaluating reactive solute degradation is needed to assess the efficiency of reducing fertilizer loads, to predict the long term evolution of in stream solute concentrations and the eutrophication potential of freshwater bodies. Modeling the reactivity at the catchment scale is the missing link to understand, quantify and predict the effect of anthropogenic pressure on the critical zone.