



HAL
open science

**Dispersion, melange et reaction dans les milieux
heterogenes:caracterisation experimentale et
modelisation**

Tanguy Le Borgne

► **To cite this version:**

Tanguy Le Borgne. Dispersion, melange et reaction dans les milieux heterogenes:caracterisation experimentale et modelisation. Sciences de la Terre. Universite Rennes 1, 2015. tel-01140444

HAL Id: tel-01140444

<https://insu.hal.science/tel-01140444v1>

Submitted on 9 Apr 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

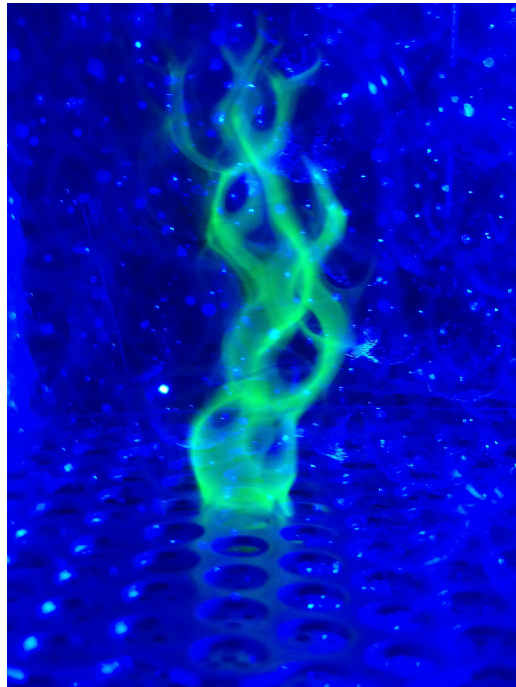
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Université de Rennes 1
Habilitation à diriger des recherches

Dispersion, mélange et réaction dans les milieux hétérogènes:
caractérisation expérimentale et modélisation

Tanguy Le Borgne

Physicien adjoint CNAP, Observatoire des sciences de l'univers de Rennes



Contents

1	Préambule	1
2	Forewords	1
3	Résumé	1
3.1	Activités scientifiques	1
3.1.1	Introduction	1
3.1.2	Dispersion et mélange dans les milieux poreux	2
3.1.3	Cinétique effective des reactions chimiques sous écoulement	3
3.1.4	Imagerie in situ des écoulements et de processus de transport	4
3.1.5	Coordination du service national d'observation H+	5
3.1.6	Conclusion	5
3.2	Questions de recherche et perspectives d'évolution	6
3.2.1	Introduction	6
3.2.2	Défis scientifiques	7
3.2.3	Conclusion	8
3.3	Liens établis avec des partenaires industriels	8
3.3.1	ADEME: remédiation des sites et sols contaminés	8
3.3.2	Antea group: Processus de colmatage microbiologique des systèmes géothermiques	9
3.3.3	TOTAL: Récupération assistée du pétrole	9
4	Scientific activity 2004-2014	10
4.1	Context	10
4.2	Upscaling dispersion processes	11
4.2.1	Linking Non-Fickian transport to velocity distribution and correlation	12
4.2.2	Field evidence of the role of velocity correlation in Non-Fickian dispersion processes	13
4.3	Mixing	16
4.3.1	The difference between spreading and mixing in heterogeneous porous media	16
4.3.2	The link between mixing and chemical reactions	16
4.3.3	The lamellar representation of mixing	18
4.4	Reaction kinetics	26
4.4.1	The impact of mixing on effective reactivity	26
4.4.2	The reactive lamella model	27
4.4.3	Imaging and modeling reactive front dynamics	30
4.4.4	In situ characterization of reactive transport processes	30
4.5	Hydrogeophysical imaging of flow structures and transport processes	32
4.5.1	Context	33
4.5.2	Inversing in situ flow measurements for fracture hydraulic properties and connectivity	34
4.5.3	Thermal imaging of fractured media with distributed temperature sensing fibre optic	36
4.5.4	Radar imaging of transport in fractured media	37
4.5.5	Large scale signature of flow heterogeneity	38
4.6	Conclusions	38
5	Scientific challenges and perspectives	40
5.1	Context	40
5.2	A paradigm shift from dispersion to mixing	41
5.3	Major open scientific questions and key experimental challenges	42
5.4	Methodology that will be developed in the ERC project ReactiveFronts	44

5.4.1	The reactive lamella approach for upscaling the impact flow dynamics on chemical reactions in porous media	44
5.4.2	Millimicro fluidics to open a new window on micro-scale flow-mixing-reaction interactions	45
5.4.3	Uncovering the coupling of fluid dynamics and biological activity in porous media flows	46
5.4.4	3D flow topologies and the role of chaotic mixing in reactivity enhancement . .	46
5.4.5	In situ imaging of fluid mixing and biochemical processes	47
5.5	Perspective in field experimentation: the ENIGMA network proposal	49
5.6	Conclusions	49
6	Curriculum Vitae	50
6.1	Identification	50
6.1.1	Etat civil	50
6.1.2	Cursus académique	50
6.1.3	Carrière professionnelle	50
6.2	Projets de recherche financés	50
6.3	Organisation de conférences (école d'été et sessions dans des conférences internationales)	51
6.4	Conférences invitées	52
6.5	Séminaires invités	52
6.6	Lien avec la formation à la recherche, capacité d'encadrement et prise de responsabilités collectives	53
6.7	Liste complète de publications	54
	Bibliography	57

1 Préambule

Ce manuscrit d'HDR synthétise les travaux de recherche que j'ai menés durant les dix dernières années au sein de l'équipe d'hydrogéologie de Rennes. Ces derniers sont le résultat d'un travail collectif en interaction avec les thésards, les ingénieurs et les chercheurs de Rennes. Ils ont également bénéficié de collaborations étroites avec un certain nombre de chercheurs en Europe et aux Etats Unis. Le manuscrit est organisé de la façon suivante: la première partie est un résumé en français de l'ensemble du dossier, incluant une brève description de mes activités de recherche, des questions de recherche que je souhaite aborder dans les prochaines années et des liens établis avec les partenaires industriels. Dans les parties suivantes ces éléments sont repris et détaillés en anglais. Un CV complet en français conclut le dossier.

2 Forewords

This HDR manuscript synthesizes the work that I have been developing during the last ten years within the Rennes hydrogeology group. These investigations are the result of a collective work in close interaction with the PhD students, engineers and researchers in Rennes. They have also benefited from close collaborations with a number of researchers in Europe and the United States. The manuscript is organized as follows: the first section is a summary in French of the whole document, including a brief description of my research activities, of the research issues that I propose to address in the next years and of the links established with industrial partners. In the following parts these elements are detailed in English. A complete CV in French concludes the manuscript.

3 Résumé

3.1 Activités scientifiques

3.1.1 Introduction

Mes activités de recherche portent sur la caractérisation et la modélisation des transferts de fluide et d'éléments en solution dans les milieux poreux et fracturés, avec des applications pour la gestion des ressources en eau et énergie dans les environnements de subsurface. J'associe pour cela des approches de modélisation et d'expérimentation en laboratoire et sur le terrain. La modélisation a pour but de comprendre et quantifier les interactions entre structure du milieu, écoulements et phénomènes de transport inerte et réactif. **Il s'agit d'aboutir à une réduction de la complexité suffisante pour pouvoir effectuer des prédictions sur l'évolution des systèmes, tout en conservant les lois émergent de l'hétérogénéité du milieu à différentes échelles.** Les expériences de laboratoire permettent d'isoler certains processus dans des milieux poreux simplifiés dans des conditions très bien contrôlées. Elles guident ainsi la réflexion pour le développement de modèles pertinents. Enfin, l'expérimentation sur le terrain est une étape indispensable pour la validation des modèles dans des conditions réelles. Les phénomènes observés au cours de ces expériences nourrissent également les questions théoriques, conduisant ainsi à de nouveaux champs de recherche. Alors que ces approches sont souvent développées séparément, j'ai pu coupler ces différentes méthodes au cours des dix dernières années, grâce à des collaborations internationales établies sur le long terme, et à des conditions très favorables offertes au sein de l'équipe d'hydrogéologie de Géosciences Rennes et de l'Observatoire des Sciences de l'Univers de Rennes.

Après mon doctorat, focalisé sur la caractérisation expérimentale et la modélisation des écoulements dans les milieux poreux hétérogènes et fracturés, je me suis orienté vers l'étude de l'impact de ces distributions de vitesses sur les processus de transport d'éléments en solution (ex : contaminants) avec des approches expérimentales (post-doctorat à l'université de Montpellier 2) et théoriques (post-doctorat à l'université polytechnique de Catalogne). Suite à mon recrutement en tant que Physicien adjoint

du CNAP à l'Observatoire des Sciences de l'Univers de Rennes, j'ai initié une nouvelle thématique de recherche portant sur l'étude des processus de mélange des éléments en solution, qui constitue un mécanisme fondamental de contrôle des réactions chimiques dans les milieux poreux. Dans le cadre de mes activités d'observation de physicien adjoint, attaché au service d'observation H+ (réseau national des sites de recherche en hydrogéologie hplus.ore.fr), j'ai développé de nouvelles méthodes expérimentales ayant pour objectif d'imager l'organisation spatiale des structures d'écoulement et de quantifier les processus de transport in situ, permettant de valider les modèles développés sur le terrain. Ces différentes activités scientifiques sont détaillées dans cette partie.

3.1.2 Dispersion et mélange dans les milieux poreux

L'étude des processus de transport dans les milieux poreux vise à caractériser et modéliser la distribution spatiale et la dynamique temporelle des concentrations en éléments dissous transportés par les écoulements souterrains. Les processus de dispersion, mélange et réaction associés contrôlent la qualité des eaux souterraines, exploitées en tant que ressource en eau, ainsi que les flux géochimiques dans le cycle hydrologique. Ils sont fortement déterminés par l'hétérogénéité des structures au sein desquelles s'organise les écoulements : arrangement des grains et géométrie des réseaux de pores à petite échelle, alternance des lithologies, fracturation et distributions de perméabilités à plus grande échelle. **La question du changement d'échelle est donc centrale pour relier les propriétés des milieux aux lois de transport effectives.** Cette question est relativement bien résolue dans le cadre des approches dites macrodispersives, où l'équation de transport effective est supposée suivre une loi diffusive simple intégrant l'effet de l'hétérogénéité via un coefficient de dispersion effectif. Cependant, de nombreuses observations ont mis en évidence deux éléments majeurs en contradiction directe avec cette hypothèse (e.g. Dentz et al., 2011): **i) le transport non-Fickien:** les distributions de concentration sont en générales non-Gaussiennes du fait de la très forte hétérogénéité des champs de vitesses les déterminant, **ii) le mélange incomplet:** alors que les théories dispersives s'attachent à prédire la concentration moyenne sur un volume représentatif, l'hétérogénéité du milieu implique que les échelles caractéristiques de variation des concentrations peuvent être bien inférieures. Ainsi, la modélisation des taux de réaction effectifs, qui dépendent de manière non linéaire des concentrations, nécessite de prendre en compte la distribution complète de concentration, la moyenne étant insuffisante.

Suite à mes travaux de thèse, essentiellement focalisés sur la caractérisation expérimentale et la modélisation des distributions de vitesses dans les milieux poreux et fracturés, j'ai orienté mes recherches vers l'étude des processus de dispersion qui consistent l'une des conséquences les plus remarquable de l'hétérogénéité des vitesses. Lors de mon postdoctorat au laboratoire de Géosciences de Montpellier, j'ai développé des méthodes de mesure expérimentales des propriétés de transport in situ par traçages artificiels. Ces mesures ont notamment apporté de nouveaux éléments sur l'origine du transport non-Fickien dans les milieux hétérogènes (Gouze et al., 2008a,b; Le Borgne and Gouze, 2007). Suite à ces observations, j'ai initié une collaboration avec M. Dentz et J. Carrera, de l'université polytechnique de Catalogne à Barcelone, sur le lien entre l'hétérogénéité des champs de vitesse et les modèles de dispersion effectifs non-Fickiens. Cette collaboration a fait l'objet d'une bourse postdoctorale Marie Curie. Nous avons développé un nouveau cadre théorique, appelé correlated CTRW (Continuous Time Random Walk), qui étend le cadre des modèles CTRW pour quantifier l'impact de la corrélation spatiale des champs de vitesse sur la dispersion anormale (Le Borgne et al., 2008a,b). Ces résultats ont motivé de nouvelles collaborations avec des laboratoires américains (MIT, Pacific Northwest National Lab, Notre Dame University) à travers lesquelles nous avons démontré la validité de ce modèle théorique pour modéliser le transport dans des réseaux de fractures (Kang et al., 2015) et à l'échelle du pore (Le Borgne et al., 2011a; de Anna et al., 2013; Bolster et al., 2014).

Ces travaux, essentiellement issus de mes recherches post-doctorales, ont permis de faire évoluer les modèles de transport non-Fickien depuis des approches essentiellement phénoménologiques vers des modèles directement issus des propriétés des champs de vitesses. Cependant, ils n'ont pas répondu directement à **la question de la modélisation du mélange incomplet et de son impact sur**

les cinétiques de réaction. J'ai abordé cette question lors mon recrutement à l'université de Rennes 1 en 2007, en collaboration avec l'équipe de Rennes et un certain nombre de collaborateurs étrangers. Nous avons en particulier montré l'effet de l'hétérogénéité des écoulements sur le mélange effectif (Le Borgne et al., 2010, 2011b; de Dreuzy et al., 2012). Depuis 2011, j'ai débuté une nouvelle collaboration avec Emmanuel Villermaux (IRPHE Marseille) qui a permis des avancées significatives dans l'objectif d'établir une théorie du mélange dans les milieux poreux en montrant l'équivalence entre le mélange dans les écoulements turbulents et dans les milieux poreux (Le Borgne et al., 2013, 2015). Ce nouveau cadre théorique quantifie le couplage entre l'hétérogénéité des champs de vitesse et l'évolution des champs de concentration. Cette représentation, dite lamellaire, permet de prendre en compte en particulier l'accélération du mélange diffusif par la déformation des volumes élémentaires de fluide sous l'effet des gradients de vitesse.

Ces travaux ouvrent un nouveau champ de recherche pour **l'étude de la dynamique de déformation fluide dans les milieux poreux hétérogènes et ses conséquences sur le mélange**, un domaine relativement inexploré jusqu'à présent. Ils se poursuivent actuellement dans le cadre de la thèse de Régis Turuban (2012-2015), que je co-encadre avec Yves Méheust, et en collaboration avec Daniel Lester (RMIT Melbourne, Australie). L'enjeu est en particulier de cerner les conditions d'apparition de mélanges chaotiques, impliquant une déformation exponentielle des volumes de fluide, suggérés par Lester et al. (2013). Si cette prédiction théorique s'avérait vérifiée par l'expérience, cela constituerait un résultat majeur de la discipline. L'une des raisons pour laquelle ce résultat important aurait échappé jusqu'à présent aux observations, est que l'essentiel des expériences est réalisé en deux dimensions. Depuis peu, des technologies émergentes offrent de nouvelles perspectives pour la réalisation d'expériences en trois dimensions, avec, en particulier, le développement récent des technologies d'impression 3D. A partir de cette technique, nous proposons de construire un dispositif expérimental unique à l'échelle internationale, pour l'étude du mélange dans les milieux poreux tri-dimensionnels (figure 30).

Enfin, dans le cadre de la chaire internationale de la fondation Rennes 1 obtenue par Joaquin Jimenez (2012-2014), nous avons initié en 2011 un programme de recherche sur **l'étude expérimentale du mélange dans les écoulements non saturés**. La zone insaturée se situe entre la surface du sol et les nappes phréatiques est une interface où coexistent l'air et l'eau sur des épaisseurs pouvant atteindre plusieurs dizaines de mètres. Elle joue un rôle fondamental dans le transport des matières dissoutes dans le cycle hydrologique. La question de l'impact de la saturation (en eau) incomplète du milieu sur le transport des solutés est actuellement totalement ouverte. Dans la zone insaturée, les chemins d'écoulements de l'eau sont distribués de manière très hétérogène, et suivent des chenaux séparés par des clusters d'air (figure 26). Le transport de solutés est assuré par la phase aqueuse, et est donc fortement contraint par la distribution des deux phases (eau et air) dans le milieu. Nous avons développé un dispositif expérimental original permettant de visualiser la distribution des deux phases (eau et air) dans le milieu et quantifier son contrôle sur la dispersion et le mélange des solutés (figure 26).

3.1.3 Cinétique effective des réactions chimiques sous écoulement

La cinétique effective des réactions chimiques est directement liée à la distribution des concentrations dans le milieu, et donc aux propriétés de mélange évoquées dans le paragraphe précédent. Nous avons initié cette thématique à Rennes avec la thèse de Pietro de Anna (2009-2012). Après une étude théorique qui a permis de quantifier l'impact du mélange incomplet sur les cinétiques de réaction (de Anna P. et al., 2011; de Anna et al., 2014a), nous avons mis en place un dispositif expérimental basé sur les réactions chimioluminescentes, permettant une imagerie haute résolution des concentrations et des cinétiques de réaction en deux dimension (de Anna et al., 2014b). Ce dispositif, réalisé en collaboration avec Yves Méheust (Géosciences Rennes) et Hervé Tabuteau (Institut de Physique de Rennes), nous permettra dans les prochaines années d'**explorer la cinétique des fronts de réaction dans différentes conditions d'écoulement et pour différents types d'hétérogénéités**. Ces travaux

expérimentaux se poursuivent en collaboration avec Pietro de Anna (actuellement en postdoctorat au MIT, USA).

Le couplage de l'approche lamellaire pour modélisation du mélange avec la réactivité chimique (Le Borgne et al., 2014) apparaît particulièrement prometteur pour établir une théorie de mélange réactif dans les milieux poreux prenant en compte la distribution complète des concentrations et sa dynamique temporelle dans les champs de vitesse hétérogènes. Cette idée sera explorée dans le cadre du projet ERC ReactiveFronts (2015-2020) avec des approches expérimentales de laboratoire et de terrain, en lien avec les développements théoriques.

3.1.4 Imagerie in situ des écoulements et de processus de transport

Dans le cadre de mes activités d'observation en tant que physicien adjoint du CNAP, je m'attache à obtenir des données in situ permettant d'apporter de nouvelles contraintes sur les distributions de vitesse d'écoulement et sur les processus de transport associés. Cette démarche expérimentale de terrain est essentielle pour valider les modèles développés à partir des concepts théoriques et des observations en laboratoire. Les sites expérimentaux du service national d'observation H+ (hplus.ore.fr) représentent des infrastructures uniques pour tester de nouvelles approches expérimentales en bénéficiant des connaissances accumulées sur les sites depuis plus de dix ans.

Pour développer ces expériences in situ, je travaille en collaboration étroite avec Olivier Bour, responsable du site expérimental de Ploemeur (H+). Nous avons également développé des collaborations avec N. Linde (Université de Lausanne), V. Bense (University of East Anglia) et J. Selker (Oregon State University). J'ai co-encadré les thèses de Maria Klepikova (Université de Rennes 1, actuellement en postdoctorat à l'ETH Zurich), Nicolas Guiheneuf (Université de Rennes 1, actuellement ATER) et Caroline Dorn (Université de Lausanne, actuellement en postdoctorat à l'université de Bern) sur ce sujet. Je co-encadre actuellement la thèse de Olivier Bochet et Jerome Bondet de la Bernardie (Université de Rennes 1) sur cette thématique. Nous avons en particulier développé de nouvelles méthodes d'inversion conjointe de différentes données hydrologiques (ex: traçages, mesure distribuée de température) et géophysiques (radar). Les campagnes expérimentales ont lieu principalement sur le site de Ploemeur (réseau H+), impliquant chaque année des chercheurs étrangers.

Traçage thermique des flux souterrains : les écoulements souterrains induisent des anomalies thermiques (en référence au gradient géothermique moyen) mesurables sur le terrain. Ainsi, durant la thèse de Maria Klepikova nous avons démontré la possibilité d'inverser les mesures de température en forage, par une approche tomographique sous différentes sollicitations hydrauliques, pour estimer les distributions d'écoulement (Klepikova et al., 2011) et caractériser la connectivité des fractures entre forages (Klepikova et al., 2013). Cette approche est d'autant plus prometteuse que de nouvelles technologies ont émergées permettant de mesurer la distribution spatiale de la température avec une haute précision. Ainsi, depuis 2006, la fibre optique est apparue comme une innovation technologique majeure en hydrologie pour suivre les variations de températures et les flux d'eau. Pour tester son potentiel en hydrogéologie, des expériences innovantes ont été réalisées en 2012 et 2013 en collaboration avec les universités d'Oregon State University (John Selker, USA) et celle d'East Anglia (T. Read et V. Bense, UK). Ces travaux ont montré tout l'intérêt de la fibre optique pour caractériser les écoulements et le transport thermiques en milieu hétérogène (Read et al. (2013, 2014)) et permettent d'envisager de nombreuses applications innovantes. Alors que cette technique avait été testée principalement en rivière auparavant nous en avons développé les premières applications pour les eaux souterraines. En nous basant sur le principe de l'anémométrie à fil chaud, nous avons pu montrer que la température de chauffe d'un câble de fibre optique dans lequel on faisait passer un courant dans l'armature métallique du câble était fonction de la vitesse du fluide. En utilisant ce principe, nous avons montré qu'il était possible de mesurer avec une excellente résolution spatiale et temporelle (respectivement 25 cm et 30s), la vitesse d'écoulement de l'eau le long d'un forage (Read et al., 2014). Les perspectives à ce travail préliminaire sont très nombreuses en hydrologie et en hydrogéologie. Afin de mieux tester les potentialités de la méthode, un banc expérimental a été réalisé. Il permet de faire circuler de l'eau

à un débit contrôlé dans un tube transparent de 5 m de long dans lequel sont installées les fibres optiques. Durant son stage de Master 2, Hugo le Lay a confirmé les résultats obtenus sur le terrain et a montré que la méthode pouvait être améliorée en assurant un meilleur contrôle du courant utilisé pour chauffer le câble de renfort de la fibre optique. .

Imagerie radar du transport dans les milieux fracturés: Malgré les innovations métrologiques pour l'instrumentation des forages, dont la fibre optique discutée dans le paragraphe précédent, notre capacité d'imagerie du milieu souterrain décroît fortement avec la distance au forage. Des progrès importants sont attendus dans ce domaine par le couplage de méthodes de monitoring géophysique (ex: profils géophysiques répétés dans le temps) avec des expériences de traçage in situ. J'ai initié une collaboration avec Niklas Linde (Université de Lausanne) et Olivier Bour pour explorer de nouvelles méthodes d'imagerie du transport dans les milieux fracturés. Les résultats obtenus dans la cadre de la thèse de Caroline Dorn (2010-2013) ont produit les premières images radar de la distribution spatiale des traceurs dans des fractures millimétriques à une centaine de mètres de profondeur. Ceci ouvre de nouvelles perspectives pour obtenir des images in situ du transport dans les réseaux de fracture (Dorn et al., 2013, 2012a,b, 2011). Ces résultats probants ont motivé le dépôt d'un nouveau projet de thèse par Niklas Linde, en collaboration avec moi-même et Olivier Bour, financé par la fondation Suisse pour la recherche (thèse Alexis Shakas 2014-2017).

3.1.5 Coordination du service national d'observation H+

En tant que Physicien adjoint du CNAP, je suis en charge, avec Philippe Davy, de la coordination du service national d'observation H+, réseau national de sites hydrogéologiques (hplus.ore.fr). Le réseau national de sites hydrogéologiques (H+) a été créé en 2002 comme Observatoire de Recherche en Environnement. Il est devenu Service National d'Observation de l'INSU en 2005, puis SOERE (Système d'Observation et d'Expérimentation au long terme pour la Recherche en Environnement) après évaluation en 2011 par l'alliance nationale de recherche pour l'environnement (ALLENVI). Le SOERE H+ international regroupe le SO H+ (sites de Ploemeur, Poitiers, Majorque et Larzac), ainsi que 4 sites pilotés par des partenaires français et européens (Hyderabad, Laboratoire Souterrain à Bas Bruit, Krauthausen et Llobregat). Ces sites sont instrumentés pour permettre la réalisation d'expériences de longue durée et/ou pour documenter les constantes de temps des évolutions du milieu. Ils sont tous potentiellement des références internationales en termes d'expérimentation hydrogéologiques. Le budget global du réseau est de 500 k€ par an en moyenne. 70 chercheurs, ingénieurs et techniciens interviennent pour le suivi des sites, l'expérimentation, l'exploitation et la mise à disposition des données. Dans le cadre de mes tâches de service, je prend en charge les tâches reliées au fonctionnement global de l'observatoire en tant que réseau de sites hydrogéologiques, d'instruments de mesure et d'équipes de recherche. Celles-ci comprennent notamment la coordination des expériences impliquant différentes équipes, la mise en commun des outils et des compétences, la coordination de la base de données et l'organisation des rencontres H+ (environ deux par an). J'assure également la gestion administrative du service d'observation: la diffusion de l'information au sein du réseau et vis-à-vis de la communauté scientifique (mise en ligne des informations et diffusion des données), la supervision (webmaster) du site web, la gestion des crédits et la rédaction des rapports scientifiques et projets visant à faire évoluer le service d'observation. De ce point de vue, l'année 2011 a été marquée par une évolution importante du réseau, par l'agrégation d'équipes françaises et européennes dans le cadre du SOERE H+ international et par le rapprochement avec le réseau de bassins versant RBV, avec la rédaction conjointe du projet d'équipex CRITEX ("Parc national d'équipements innovants pour l'étude spatiale et temporelle de la Zone Critique des Bassins Versants").

3.1.6 Conclusion

Les recherches expérimentales et théoriques que je mène depuis une dizaine d'années ont ouvert de nouvelles perspectives, notamment pour l'exploration et la quantification des processus de mélange

réactifs dans les milieux poreux, qui jouent un rôle fondamental dans le contrôle des transformations biogéochimiques affectant les systèmes hydrologiques, et des applications sociétales et industrielles de première importance, telles que la gestion des ressources en eau, la dépollution des sols et aquifères, l'exploitation des ressources énergétiques souterraines (pétrole, gaz, géothermie), le stockage souterrain des déchets, et la séquestration du CO_2 . De grandes avancées expérimentales et théoriques sont attendues dans les prochaines années dans le cadre du projet ERC ReactiveFronts qui permettra de recruter trois doctorants et deux postdoctorants, dont je souhaite diriger les recherches en tant qu'encadrant principal.

3.2 Questions de recherche et perspectives d'évolution

3.2.1 Introduction

Dans les prochaines années, je souhaite faire évoluer mes recherches vers la caractérisation expérimentale et la modélisation des processus de mélange réactifs dans les milieux hétérogènes, qui représente la thématique centrale du projet ERC ReactiveFronts. Le mélange des éléments chimiques et des nutriments dans les milieux souterrains (sols, lits de rivière, eau souterraine) est un processus fondamental pour le transport des éléments chimiques et des contaminants dans les environnements continentaux. Dans ces milieux, l'activité biochimique est souvent localisée dans des zones de mélange, appelées "hotspots", telles que l'interface entre les eaux souterraines et les eaux de surface. Ces zones de mélange sont généralement caractérisées par une dynamique complexe des écoulements, une saturation en eau potentiellement variable, des conditions redox fluctuantes et des communautés biologiques multifonctionnelles. **Bien que des progrès importants aient été obtenus dans la caractérisation et la modélisation des processus de transport dans les milieux souterrains, leur couplage avec les réactions biochimiques reste une question largement ouverte.** En particulier, la forte variabilité spatiale des vitesses d'écoulement dans ces milieux induit des fluctuations spatiales significatives des concentrations en soluté, avec pour conséquence une dépendance d'échelle attendue, mais actuellement inconnue, des cinétiques de réaction effectives. En conséquence, les prédictions effectuées à partir de mesures de laboratoire en batch bien mélangés, peuvent différer par des ordres de grandeur des observations sur le terrain. Mon objectif dans les prochaines années est de développer et valider un cadre de modélisation du transport réactif dans les milieux souterrains, intégrant la variabilité spatiale des écoulements et des concentrations via de nouveaux concepts de représentation du mélange des fluides dans les milieux poreux.

Ce programme scientifique fait l'objet d'un projet ANR jeune chercheur (accepté, 2015-2019) et un projet ERC plus ambitieux (accepté, 2015-2020). Il se décline globalement en trois objectifs. Le premier objectif vise à étendre le cadre théorique de modélisation du mélange des éléments conservatifs dissous dans les milieux poreux, que j'ai récemment proposé (Le Borgne et al., 2013, 2015), à la modélisation des processus réactifs résultant du mélange. L'originalité de l'approche, issue des théories de mélange dans les écoulements turbulents, est de quantifier le couplage entre déformation fluide, transfert de masse diffusif, et réactions chimiques, contrôlant les taux de réaction effectifs dans les fronts de mélange complexes. Le second objectif est de mettre en place des dispositifs expérimentaux milli et micro-fluidiques innovants en vue d'imager la distribution spatiale complète des concentrations et des taux de réaction à l'échelle élémentaire du pore. Cette étape de validation des modèles en conditions de laboratoire bien contrôlées est indispensable avant l'application à l'échelle de terrain, par essence beaucoup plus complexe. L'étape de validation in situ, qui constitue le troisième objectif, sera entreprise en tirant profit des synergies avec des projets en cours au sein de l'équipe d'hydrogéologie de Rennes (thèse ADEME, ANR stock-en-socle), et en s'appuyant sur les infrastructures expérimentales nationales (observatoire H+, equipex CRITEX), qui fourniront des premières données expérimentales quantitatives permettant d'étudier les taux de réaction in situ dans différentes conditions d'écoulement et d'étudier les effets d'échelles sur les taux de réaction effectifs.

3.2.2 Défis scientifiques

1. Modélisation de l'impact de la dynamique des fluides sur les cinétiques de réaction dans les milieux poreux: Bien que l'importance de la déformation des interfaces de mélange pour le contrôle des réactions chimiques soient bien reconnues dans les contextes d'écoulements turbulents et chaotiques (Ranz, 1979; Ottino, 1989; Tel et al., 2005), ce couplage demeure largement inexploré dans le cadre des milieux poreux. L'une des raisons pour cela est la difficulté liée à l'observation des fluides réactifs dans ces systèmes opaques. La figure 26 illustre une expérience bidimensionnelle de front de mélange dans un milieu poreux (Jimenez-Martinez et al., under review). Le front de mélange, initialement orienté perpendiculairement à la direction principale d'écoulement, est déformé pour former une topologie lamellaire (Ottino, 1989). Ce processus de déformation, généré par l'hétérogénéité spatiale des vitesses, augmente fortement le transfert de masse diffusive à travers l'interface, et donc la réactivité effective. La même expérience effectuée en conditions non saturées montre la formation de structures de mélange complexes liées à l'existence de chemins préférentiels d'écoulement et de zones de stagnation se développant autour des clusters d'air. Ceci met en évidence le contrôle des processus de mélange par l'hétérogénéité du champ de vitesse. La représentation lamellaire du mélange dans les milieux poreux, que j'ai récemment proposée en collaboration avec Emmanuel Villermaux et Marco Dentz (Le Borgne et al., 2013) offre de nouvelle perspective pour quantifier cette interaction et son impact sur les cinétiques de réaction effective. Dans une étude préliminaire (Le Borgne et al., 2014) nous avons montré par cette approche que les cinétiques globales de réaction peuvent varier sur des ordres de grandeur en fonction de la topologie des écoulements (figure 14).

2. Imagerie millifluidique et microfluidique des écoulement, du mélange et des cinétiques de réaction biochimiques: Une difficulté intrinsèque aux milieux poreux est l'accès limité à l'imagerie de la distribution spatiale des écoulements, des champs de concentration, des interfaces réactives et des interactions avec les micro-organismes. Les expériences traditionnelles sont faites dans des colonnes ou les concentrations des éléments réactifs peuvent être mesurées uniquement à la sortie du système ou en quelques points. Les méthodes expérimentales émergentes, basées sur des dispositifs micro et milli fluidique, changent profondément notre vision des couplages entre écoulements et réaction à l'échelle du pore (Willingham et al., 2008; Rolle et al., 2009; de Anna et al., 2014b). Dans une publication parue en 2013 dans la revue *Physical Review Letters*, des collègues Australiens, avec lesquels nous avons récemment initié une collaboration, ont formulé une hypothèse remettant en cause les fondements des modèles conceptuels de transport dans les milieux souterrains (Lester et al., 2013). A partir d'une représentation théorique simplifiée, ils ont fait état de propriétés chaotiques des processus de mélange dans les sols et les roches, lié à la topologie tridimensionnelle des chemins d'écoulement dans ces milieux. Si leurs prédictions théoriques s'avéraient vérifiées par l'expérience, cela constituerait un résultat majeur de la discipline. Quelques groupes ont développé récemment des expériences tridimensionnelles pour étudier la distribution des vitesses d'écoulement à l'échelle du pore (Moroni and Cushman, 2008) ou la distribution spatiale des biofilms par microscopie confocale ou micro-tomographie (Itis, 2011). Cependant, il existe très peu d'études expérimentales sur l'imagerie des champs de concentration en trois dimensions. Le dispositif d'imagerie 3D récemment mis en place dans le cadre de la thèse de Regis Turuban offre de nouvelles perspectives pour l'exploration des processus de mélange et de réaction en 3D. De plus, je souhaite étendre ce dispositif pour créer un laboratoire de bio-microfluidique permettant d'étudier le rôle des micro-organismes dans la réactivité et le couplage entre la formation des biofilm et l'organisation spatiale des écoulements, en collaboration avec Alexis Dufresne et Yvan Lagadeuc (ECOBIO). Ceci fait l'objet du projet CNRS de Pietro de Anna, déposé en Janvier 2015 pour une candidature à Géosciences Rennes.

3. Caractérisation des processus de transport réactif in situ : La prise en compte des processus de mélange et dispersion dans la prédiction des réactions biogéochimiques constitue un défi scientifique majeur qui a reçu une attention accrue ces dernières années. Il est en particulier reconnu que les prédictions faite classiquement à partir de cinétiques réactionnels mesurées en batch de laboratoire peuvent difficilement être extrapolées sur le terrain du fait de l'hétérogénéité des écoulements et

de la réactivité. Le réseau H+, que je coordonne, a les moyens d'apporter des données potentiellement décisives dans ce débat. Dans le cadre d'un Work Package que je pilote au sein du projet equipex CRITEX ("Parc national d'équipements innovants pour l'étude spatiale et temporelle de la Zone Critique des Bassins Versants"), un laboratoire mobile a été développé pour suivre sur le terrain l'évolution des concentrations chimiques, y compris les gaz dissous, et l'activité microbiologique lors d'expériences de traçages réactifs. Cet équipement vient d'être terminé et a été testé sur le terrain pour la première fois en Juin 2014. Il sera déployé à partir de 2015 dans le cadre de différentes campagnes menées sur les sites H+ et RBV (Réseau des Bassins Versants).

3.2.3 Conclusion

Mon programme de recherche pour les prochaines années vise ainsi à promouvoir le développement d'une nouvelle activité de recherche au sein de l'OSUR pour la caractérisation expérimentale et la dynamique des fronts de mélange réactifs (projet ERC ReactiveFronts). Ce projet s'appuiera sur des collaborations interdisciplinaires à l'échelle nationale (Géosciences Rennes, ECOBIO, IPR, IRPHE Marseille), ainsi que sur des collaborations internationales bien établies (CSIC Barcelona) et naissantes (UC Davis, CSIRO Melbourne) avec les groupes leaders dans ce domaine.

3.3 Liens établis avec des partenaires industriels

Le développement de liens avec les industriels est important pour transférer les progrès effectués en modélisation et les innovations expérimentales vers les applications. Ces liens permettent aussi d'analyser des jeux de données uniques qui ne seraient pas accessibles dans un cadre purement académique (ex: pilotes d'installation géothermiques). Ils nourrissent également les questionnements scientifiques en mettant en évidence des problèmes fondamentaux non résolus.

3.3.1 ADEME: remédiation des sites et sols contaminés

L'une des méthodes de remédiation in situ consiste à injecter un fluide dans un milieu naturel pour fixer un contaminant afin de le rendre moins nocif ou de le neutraliser. Les réactions biochimiques se passent dans ce cas à l'interface entre le fluide injecté et le contaminant. Le fluide peut contenir un agent oxydant ou réducteur susceptible de dégrader les contaminants, ou un biostimulant (i.e. des nutriments) favorisant l'activité bactérienne. Une thèse a été co-financée par l'ADEME (Agence de l'Environnement et de la Maîtrise de l'Energie) sur thématique (Olivier Bochet, 2014-2017, co-directeurs Tanguy Le Borgne, Luc Aquilina).

Les réactions chimiques entrant en jeu dans l'évolution chimique et biologique des eaux souterraines, ainsi que dans l'atténuation naturelle des sites contaminés ou les méthodes de remédiation, sont très variées (oxydo-réduction, adsorption, précipitation, dissolution). Dans le cadre de cette thèse des réactions spécifiques sont choisies pour quantifier l'effet de l'hétérogénéité sur les cinétiques de réaction. Nous étudions en particulier des réactions mettant en jeu une activité bactérienne, telle que la dénitrification. Il s'agit d'étudier de manière systématique l'influence des conditions d'écoulement, des volumes investigués, des temps de résidence et de la variabilité spatiale sur les cinétiques mesurées. Les expériences sont complétées par des mesures en batch au laboratoire. Les résultats des traçages réactifs seront modélisés à l'aide du logiciel COMSOL multiphysics, qui permet le couplage de la simulation des écoulements avec le calcul de la spéciation des espèces chimiques. L'objectif sera de mettre en évidence l'intérêt du développement technologique proposé (contrôle précis de l'injection, capteurs chimiques in situ, et suivi en continu des concentrations des réactifs et produits) pour améliorer les investigations sur site, améliorer la représentativité des mesures de contamination des sols, mieux prédire le devenir des polluants dans les eaux souterraines et optimiser les procédés de traitement in situ. La méthodologie mise en place durant la thèse sera, à terme, étendue à différentes réactions chimiques intervenant dans l'atténuation naturelle et la remédiation des contaminants.

3.3.2 Antea group: Processus de colmatage microbiologique des systèmes géothermiques

Une autre application intéressante se situe dans le domaine énergétique : on constate que 30% des doublets en géothermie peu profonde (< 300 mètres) sont affectés par des problèmes de colmatages physiques (transport de particules) ou biologiques (biofilms). Le développement dommageable de ces biofilms est un problème bien connu : en injectant de l'eau froide (oxygénée) dans le sous-sol pour qu'elle se mélange avec des eaux chaudes, plus minéralisées, on crée à l'interface entre ces deux masses d'eau les conditions d'un développement microbiologique conduisant à la formation de biofilms. Ces processus de colmatage impliquent des interactions complexes entre les écoulements d'eau souterraine, les réactions chimiques et l'activité biologique. Un projet sur cette thématique, en collaboration avec antea group, un bureau d'étude international dans le domaine de l'eau et de l'environnement, a été financé par l'ADEME en 2015. Une bourse CIFRE en collaboration entre antea group et l'université de Rennes a été également déposée cette année pour financer un doctorant qui travaillera sur cette thématique.

Les objectifs du projet sont : 1) L'étude des processus bio-géochimiques et physiques impliqués dans les processus de colmatage et leur couplage avec les écoulements induits par la mise en place d'un doublet géothermique. Le but est de mettre au point un outil prédictif fiable permettant d'évaluer sur la base d'une approche multicritère validée par un suivi in situ le risque de colmatage des puits dans le cadre d'installations de pompes à chaleur sur nappes. 2) La mise en place de sites pilotes pour tester et suivre dans le temps l'efficacité des traitements curatifs et préventifs, l'analyse de leur impact environnemental et de leur viabilité sur les plans techniques et économiques en regard des problématiques rencontrées. 3) La synthèse des résultats scientifiques et techniques obtenus pour l'élaboration d'un guide d'aide à la décision visant, à partir de l'évaluation des risques encourus et des solutions de traitements curatifs ou préventifs envisageables à juger de la faisabilité du projet sur les plans techniques ou économiques en respectant les contraintes environnementales.

3.3.3 TOTAL: Récupération assistée du pétrole

La récupération assistée du pétrole (EOR: enhanced oil recovery) permet d'améliorer le taux de récupération du pétrole, c'est-à-dire d'extraire du réservoir une fraction plus importante du pétrole initialement présent. L'optimisation des méthodes de récupération du pétrole représente un enjeu considérable car le taux de récupération des méthodes classiques est relativement faible : 30% en moyenne et seulement de 3 à 10% pour le pétrole lourd. Différentes stratégies sont employées en EOR pour améliorer le rendement du processus. Dans le cas des pétroles lourds en particulier, on utilise des polymères pour réduire le rapport de mobilité, initialement très défavorable au déplacement. Une autre approche consiste à réduire la tension superficielle entre le pétrole et le fluide injecté par utilisation de solutions alcalines. Les alcalins réagissent sur des acides gras naturels du pétrole, ce qui génère in situ des surfactants qui abaissent la tension de surface entre les deux liquides, d'un rapport pouvant atteindre quelques ordres de grandeur. Ce processus provoque une émulsification, soit du pétrole dans l'eau, soit de l'eau dans le pétrole, selon la concentration en alcalin. Dans le cas de pétroles lourds, en particulier, une concentration importante en alcalin permet l'émulsification de l'eau dans le pétrole, ce qui peut grandement améliorer l'efficacité du déplacement du pétrole par la solution, par blocage des zones de grande perméabilité dans le milieu. Par contre, une concentration faible en alcalin conduit généralement à la formation d'une émulsion de pétrole dans l'eau, dont la mobilité est bien supérieure à celle de la phase pétrole initiale. L'efficacité de la technique dépend ainsi de l'évolution spatiale et temporelle des concentrations en ions alcalins dans le milieu. Cette évolution est contrôlée par la dispersion et le mélange de la solution injectée dans la phase fluide concernée, qui est soumise à un écoulement diphasique avec le pétrole. La caractérisation et la modélisation d'un tel processus de transport(-réaction) constitue actuellement un défi scientifique majeur, avec des applications potentielles dans l'EOR, l'extraction du gaz, le stockage de CO_2 , la remédiation des sites contaminés ou encore les processus de transport dans la zone non saturée.

Un stage de master 2 (co-encadré par Yves Méheust et Tanguy Le Borgne), potentiellement suivi

d'une thèse, a été financé en 2015 par TOTAL pour étudier ces processus grâce à un dispositif expérimental permettant d'imager la distribution spatiale des concentrations de traceurs transportés par des fluides dans des milieux poreux. Ce dispositif offre une vision nouvelle des processus de transport dans ces milieux, ouvrant des perspectives pour la modélisation prédictive de l'évolution temporelle et spatiale des concentrations et ses conséquences sur la réactivité des fluides. Le dispositif bidimensionnel permet de faire s'écouler deux fluides (liquides ou gaz) dans un milieu poreux transparent constitué de grains cylindriques disposés dans une cellule de Hele-Shaw, et d'enregistrer à intervalles de temps réguliers la géométrie des phases liquides dans le milieu, la différence de pression entre l'entrée et la sortie du milieu, mais également le champ de concentration d'un soluté présent dans l'une des phases. Nous préparerons une géométrie dans laquelle des amas de liquide non-mouillant (le pétrole) seront entourés de liquide mouillant (le fluide aqueux), et nous injecterons ce même fluide chargé en alcalins (de la soude NaOH, par exemple). Nous étudierons comment la distribution spatiale des concentrations en ions alcalins impacte l'émulsification du pétrole et sa mobilisation. Pour ce faire de la fluorescéine sera injectée en même temps que la solution alcaline; leurs coefficients de diffusion moléculaire étant identiques, on s'attend à ce que l'évolution temporelle de leurs champs de concentration le soient également. Nous rechercherons ainsi la concentration en alcalin, le volume injecté et la vitesse d'injection optimaux, et nous examinerons différentes géométries et protocoles d'injection afin de déterminer la configuration la plus efficace.

4 Scientific activity 2004-2014

In this part and the following my past research activities and perspectives, summarized in the first section in French, are detailed in English.

4.1 Context

While the surface components of continental waters, such as streams, lakes and glaciers, are a very familiar part of our landscapes, the vast majority of continental water resources resides and flows in the subsurface, and is thus broadly inaccessible to direct observation. The growing societal needs for freshwater, energy and waste management imply that subsurface environments are increasingly subject to multiple (possibly competing) uses of water resources (e.g. groundwater abstraction, artificial recharge, contamination) and energy (e.g. geothermal energy, CO_2 sequestration, oil and gas extraction) while being endangered by anthropogenic contamination. In some parts of the world, subsurface hydrological systems are experiencing profound modifications, such as large-scale groundwater level depletion in response to increasing water consumption and massive CO_2 injection or fracking activities in enhanced geothermal systems and shale gas exploration, with debated effects on the environment. Intensification of agriculture, industrial activity, and urbanisation leads to a growing input of chemicals and pathogens to soils that subsequently endanger the quality and potential use of groundwater resources.

The last decade has seen great advances in stochastic hydrology, on 2D and 3D microscale imaging, and on geophysical methods. These advances have made it clear that (1) the subsurface is highly heterogeneous, (2) heterogeneity controls most flow, transport and biochemical processes. However, **there still exists a wide gap between modeling hypotheses and field reality** (e.g. common homogeneous or multi-gaussian representations of field parameters). Furthermore, there are very few experimental datasets documenting in situ spatial patterns in hydraulic properties and processes at scales relevant to applications. This deficiency is particularly critical for solving current scientific questions of strong societal and industrial relevance, including anomalous dispersion of dissolved compounds, impact of mixing on chemical reactivity, coupling of flow and microbiological activity, fluxes and processes at boundaries between surface and subsurface compartments including unsaturated, river-groundwater and saline intrusion systems.

Since my doctorate PhD graduation in December 2004, I have addressed some of these scientific challenges by blending theory, numerical simulations and experiments in a synergistic manner, in collaboration with a number of researchers in Europe and the US. The main results of these investigations are summarized in this section. I first present the modeling framework that we have developed, and validated from field experiments, to upscale non-Fickian dispersion in heterogeneous velocity fields (section 3.2). The latter quantifies the distribution of residence times in the subsurface and the spatial extent of dissolved plumes. I then discuss the analysis and modeling of mixing processes that control the distribution of concentrations and the reactive processes that depend non-linearly on these concentrations (section 3.3). I present a new theoretical framework for mixing in heterogeneous porous media, which is validated from detailed numerical simulations. This opens new perspectives for predicting reactive transport processes, which are discussed in section 3.4. This research topic has motivated the development of a new experimental lab in Rennes to image the microscale coupling of mixing and reaction processes, and the design of new field experiments to quantify these interactions in situ. Finally, section 3.5 discusses the experimental progresses that we have obtained to characterize the spatial distributions of flow in the field, which are the fundamental driver of transport processes.

4.2 Upscaling dispersion processes

The ability to upscale dispersion is an important step in predicting solute transport through porous media. This topic has received continuous attention since the pioneering work of Taylor, who studied dispersion in a tube (Taylor, 1953). Since this seminal study there has been a large amount of work dedicated to quantifying dispersion in more complex flow fields. A variety of methodologies including the method of local moments (Brenner, 1980; Brenner and Adler, 1980; Brenner and Edwards, 1993) and volume averaging (Bear, 1972; Whitaker, 1999; Quintard and Whitaker, 1994) among others have emerged. The main goal of these methods is to develop an effective asymptotic dispersion coefficient that quantifies solute spreading in an upscaled effective equation and in many cases they have been successful.

Macro-dispersion approaches describe asymptotic heterogeneity-induced transport, which can be cast in an advection-dispersion equation for the macroscale solute concentration. Such Fickian models are characterized typically by a diffusive growths of the plume size. In many applications, however, such an asymptotic regime is often not reached on realistic space and time scales. In fact, there is a large amount of data from field and laboratory experiments (Adams and Gelhar, 1992; Gelhar et al., 1992; Le Borgne and Gouze, 2007; Silliman et al., 1987; Moroni et al., 2007) that suggests that such **Fickian behaviour is often not observed**. Theoretical predictions in heterogeneous velocity fields anticipated this (Matheron and de Marsily, 1980; Deng et al., 1993; Dentz et al., 2000; Berkowitz et al., 2006; Bijeljic and Blunt, 2006). Such behavior can be traced back to incomplete mixing on the macroscopic support scale (Le Borgne et al., 2011b; Dentz et al., 2011).

Thus, for the realistic modeling of transport in heterogeneous porous media, it is necessary to predict transport during this pre-asymptotic regime and in particular to capture the anomalous non-Fickian behaviour. Several nonlocal models have emerged to model this behaviour in porous media, including moment equation approaches (Neuman, 1993; Morales-Casique et al., 2006), projector formalisms (Cushman and Ginn, 1993, 1994), multi-rate mass transfer (Haggerty and Gorelick, 1995; Carrera et al., 1998; Cherblanc et al., 2007; Chastanet and Wood, 2008), fractional advection-dispersion equations (Benson et al., 2000, 2001; Cushman and Ginn, 2000), continuous time random walks (Berkowitz et al., 2006) and continuous Markovian stochastic processes in time (Meyer and Tchelepi, 2010). A review of these models is provided in Neuman and Tartakovsky (2009).

One of the main open question within such nonlocal modeling approaches is how to relate microscale properties (e.g., velocity statistics) to the effective macroscale models. In this context, my main contribution has been to establish a quantitative relationship between the velocity distribution and correlation properties and the upscaled non-Fickian dispersion behavior (Le Borgne et al., 2008a) through the development of a new correlated Continuous Time Random

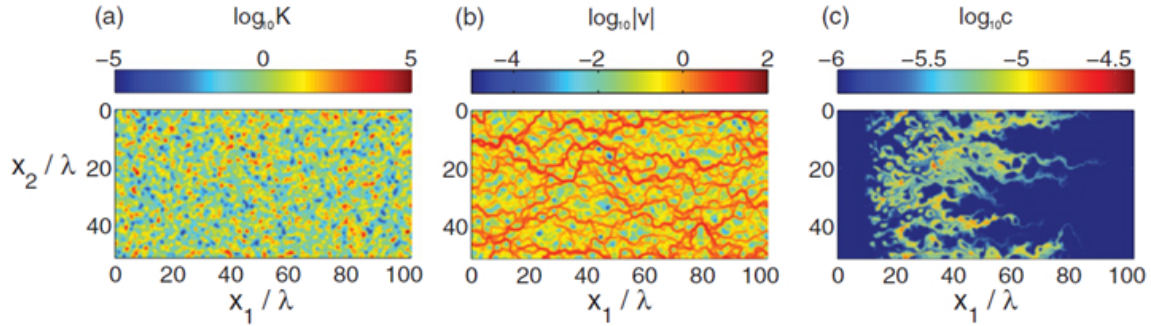


Figure 1: (a) Lognormal conductivity field with variance $\sigma_{\ln K}^2 = 9$ and a correlation length $\lambda = 10$, (b) simulated velocity field, (c) simulated concentration field at time $t = 10\tau_a$, where the mean advection time $\tau_a = \lambda/\bar{v}$, for an initial line injection at longitudinal position $x(0) = 10\lambda$ and a Péclet number $Pe = \lambda\bar{v}/D = 10^2$ (Le Borgne et al., 2011b).

Walk model, as discussed in the following section.

4.2.1 Linking Non-Fickian transport to velocity distribution and correlation

Let us consider the one-dimensional space-time random walk model,

$$x^{(n+1)} = x^{(n)} + \xi^{(n)}, \quad t^{(n+1)} = t^{(n)} + \tau^{(n)}, \quad (1)$$

where both the spatial and temporal increments, $\xi^{(n)}$ and $\tau^{(n)}$ are random. Equation (1) describes a continuous time random walk (CTRW) (e.g., Montroll and Weiss, 1965). The particle velocity at step n is given by the kinematic relationship $v^{(n)} = \xi^{(n)}/\tau^{(n)}$. Note that it may include advection and diffusion processes. The space time positions of a particle after n steps is denoted by $(x^{(n)}, t^{(n)})$. Non-Fickian transport can be modeled in this framework by choosing the spatio-temporal increments from distributions whose widths are of the order of or larger than the observation scales. Fickian behavior is obtained if both the widths of the distributions of the spatial and temporal increments are small compared to the observation lengths and times.

The application of effective random walk models to the description of effective transport in heterogeneous velocity fields is often based on the postulation of a joint distribution of the spatial and temporal increments and the subsequent fit of the model to some dispersion measurements, such as the evolution of the spatial moments of the solute cloud or breakthrough curves (Berkowitz et al., 2006). However, the relationship between the flow field organization and the distribution of spatial and temporal increments is unknown in general. In particular, in many effective random walk descriptions velocity correlation properties, which carry information on the velocity field organization, cannot be included easily (Montero and Masoliver, 2007).

Through a collaboration developed during my postdoc with Marco Dentz and Jesus Carrera, we derived a joint distribution of spatial and temporal increments from the Lagrangian velocity statistics and correlation properties instead of postulating it (Le Borgne et al., 2008b). The Lagrangian statistics were obtained from numerical simulations of flow and transport in highly heterogeneous porous media (Figure 1). Lagrangian flow characteristics play an important role for the qualitative and quantitative understanding of non-Fickian transport in heterogeneous flow fields (Le Borgne et al., 2007). Specifically, strong correlations have been identified as a cause for non-Fickian transport patterns, (e.g., Bouchaud and Georges, 1990). A different source for non-Fickian transport are broad disorder distributions (e.g., Dentz and Berkowitz, 2005). Long disorder correlations on one hand and broad heterogeneity distributions on the other hand are possible causes for anomalous transport patterns with different impact on the effective transport behavior.

Our objective was to define an effective transport model that is consistent with the velocity fields organization and that is fully characterized by the Lagrangian velocity statistics. To this end, we analyzed the Lagrangian flow characteristics with the aim to obtain a simple formulation for effective particle dynamics as a Markovian model. We set up a numerical random walk model for transport in a heterogeneous Darcy flow field, project the transport process on the direction of the mean flow and analyze the Lagrangian velocity statistics along the projected particle trajectories. The latter defines a $d = 1$ dimensional stochastic process that turned out to be a Markov chain for constant spatial increments, i.e., the velocity at a given position along the trajectory depends only on the velocity value at the previous positions. This implies that velocities at equidistant positions along a particle trajectory form a Markov process, which means that here Lagrangian velocities are Markovian in space and not in time. This fundamental property leads naturally to a representation of effective particle motion as a random walk in space-time (Le Borgne et al., 2008a),

$$x^{(n+1)} = x^{(n)} + \Delta x \quad (2a)$$

$$t^{(n+1)} = t^{(n)} + \frac{\Delta x}{v^{(n)}}, \quad (2b)$$

where the series of successive particle velocities $\{v^{(n)}\}_{n=0}^{\infty}$ at equal distances Δx along the particle trajectory form a Markov chain in space, whose transitions are characterized by the conditional probability density $r(v, x|v', x')$. The probability for a particle to make a transition from v' at travel distance x' to v at travel distance $x = x' + \Delta x$ is given by (e.g., Risken, 1996)

$$r(v, x|v', x')dv = \left\langle \delta \left(v - v^{(n+1)} \right) \right\rangle \Big|_{v^{(n)}=v'}, \quad (3)$$

where the angular brackets denote the average over all realization of $\{v^{(n)}\}_{n=0}^{\infty}$.

The random walk (2) is a Markov process in the phase space (x, t, v) . It can be viewed as a correlated CTRW. Unlike classical CTRW models (e.g., Metzler and Klafter, 2000; Berkowitz et al., 2006), here the successive particle velocities are not independent, but depend on the velocity at the previous step. Correlated CTRW models have been recently studied in the literature (e.g., Montero and Masoliver, 2007; Chechkin et al., 2009; Magdziarz et al., 2012; Meerschaert et al., 2009; Tejedor and Metzler, 2010). While these studies postulate some correlation, here the correlated CTRW approach derives from the Markovian nature of the spatial (Lagrangian) velocity transitions. The proposed Lagrangian statistical model was shown to provide accurate predictions for transport in the pre-asymptotic non-Fickian transport regime for different velocity organizations (Figure 2). It describes a wide range of transport behaviors, which can be related directly to the Lagrangian velocity correlation properties and thus to the velocity field organization. The effect of including velocity correlation was studied by comparison with the predictions of the corresponding classical CTRW model.

This study was followed by a numbers of papers that examined the relevance of the newly developed correlated CTRW framework for different structural properties and at different scales (Kang et al., 2011; de Anna et al., 2013). This led to the development of a collaboration with the team of Ruben Juanes at MIT through the PhD thesis of Peter Kang (2010-2014). Discussions with Sylvie Lorthois (IMFT Toulouse) are on-going for application of this modeling framework to transport in biological networks, in the context of blood micro-circulation in the brain.

4.2.2 Field evidence of the role of velocity correlation in Non-Fickian dispersion processes

The theoretical findings presented above motivated a series of field tracer tests to validate the developed modeling framework. The objective was in particular to bring field evidence of velocity correlation effects which are quantified in the correlated CTRW model. These experiments were performed on the H+ Ploemur site in collaboration with Olivier Bour and Peter Kand (MIT).

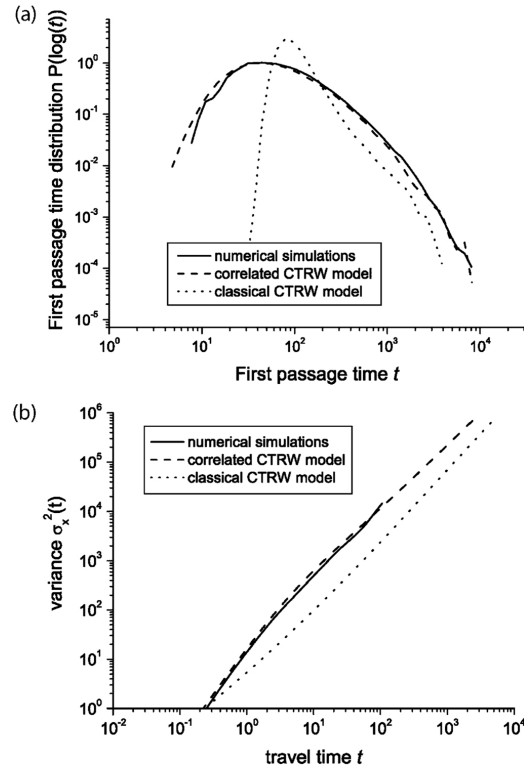


Figure 2: Comparison of the numerical simulations for the multilognormal fields (figure 1) with the predictions given by the correlated CTRW model and the standard CTRW model. (a) First passage time distribution at a distance of 100 elements ($12,5\lambda$) from the inlet (b) variance of the spatial concentration distribution $\sigma_x^2(t)$ as a function of time (Le Borgne et al., 2008b).

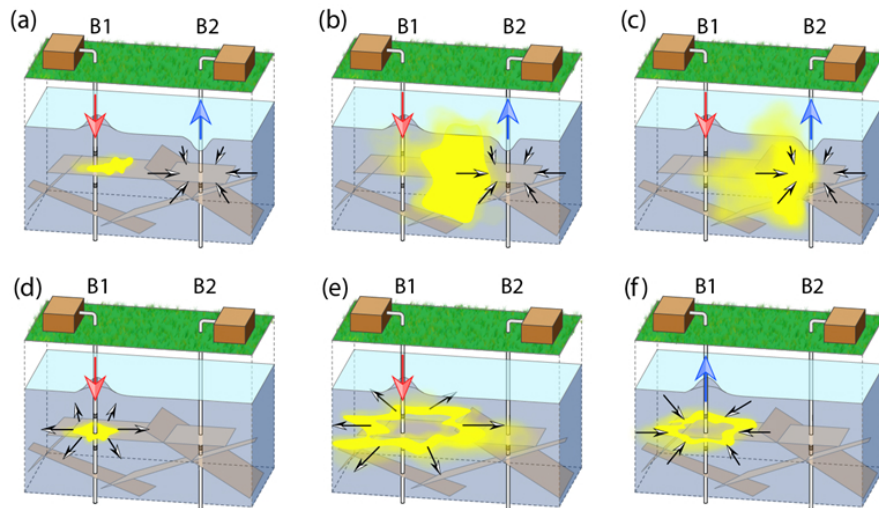


Figure 3: Schematic of the tracer tests conducted. (a,b,c) Convergent test with tracer placement at borehole $B1$ and pumping from borehole $B2$. Two different fracture planes at different depths ($B1-2$ and $B1-4$) are used for two separate tests. (d,e,f) Pushpull test from borehole $B1$. The same two fracture planes $B1-2$ and $B1-4$ are used.

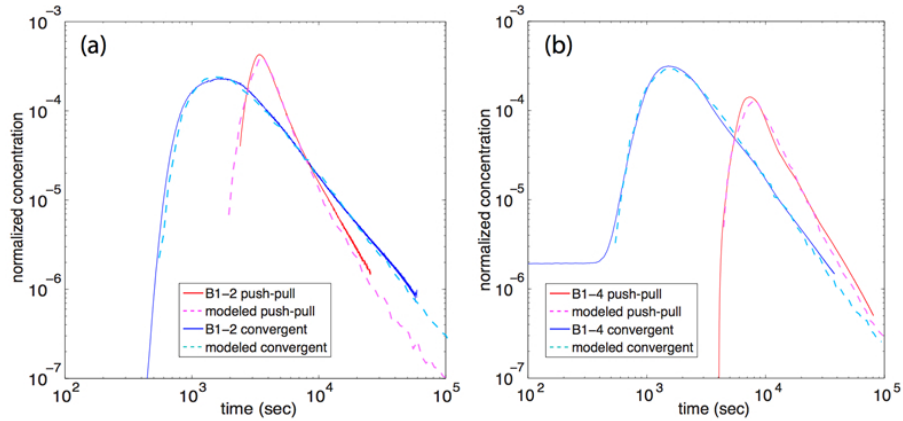


Figure 4: Comparison of measured and modeled tracer breakthrough curves for both convergent and push-pull tests, modeled with the same set of parameters. (a) $B1 - 2$ fracture; correlated CTRW model with parameters (b) $B1 - 4$ fracture; correlated CTRW model.

A signature of anomalous transport in the field is the late-time tailing of breakthrough curves (BTCs), that is, time series of tracer concentration at the pumping well (Figure 4). Breakthrough curves are affected by both the underlying fracture geometrical properties and the physical transport processes such as advection, diffusion, dispersion and adsorption. Thus, they are sensitive to both velocity distribution and velocity correlation. To differentiate velocity distribution from velocity correlation effects, we have proposed a framework combining single-well (push-pull) and two-well (convergent) tests to extract transport parameters (Figure 3). Flow reversibility is strongly dependent on velocity correlation, whereas late-time scaling of breakthrough curves is mainly controlled by velocity distribution. We used two boreholes, B1 (83 m deep) and B2 (100 m deep), which are 6 m apart. Previous work (Dorn et al., 2012b, 2013) has identified four major conductive fractures intersecting B1, labelled B1-1 (24 m deep), B1-2 (50 m), B1-3 (63 m) and B1-4 (79 m), and four major conductive fractures intersecting B2, labelled B2-2 (56 m), B2-3 (59 m), B2-4 (79 m) and B2-5 (97 m). We designed and conducted convergent and push-pull tests at two different fractures: B1-2 and B1-4.

In the convergent test, we injected a known mass of tracer into an injection borehole (B1) and measured the tracer concentration at the pumping borehole (B2) (figure 4(a,b,c)). In the push-pull test, we first injected a known mass of tracer into borehole B1, and continued to inject fresh water for a fixed duration of time (“push” phase). We then reversed the flow and pump water from the same borehole with the same flow rate (“pull” phase), and measured the arrival tracer concentration. In all experiments, a double-packer system was installed to isolate the injection into the desired fracture plane. As expected, the BTCs were broader for the convergent tests than for the push-pull tests, given that in the latter the spreading during the “push” phase is partially recovered during the “pull” phase. Indeed, the degree to which the initial tracer spreading is reversed is an indication of the strength of velocity correlation. Analyzing the two convergent tests, we note that the power-law late-time scalings are different, exhibiting a slope of ~ 1.75 for B1-2 and ~ 1.85 for B1-4. This difference reflects different velocity distributions, and can be interpreted as different levels of heterogeneity. The gentler slopes in the BTCs indicate a broader velocity range (higher probability) towards small velocities.

Based on this field evidence, we have proposed a stochastic transport model that incorporates local dispersivity, Lagrangian velocity distribution, and Lagrangian velocity correlation as the three key transport processes, through a correlated CTRW formulation (Kang et al., 2015). We have shown analytically that our model embodies other existing models of transport as particular cases: it is equivalent to the Multi-Rate Mass Transfer model under the assumption of negligible velocity correlation, and to the Stochastics Stream Tube model under the assumption of infinite correlation. The transport model accurately captures the anomalous behavior in the breakthrough curves for both

push-pull and convergent flow geometries, with the same set of parameters. Thus, the proposed correlated CTRW modeling approach provides a simple yet powerful framework for characterizing the impact of velocity distribution and correlation on transport in fractured media. **This study represents the first field scale validation of the correlated CTRW approach.**

4.3 Mixing

4.3.1 The difference between spreading and mixing in heterogeneous porous media

The upscaling of dispersive or spreading process described in the previous section is important to predict the spatial extent and residence times of contaminant plumes. However, it is not sufficient to predict reactive processes that depend non-linearly on the distribution of concentrations within the plume. In fact, the spatial extent of a mixture does not tell much about its content, but rather its average concentration, and **the knowledge of the spreading properties alone is insufficient to quantify mixing** (e.g., Kitanidis, 1994; Dentz et al., 2011; Le Borgne et al., 2011b), that is the full concentration distribution, and the local spatial structure of the concentration field in the medium. Mixing processes in porous media are particularly important for controlling fluid-fluid as well as fluid-solid chemical reactions (e.g. Cirpka and Valocchi, 2007; Cirpka et al., 2008b; Rolle et al., 2009; Dentz et al., 2011; de Anna et al., 2014b). Dissolution or precipitation processes, for instance, are often triggered by the mixing of different waters respectively at chemical equilibrium (e.g. Tartakovsky et al., 2008a). Different mixing measures have been studied to investigate these processes in porous media (Kitanidis, 1994; Fiori and Dagan, 2000; Fiori, 2001; Bolster et al., 2011; Le Borgne et al., 2010; Chiogna et al., 2012; de Barros et al., 2012).

While for homogeneous media under uniform and constant flow conditions, solute mixing is due to local scale dispersion, for heterogeneous media this is different. The spatial heterogeneity of the field leads to stretching and folding of the solute plume. At times that are smaller than the mass transfer time over a typical heterogeneity scale, these mechanisms increase the solute spread but not the mixing of the solute (e.g., Kitanidis, 1994). Thus, for heterogeneous media, the processes of spreading and mixing need to be separated (Figure 5). Both processes are of course closely coupled. The concentration contrasts that are generated by the spread of the solute enhance mass transfer due to diffusion and local dispersion and thus lead to enhanced mixing (Le Borgne et al., 2011b).

4.3.2 The link between mixing and chemical reactions

Flow heterogeneity leads to chemical reaction dynamics that are very different from the ones observed under homogeneous conditions. Hence, the quantitative relation between the heterogeneity controls of mixing and effective reaction rates is of central concern in disciplines as diverse as geophysics, chemical engineering, biology and hydrology (e.g. Tel et al., 2005; Neufeld and Hernandez-Garica, 2010; Weiss and Provenzale, 2008; Dentz et al., 2011). In porous media flows, effective reaction rates have been shown to differ significantly from those predicted by effective dispersion coefficients (e.g. Gramling et al., 2002; Luo et al., 2008; Battiato et al., 2009; Tartakovsky et al., 2009; Chiogna et al., 2012; de Anna et al., 2014b; Hochstettler and Kitanidis, 2013). Geochemical reaction kinetics can be either limited by the characteristic time of intrinsic chemical phenomena (kinetic limitation) or by the time necessary to bring reactants into contact, either in solution or in the solid phase (mixing limitation). The upscaling of kinetic limited geochemical reactions in the presence of physical and chemical medium heterogeneity has been addressed in the literature using volume averaging techniques, PDF approaches, multicontinuum approaches as well as reactive streamtube models (e.g., Dentz et al., 2011; Maher and Chamberlain, 2014). On the other hand, the upscaling of mixing limited geochemical reactions requires an explicit coupling of transport and reaction phenomena, which is still largely an open question.

Recent approaches have sought to link effective reactivity to transport at local scales using particle-based Lagrangian modeling frameworks (Tartakovsky et al., 2008b; Benson and Meerschaert, 2008; Edery et al., 2009), as well as interface deformation models (de Anna et al., 2014a). These works

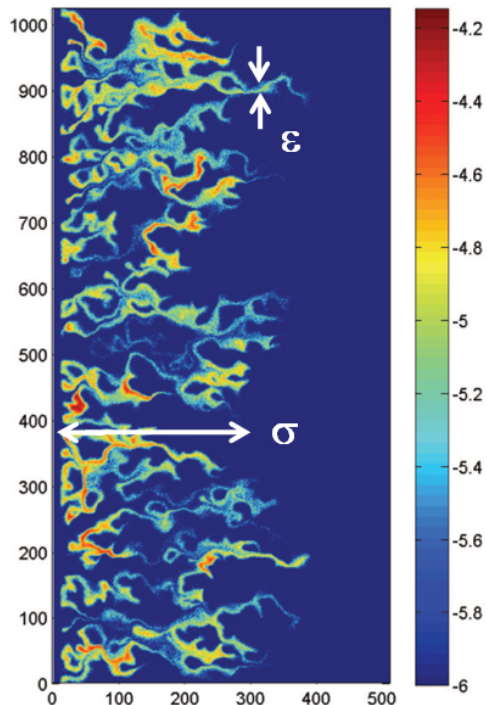


Figure 5: Concentration field simulated in a heterogeneous Darcy field (as in figure 1), illustrating the difference between the spreading scale σ that describes the spatial extent of the plume and the mixing scale ϵ that quantifies the scale at which solutes can be assumed to be fully mixed (adapted from Le Borgne et al. (2010)).

focus on irreversible bimolecular reactions, which depend mainly on the collocation of the dissolved chemical species. Here we focus on reversible chemical reactions, such as dissolution or precipitation processes, which are generally triggered by the mixing of water bodies respectively at chemical equilibrium (de Simoni et al., 2007). **The quantification of such mixing-induced chemical disequilibrium and its impact on global reaction rates remains a key challenge due to its importance in controlling geochemical processes.**

To illustrate the fundamental interactions between fluid mixing and chemical reaction let us consider the paradigmatic reversible reaction



in which C is a pure-phase mineral and therefore has activity 1. The mass action law relates the equilibrium concentrations of A and B by $c_A c_B = K$ with K the equilibrium constant. This simple reaction may represent for instance gypsum precipitation resulting from the mixing of different waters, each one at equilibrium with the rock de Simoni et al. (2005). The method developed in the following can be however extended to more complex reaction network, including dissolution processes, using the general methodology presented by de Simoni et al. (2007) to relate reactive concentration to conservative components.

Transport of the dissolved species A and B is described by the advection-dispersion reaction equation

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{v} c_i - D \nabla^2 c_i = r, \quad (4b)$$

with $i = A, B$. We set the constant porosity equal to 1, which is equivalent to rescaling time. Notice

that we adopt an approximate model of dispersion that relies on a constant dispersion coefficient D , in order to expedite the overall concept, and emphasize the impact of flow heterogeneity on the reaction efficiency, which is quantified by the reaction rate r . Furthermore, we assume the dispersion coefficients are equal for both species. The methodology can be straightforwardly extended to account for anisotropic local scale dispersion. For fast reactions, the reaction rate is determined by the mixing properties of the flow and transport system. While the reaction is locally at equilibrium at each point of the medium, this equilibrium is disturbed due to spatial mass transfer by advection and diffusion, or in other words, by mixing. Thus, the effective reaction rate depends fully on the mass transfer rates induced by the deformation of material interfaces and diffusion.

The quantitative relation between the effective reaction rate and the mixing dynamics for mixing-limited reactive transport has been shown in the papers by de Simoni et al. (2005, 2007). These authors demonstrate that the reaction rate is given by

$$r = \frac{dc_i}{dc} D (\nabla c)^2 \quad (4c)$$

where $c = c_A - c_B$ is the conservative component, (as used in conventional speciation calculations) for the bimolecular reaction, which is transported according to (4b) for $r = 0$. **Equation (4c) provides a direct link between the reaction rate and the conservative concentration gradient.**

The mixing dynamics are encoded in the scalar dissipation rate,

$$\chi = \int_{\Omega} d^d D (\nabla c)^2, \quad (5)$$

which reflects the elementary mass transfer mechanisms; the creation of concentration gradients and their attenuation by diffusion (e.g., Pope, 2000; Kapoor and Anmala, 1998; Kapoor and Kitanidis, 1998; Fedotov et al., 2005; Warhaft, 2000; Bolster et al., 2011). Note that the form (4c) of the reaction rate requires that the diffusion coefficients for both species are equal. Equation (4c) indicates that the scalar dissipation rates captures the impact of mixing on chemical reactions. Thus, we investigated the temporal scaling properties of the scalar dissipation rate in heterogeneous permeability fields with variances ranging from very small ($\sigma_{lnK}^2 = 0.01$) to very large ($\sigma_{lnK}^2 = 9$). For an initial pulse line injection, we found that moderate and strong heterogeneity induce an anomalous temporal scaling of the scalar dissipation rate, which we call non-Fickian mixing (Le Borgne et al., 2010). This effect is particularly relevant for upscaling reactive transport as it implies a non-Fickian scaling of reactive transport.

4.3.3 The lamellar representation of mixing

The dynamics of mixing can be fully quantified by the temporal evolution of the concentration probability density function (PDF), as the mixture evolves towards uniformity under the combined action of diffusion and advection. The prediction of the distribution of conservative concentrations leads to the estimation of reaction rates for fast chemical reactions, as quantified by equation (4c).

A common approach to model concentration PDFs is to assume an ad-hoc distribution, which is parametrized from analytical derivation of concentration moments obtained under different approximations (e.g., Fiorotto and Caroni, 2002; Bellin and Tonina, 2007; Tonina and Bellin, 2008; Cirpka et al., 2008b). Other approaches include mapping closures to transfer the stochasticity of the flow field to the concentration distribution (e.g., Chen et al., 1989; Dentz and Tartakovsky, 2010; Dentz, 2012) and phenomenological approaches that employ stochastic mixing models (Valiño and Dopazo, 1991; Fedotov et al., 2005) to simulate the stochastic evolution of concentration using surrogate mechanisms, see also Pope (2000) and Fox (2004) for an overview.

The study of scalar mixing in a simple stirring protocol by Meunier and Villermaux (2010) has nevertheless demonstrated that these mechanisms can be quantified from first principles using the

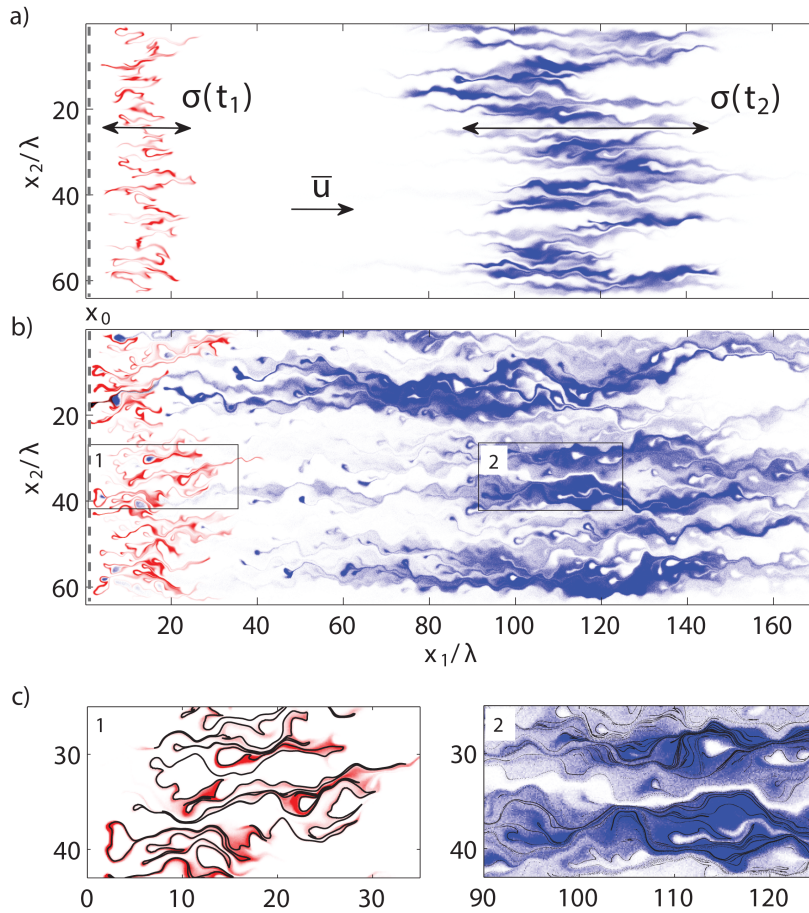


Figure 6: Simulated concentration fields c in lognormal permeability fields (figure 1). The concentration fields are shown at times $t_1 = 12.5\tau_a$ (proportional to red color intensity) and $t_2 = 112.5\tau_a$ (proportional to blue color intensity), for an initial line injection with uniform concentration $c_0 = 2 \times 10^{-3}$ at longitudinal position $x_0 = \lambda$, a Péclet number $Pe = 8 \times 10^2$ and permeability field variances equal to a) $\sigma_{\ln K}^2 = 1$ and b) $\sigma_{\ln K}^2 = 4$. The plume is transported from left to right with a mean velocity \bar{u} and a dispersion length $\sigma(t)$ increasing with time. c) zoom of the concentration fields at each time with superimposition of a purely advected line (black lines), initially located at $x_0 = \lambda$, illustrating the composition of the mixture by stretching and diffusive coalescence (Le Borgne et al., 2013).

powerful concept of the ‘diffusive strip’, or ‘lamellae’ representation of the scalar field (Ranz, 1979). Scalar lamellae are naturally formed by the repeated action of advective motions (figure 7). In this representation the coupling of diffusion to the stretching experienced by the lamellae is straightforward. **The complete PDF of concentration can thus be computed from the diffusion equation in a moving frame, and an additional principle of lamellae random coalescence** initially proposed by Villermaux and Duplat (2003) allows for the description of the mixture content up to its final uniformity. In the same line of thought, we have recently highlighted the role of stretching, diffusion and coalescence mechanisms in governing the evolution of concentration mixtures in Darcy scale porous media (Villermaux, 2012; Le Borgne et al., 2013, 2015). While the porous media structure does not deform in general, the ‘frozen’ flow heterogeneity at different scales generates similar folding and stretching mechanisms as in chaotic or turbulent flows (Metcalf et al., 2010; de Barros et al., 2012; Mays and Neupauer, 2012; Villermaux, 2012), see figure 6. In this framework, the understanding of the basic composition rule of the dispersing mixture provides an analytical description of the overall concentration distribution.

In 2010, I have developed a collaboration with Emmanuel Villiermaux (Aix-Marseille University) and Marco Dentz (CSIC Barcelona) to explore the potential of this theory for predicting mixing in Darcy scale heterogeneous porous medium over a range of Péclet numbers and structural heterogeneities. The main challenge when dealing with these highly heterogeneous flow systems is that dispersion and mixing occur simultaneously. This leads to a range of mixing behaviors at the ends of which lie two turbulent flow equivalents: the ever dispersing mixture scenario (Duplat et al., 2010) for large Péclet numbers, and the confined mixture scenario (Duplat and Villiermaux, 2008) for small Péclet numbers. We have shown that in the first case, the concentration content can be determined from the stretching history of individual lamellae alone, while for the second case, the concentration content is given by the frequency of coalescence of neighboring lamellae (Le Borgne et al., 2013, 2015). Since this modeling approach will play a central role in my future research, I detail in the following the basic principles of the theory.

Stretching enhanced diffusive mixing

The concentration field can be seen as a set of lamellae, whose concentration depends on the interaction between local stretching and diffusion (figure 7). Compression perpendicular to the stretching direction enhances diffusive mass transfer by steepening the scalar gradient. We recall here the basic interaction between stretching and diffusion at the scale of a lamella, leading to an expression for the concentration PDF across a strip that depends on the stretching history (Ranz, 1979; Duplat et al., 2010; Meunier and Villiermaux, 2010). Considering a single lamella, the temporal evolution of the concentration $c(\zeta, t)$ at a position n along the direction perpendicular to the lamella is

$$\frac{\partial c}{\partial t} + \frac{n}{s} \frac{ds}{dt} \frac{\partial c}{\partial n} = D \frac{\partial^2 c}{\partial n^2}. \quad (6)$$

where D is the diffusion coefficient and $s(t)$ is the distance between two material particles in the direction perpendicular to the lamella.

The term $-\frac{n}{s} \frac{ds}{dt} \frac{\partial c}{\partial n}$ represents the impact of compression in the direction perpendicular to the principal direction of elongation of the lamella. By mass conservation under pure advection, $s(t)$ is related to the lamella length $\ell(t)$ by $s(t)\ell(t) = s_0\ell_0$, where s_0 and ℓ_0 are the initial lamella dimensions. Therefore $s^{-1}ds/dt = -\ell^{-1}d\ell/dt$. For the initial condition $c(n, t=0) = c_0 \exp(-n^2)$, the solution is given by the Gaussian profile,

$$c(n, t) = \frac{c_0 \exp\left[-\frac{n^2 \rho(t)^2}{s_0^2(1+4\tau(t))}\right]}{\sqrt{1+4\tau(t)}}, \quad (7)$$

where we defined the dimensionless time

$$\tau(t) = \frac{D}{s_0^2} \int_0^t dt' \rho(t')^2 \quad (8)$$

from the relative strip elongation $\rho(t) = \ell(t)/\ell_0$. The maximum lamella concentration θ in $n=0$ is

$$\theta(t) = \frac{c_0}{\sqrt{1+4\tau(t)}} \quad (9)$$

This equation quantifies stretching enhanced diffusive mixing: for large elongations ρ , $\tau(t)$ becomes also large and thus the maximum lamella concentration $\theta(t)$ decreases faster than for a simple diffusive process.

The concentration PDF in the strip corresponding to the Gaussian profile (7), see also figure 7, is

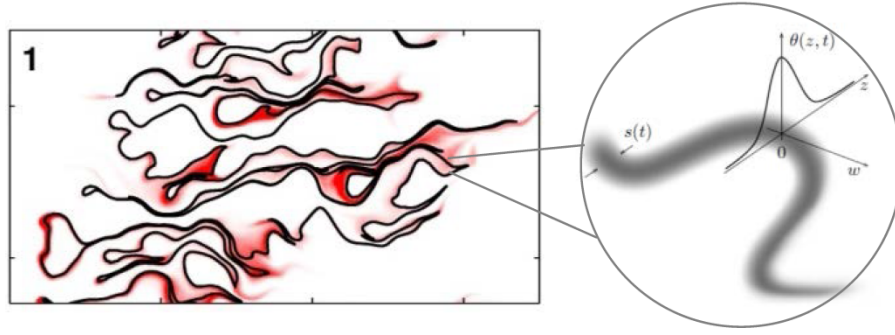


Figure 7: Illustration of the lamella concept: The scalar line, initially located perpendicular to the main flow direction, distorts into a brush made of a collection of strips, aligned on average with the direction of the mean flow. At early times, the scalar concentration is close to uniform along the stretching direction and varies rapidly along the compressive one, thus forming a lamella-like topology;

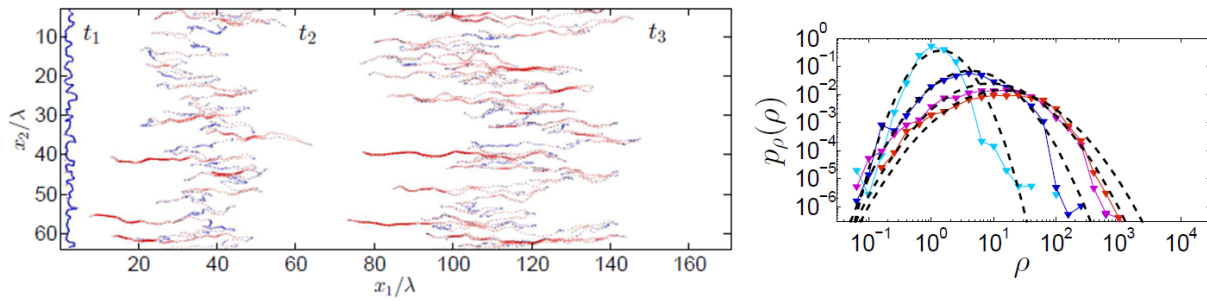


Figure 8: Left: Advected line at times $t_1 = 2.5\tau_a$, $t_2 = 37.5\tau_a$, $t_3 = 112.5\tau_a$ for $\sigma_f^2 = 1$. The initial position of the line is $x_1 = \lambda$. The red color intensity is proportional to ρ for lamella elongations $\rho \geq 10$. The blue color intensity is proportional to $1/\rho$ for $\rho < 10$. Hence, the red zones represent the parts of the line that are most elongated while the blue zones represent the portions that have been less stretched. Right: PDF of elongations at times $t_1 = 0.25\tau_a$, $t_2 = 12.5\tau_a$, $t_3 = 50\tau_a$ and $t_4 = 112.5\tau_a$. The PDF of elongations follow an approximate lognormal distribution as predicted by the stochastic stretching model of Le Borgne et al. (2013).

given by

$$p(c|\theta) = \frac{1}{2c\sqrt{\ln(\theta/\epsilon)\ln(\theta/c)}} \quad (10)$$

with $\theta \geq c$. The concentration range is $[\epsilon, \theta]$, with ϵ and θ the minimum and maximum concentrations in the strip. **Equation (10) provides the relationship between the concentration PDF of a lamella and its elongation history**, through the temporal evolution of the maximum concentration θ in the strip (9).

Random elongation processes and concentration PDFs

As quantified in equation (7) and (8), the history of lamella elongation $\rho(t)$ plays a key role in controlling stretching enhanced diffusive mixing. There is however currently no theory to predict fluid deformation in porous media. The lamella elongation can be quantified by computing the pair separation $\ell(t) = |\mathbf{x}(t|\mathbf{a}+\Delta\mathbf{a}) - \mathbf{x}(t|\mathbf{a})|$ of neighbouring particles initially located at a distance $\ell_0 = |\Delta\mathbf{a}|$ on the injection line. As illustrated in Figure 8, the width of the PDF of elongations $p_\rho(\rho, t)$ increases with increasing time as the line is distorted by the flow heterogeneity. The average elongation is found,

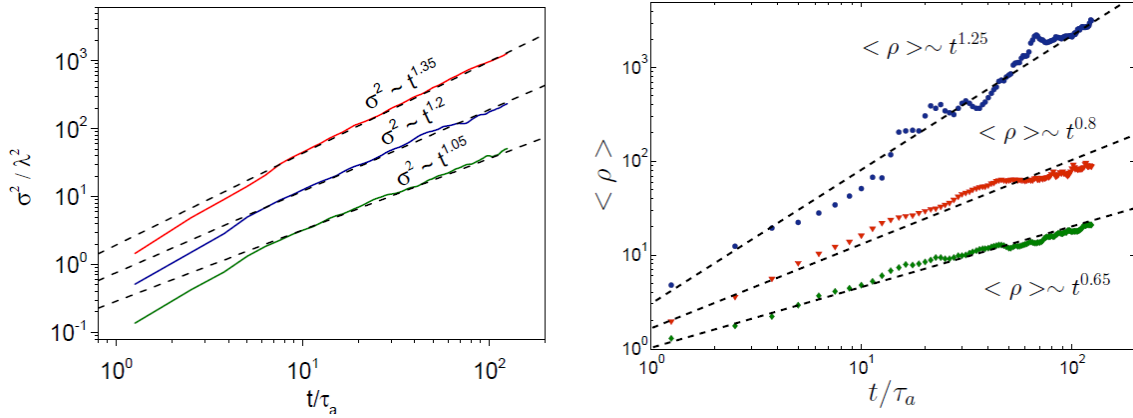


Figure 9: Left: Temporal evolution of the advective spatial variance $\sigma^2(t)$, which characterizes advective spreading for $\sigma_f^2 = 0.25$ (green curve), $\sigma_f^2 = 1$ (blue curve) and $\sigma_f^2 = 4$ (red curve) (Le Borgne et al., 2015). Right: Temporal evolution of the mean elongation $\langle \rho(t) \rangle$ for different permeability field variances : $\sigma_{\ln K}^2 = 0.25$ (green diamonds), $\sigma_{\ln K}^2 = 1$ (red triangles), $\sigma_{\ln K}^2 = 4$ (blue disks).

from our simulations, to be well fitted by a power law in time (figure 9) as

$$\langle \rho(t) \rangle \propto \left(\frac{t}{\tau_a} \right)^\alpha. \quad (11)$$

The profound nature of this behavior and the origin of its connection with the structure of the permeability field is the subject of current research. Understanding this phenomena requires exploring the fluid deformation dynamics in heterogeneous media, which represents a new line of research that I currently develop with my collaborators.

This nonlinear stretching law has important implications for the geometry of the line. During its transport, the advected line is confined in a domain whose longitudinal extent grows as the advective spreading length $\sigma(t)$ and whose lateral extent is constant, see also Figure 8. The advective spreading length $\sigma(t)$ is defined in terms of the longitudinal position of purely advectively transported particles $x_1(t)$ as

$$\sigma^2(t) = \langle [x_1(t) - \langle x_1(t) \rangle]^2 \rangle. \quad (12)$$

The angular brackets denote the average over all particles in the initial line. As shown in figure 9, the advective spatial variance increases non-linearly over the time scales of simulations, which is characteristic of non-Fickian spreading processes in heterogeneous media as discussed in the previous section (Le Borgne et al., 2008a). The anomalous scaling of advective spreading is in general persistent in time as the advective sampling of the velocity heterogeneity is not fostered by diffusion. Hence, the convergence to Fickian advective dispersion is expected to occur at a characteristic advective time corresponding to the lowest velocity in the domain. This time may be thus very large for strongly heterogeneous media as discussed in the previous section. Advective spreading in porous media has been shown to be characterized by strong intermittent properties, which can be related to the flow field heterogeneity by correlated continuous time random walk approaches discussed in the previous section. The non-linear evolution of the spatial variance $\sigma(t)$ in the non-Fickian regime is often approximated as a power law,

$$\sigma(t) \propto t^{\beta/2}, \quad (13)$$

with $1 \leq \beta \leq 2$ (figure 9).

The power law evolution of the mean elongation $\langle \rho(t) \rangle$ and the advective spreading length $\sigma(t)$

implies that the advected line support is fractal, as shown as follows. Considering a fractal line support, the number of boxes of size r needed to cover the line at a line extension $\sigma(t)$ is

$$N(r, t) \propto \left[\frac{r}{\sigma(t)} \right]^{-d_f}, \quad (14)$$

Thus, with increasing time, the number of boxes of unit size needed to cover the line increases as $\sigma(t)^{d_f}$. At the same time $N(r, t)$ increases according to $\langle \rho(t) \rangle$ so that

$$\langle \rho(t) \rangle \propto \sigma(t)^{d_f}. \quad (15)$$

Thus, since both $\langle \rho(t) \rangle$ and $\sigma(t)$ evolve as a power law of time, the line should be characterized by a stable fractal dimension d_f such as,

$$d_f = \frac{2\alpha}{\beta}. \quad (16)$$

The fractal dimension of the advected line computed by box counting, is found to be well defined over two orders of magnitude in space (Le Borgne et al., 2015). It is independent of time and ranges from $d_f = 1.3$ for the moderate heterogeneity to $d_f = 1.8$ for the strong heterogeneity, which is consistent with (16). Equation (16) thus provides a key relationship between stretching, spreading and the geometrical properties of the scalar field.

The quantification of the distribution of elongations along the line as it is transported in the heterogeneous porous media is a key step towards the prediction of the distribution of concentration. **We describe here a corresponding mixing model which maps the PDF of lamella elongations into the PDF of concentrations.** For large Péclet numbers, a well developed regime exists in which lamellae do not overlap. In this regime, the concentration PDF $p_c(c, t)$ is obtained by sampling concentration over individual lamellae, whose PDF (10) is conditional to the respective maximum concentration $\theta(t)$. The maximum concentration describes a stochastic process due to the stochasticity of the elongation $\rho(t)$. A detailed analysis of the lamella stretching process has shown that it can be well represented by a multiplicative random process (Le Borgne et al., 2015). This implies that the PDF of elongations is lognormal as well as the PDF of maximum lamella concentration $p_\theta(\theta, t)$,

$$p_\theta(\theta, t) = \frac{\exp \left\{ -\frac{[\ln(\theta/c_0) - m_z]^2}{2\sigma_z^2} \right\}}{\theta \sqrt{2\pi\sigma_z^2}}. \quad (17)$$

where

$$m_z(t) = -\mu \ln(t/\tau_a) - \frac{1}{2} \ln(t/\tau_a), \quad \sigma_z^2(t) = 2\nu \ln(t/\tau_a) \quad (18)$$

are the mean and variance of $z(t) = \ln[\theta(t)]$. The parameters μ and ν describe the power law evolution of the mean and variance of the elongation (figure 9).

The global concentration PDF is thus written as

$$p_c(c, t) = \int_c^\infty d\theta p_c(c|\theta) p_\theta(\theta, t). \quad (19)$$

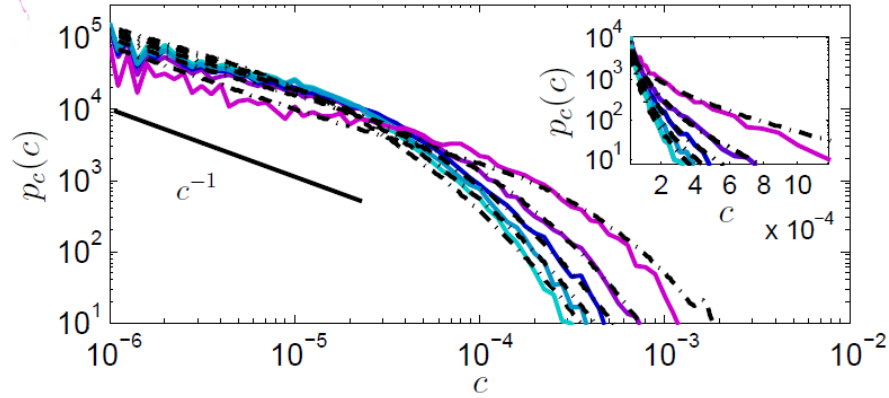


Figure 10: Concentration PDFs at times $t = 12.5\tau_a, 37.5\tau_a, 62.5\tau_a, 87.5\tau_a, 112.5\tau_a$ for a Péclet number $Pe = 8 \times 10^4$ and a permeability field variance $\sigma_f^2 = 1$. The simulations are represented by blue continuous lines and the predictions obtained from the independent lamella model (20) are represented by black dash dotted lines. Inset: same plot in semi-log representation, emphasizing the non-exponential concentration decay (Le Borgne et al., 2015).

Using (17) in (19) and rescaling the integration variable, we can write the concentration PDF as

$$p_c(c, t) = \int_{\ln(c)}^{\infty} dz \frac{\exp\left[-\frac{(z-m_z)^2}{2\sigma_z^2}\right]}{2c\sqrt{2\pi\sigma_z^2}\sqrt{[z-\ln(\epsilon)][z-\ln(c)]}} \quad (20)$$

where we used (10) for $p_c(c|\theta)$.

The concentration PDF (20) is parameterized only by the parameters μ and ν , which are obtained from the evolution of $\rho(t)$. Its predictions are in good agreement with the numerical simulations for all cases, in which the stretched lamellae that constitute the line evolve on their own and do not overlap, i.e. at early times and high Péclet numbers (figure 10). The model predicts correctly the temporal evolution of the shape of the concentration PDF, as it evolves towards uniformity. The model predicts accurately the impact of heterogeneity on mixing and represents well the decrease of the maximum concentration as the degree of heterogeneity increases (figure 10). The behavior of $p_c(c, t)$ for small concentrations is given by $p_c \propto 1/[c\sqrt{\ln(1/c)}]$, which is characteristic of the Gaussian concentration profiles across each lamella as given in (7). The PDF of large concentrations is controlled by the lognormal PDF of maximum lamella concentrations $p_m(\theta)$.

Random aggregation processes and concentration PDFs

Interactions between lamellae are enforced at later times and for smaller Péclet numbers because the average elongation $\langle \rho \rangle \propto t^\alpha$ grows faster than the longitudinal size of the dispersion area $\sigma \propto t^{\alpha/d_f}$ in which the line is confined. Recall that $d_f \geq 1$ as given in (16). When the lamella width is larger than the distance between lamellae, the concentration fields around each lamella start coalescing to form lamella aggregates as illustrated in figure 11. Due to continued diffusive broadening these lamella aggregates may overlap to form bundles. To represent this process, we have developed a mixing theory in which lamella interaction is modeled as a random aggregation process with partial or complete coalescence (Le Borgne et al., 2015).

Assuming that the lamellae that overlap have uncorrelated stretching histories, the concentrations of lamellae that aggregate can be considered as uncorrelated random variables, and the coalescence can be described as a random aggregation process. As discussed by Duplat and Villermaux (2008) and illustrated in figure 12 the concentration distribution in this regime is well described by a Gamma

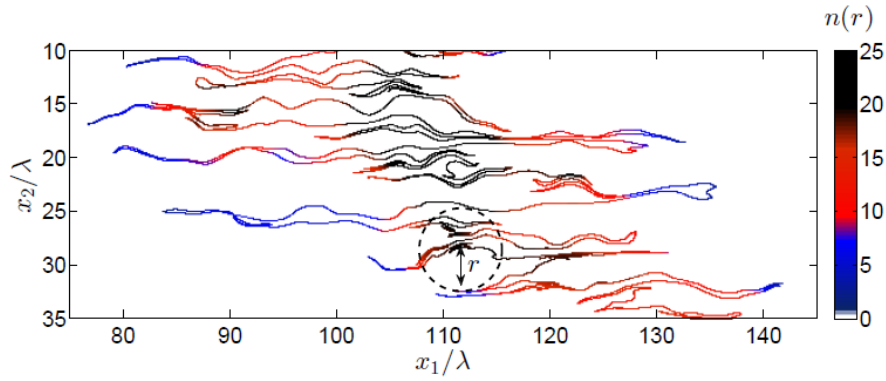


Figure 11: Estimation of the number of lamella overlap along the line $n[\mathbf{x}(t|\mathbf{b}), r, t]$ for a diffusion scale $r = 4\lambda$ at time $t = 112, 5\tau_a$ (Le Borgne et al., 2015).

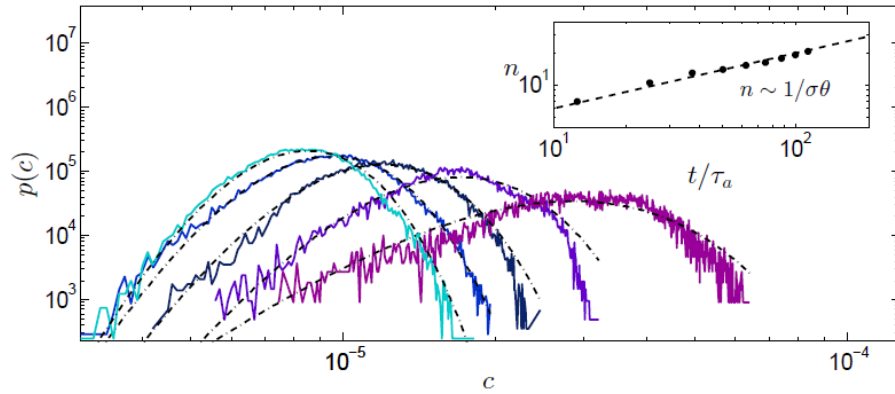


Figure 12: Concentration PDFs at the center of the plume, $\bar{x}(y) - \sigma_x(y)/2 < x < \bar{x}(y) + \sigma_x(y)/2$, at times $t = 12.5\tau_a, 37.5\tau_a, 62.5\tau_a, 87.5\tau_a, 112.5\tau_a$ for a Péclet number $Pe = 8$ and a permeability field variance $\sigma_{\ln K}^2 = 1$ (blue continuous lines). The predictions of the random aggregation model (equation (21)) are shown in black dash dotted lines. Inset: temporal evolution of the average coalescence number $\bar{n}_c(t)$ corresponding to each (Le Borgne et al., 2015).

distribution that results from the random lamella aggregation process:

$$p_c(c, t) = \frac{c^{\bar{n}-1}}{\langle \theta \rangle^{\bar{n}} \Gamma(\bar{n})} \exp[-c/\langle \theta \rangle]. \quad (21)$$

where $\bar{n}(t)$ is the average lamella coalescence number at time t , which increases in time such as it restores the average concentration,

$$\bar{n}_c(t) \propto \frac{1}{\sigma(t) \langle \theta(t) \rangle}, \quad \text{for } t > \tau_D \quad (22)$$

We expect this distribution of concentration values around the center of the plume because there the lamella density is highest, see figure 11. In Le Borgne et al. (2015), we developed a more general expression that accounts for the spatial distribution of coalescence number.

The establishment of the lamellar mixing theory for porous media is a significant contribution as it represents an important step for upscaling mixing processes in heterogeneous porous media, as well as associated chemical rate laws (see perspective section). This framework provides analytical expressions for the concentration distributions (both in one point, and for the concentration differences at a given spatial distance) in the different regimes experienced by the

scalar mixture as it progresses towards uniformity. The predictions, which are entirely parametrized by the elongation distribution, line geometry and diffusion coefficient, are in good agreement with numerical simulations for all investigated permeability field variances, Péclet numbers and times. These expressions characterize the impact of the permeability field heterogeneity on the temporal evolution of mixing, as quantified by the concentration moments, scalar dissipation rate or entropy. The effective mixing behavior is thus directly related to the mean elongation exponent μ , the elongation variance exponent ν and the line fractal dimension d_f .

As discussed in the following section, the proposed framework is expected to be particularly relevant for upscaling chemical reactivity in porous media flows since the distribution of concentration gradients resulting from the interaction of stretching and coalescence governs the mixing of chemical elements liable to react. Furthermore, this modeling framework is directly applicable for risk assessment studies, in which uncertainty in transported contaminant concentration is given by the concentration PDFs. While the present study focuses on Darcy scale heterogeneity, the developed theory is expected to be applicable at pore scale, as very similar stretching and coalescence processes are induced by the pore scale flow heterogeneity de Anna et al. (2014a). Extension of the theory to 3D porous media is currently under investigation. We anticipate that the additional dimension can be treated by considering stretched sheets instead of lamellae as elementary objects. Furthermore, the stretching behavior is likely to be impacted by the additional degree of freedom (Lester et al., 2013).

4.4 Reaction kinetics

Based on the new theoretical and experimental tools presented above, my objective is to develop and validate a reactive transport modeling framework for subsurface flows, integrating the spatial variability of flow and concentrations via new concepts for representing fluid mixing. The results are expected to have fundamental implications for predicting biochemical transformation in hydrological systems, as well as practical impacts for estimating effective reaction rates in industrial applications, such as geothermal activities or subsurface remediation operations. I present here the recent results that I have obtained. The perspectives are presented in the following section.

4.4.1 The impact of mixing on effective reactivity

Subsurface reactive transport has long been the focus of research projects designed to elucidate both fundamental isolated processes and collective behaviors in natural porous media. As a result, a great deal has been learned about biogeochemical reactions in the subsurface (e.g. Appelo and Postma, 2005). However, while the role of mixing processes in governing reactive front kinetics is generally recognized, existing modeling frameworks have largely sidestepped the complexities associated with heterogeneous porous media (Dentz et al., 2011). In particular, the strong spatial variability of subsurface flow velocities, characterized by the coexistence of fast and slow flow paths, is known to induce a significant spatial variability of solute concentrations. The consequent small scale chemical gradient variability, exerting a direct control on reactive fluxes, is expected to strongly impact upscaled effective reaction kinetics, although this relationship is currently quantitatively unknown (Meile and Tuncay, 2006). This implies that **reaction rates classically estimated in the laboratory, in well mixed batch reactors with no chemical gradients, may differ by orders of magnitude from those controlling reactive processes on the field scale.**

As discussed in the previous section, as solutes are transported in heterogeneous flow fields, they tend to organize into elongated structures that naturally formed by the repeated action of the advection motions (Villiermaux, 2012; Le Borgne et al., 2013; de Anna et al., 2014a). This is illustrated in figure 13, where the shear action of a stratified flow field induces a deformation of the reactive fronts that may be viewed as a collection of stretched lamellae. The lamellar representation allows to quantify the enhancement of diffusive mass transfer induced by the increase of the surface available for diffusion and by the steepening of concentration gradients arising from compression in the direction perpendicular

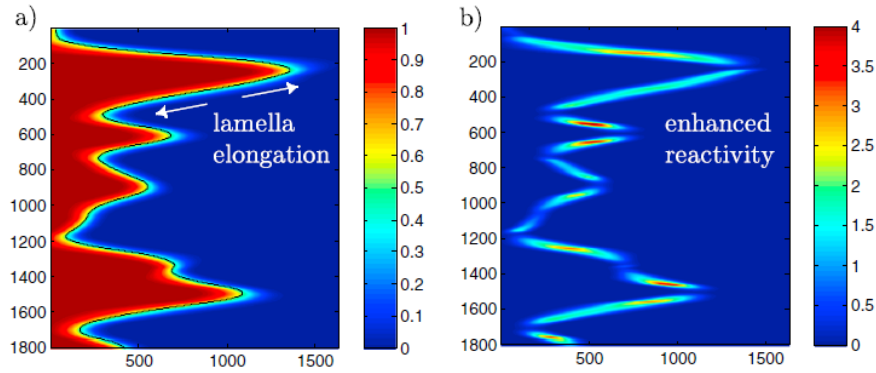


Figure 13: Illustration of a reaction front in a stratified random flow field based on lamellar mixing (from Le Borgne et al. (2014)). (a) Concentration profile of the conservative component illustrating the interface between displacing and resident waters, which is deformed by the action of the flow heterogeneity and develops a lamellar structure. (b) Reaction rates along the interface normalized by the reaction rates for homogeneous flow. Interface elongation enhances concentration gradients by decreasing the lamella width and thus increases chemical reactivity.

to the maximum stretching direction (Ranz, 1979; Duplat and Villermaux, 2008). In the following, we **generalize this concept to fast reversible reactions**. Extension to different Damkohler numbers will be investigated in the next years.

4.4.2 The reactive lamella model

We detail here the basic principle of the reactive lamella model, which couples fluid stretching, mixing and chemical reactions. We thus now write equation (6) for reactive species c_i as (Ranz, 1979),

$$\frac{\partial c_i}{\partial t} - \gamma(t)n \frac{\partial c_i}{\partial n} - D \frac{\partial^2 c_i}{\partial n^2} = r(t), \quad (23)$$

where n is the coordinate perpendicular to the main direction of elongation of the lamella, D is the local diffusion coefficient for mass transfer in the n direction exclusively, and $\gamma = d \ln(\rho)/dt = -d \ln(s)/dt$ is the elongation rate. Concentration gradients in the stretching direction are much smaller than the ones perpendicular to the lamella and are ignored here. Concentration gradients in the direction perpendicular to the lamella are steepened due to compression. The width s of the lamella is a measure for the concentration gradient scale.

Notice that this picture of lamellar transport is valid as long as the lamellae can be considered as independent. This is the case for linear shear flows and radial flow scenarios, for example. In heterogeneous flows, lamellae may start interacting through coalescence (Villermaux, 2012; Le Borgne et al., 2013). The time scale for the transition from the stretching enhanced mixing regime to coalescence is typically set by the mixing time scale τ_m (Villermaux, 2012), which quantifies the competition of fluid deformation to decrease the lamella width and diffusion to increase it.

Dispersion and Reaction at the Lamella Scale

Equation (23) can be transformed into a diffusion-reaction equation with constant parameters by considering the variable transform (Ranz, 1979; Meunier and Villermaux, 2010) to the reduced coordinate \tilde{n} and warped time τ , which are defined by

$$\tilde{n} = \frac{n}{s_0} \rho, \quad \tau = \int_0^t dt' D \frac{\rho^2}{s_0^2} \quad (24)$$

where s_0 is the initial lamella width in the n -direction. This transformation leads to the following reaction diffusion equation:

$$\frac{\partial \tilde{c}_i}{\partial \tau} - \frac{\partial^2 \tilde{c}_i}{\partial \tilde{n}^2} = \tilde{r}(\tilde{n}, \tau), \quad (25)$$

where the concentration $c(n, t)$ and the reaction rate $r(n, t)$ are related to $\tilde{c}_i(\tilde{n}, \tau)$ and $\tilde{r}(\tilde{n}, \tau)$ as

$$c(n, t) = \tilde{c}[\tilde{n}(n), \tau(t)] \quad r(n, t) = \frac{D\rho^2}{s_0^2} \tilde{r}[\tilde{n}(n), \tau(t)]. \quad (26)$$

Note that the transformation (26) assumes constant and isotropic dispersion coefficient. Extension to a velocity dependent dispersion tensor is the subject of current investigations.

The reaction rate $r(n, t)$ integrated over a lamella segment is given by

$$R_\ell(t) = \ell_0 \rho \int_{-\infty}^{\infty} dn r(n, t) = \frac{D\ell_0 \rho^2}{s_0} \int_{-\infty}^{\infty} d\tilde{n} \tilde{r}[\tilde{n}, \tau(t)], \quad (27)$$

where we used (24) and (26). This equation relates the reaction rate of a lamella to that of a one-dimensional diffusion-reaction system. The global, upscaled reaction rate then is given by the sum of the contributions of the individual lamellae as

$$R(t) = \sum_{\ell} R_\ell(t). \quad (28)$$

Fast reversible bimolecular reaction

We illustrate this approach for the fast reversible bimolecular reaction system (4), which is fully determined by the mixing properties of the flow and transport system. In the coordinate system attached to the material strip, the conservative component $c = c_A - c_B$ now satisfies the diffusion equation in reduced coordinates

$$\frac{\partial c}{\partial \tau} - \frac{\partial^2 c}{\partial \tilde{n}^2} = 0. \quad (29)$$

The general expression (4c) for the reaction rate is now given in reduced coordinates by

$$\tilde{r}(\tilde{n}, \tau) = \frac{d^2 c_A}{dc^2} \left(\frac{\partial c}{\partial \tilde{n}} \right)^2. \quad (30)$$

The concentration of species A in terms of u is obtained from the mass action law $c_A c_B = K$ and $c = c_A - c_B$ as

$$c_A(c) = \frac{c}{2} + \sqrt{\frac{c^2}{4} + K}. \quad (31)$$

In the following, we solve the mixing-induced reactive transport problem for a reaction front in a spatially variable flow.

Reaction Front

We consider the scenario of miscible displacement of solutions of two different chemical compositions, each at chemical equilibrium. Between the two solutions, a mixing interface develops, that is deformed due to velocity gradients. Mass transport across the interface is, as outlined above, determined by the interaction of interface compression and diffusion/dispersion. This scenario can be described by the initial distribution $c(\tilde{n}, \tau = 0) = \frac{1}{2} \Delta c_0 \operatorname{erfc}(\tilde{n}/\sqrt{2}) + c_r$, where $\Delta c_0 = c_d - c_r$, and c_d and c_r the differences of the species concentrations in the displacing and resident fluids. As boundary

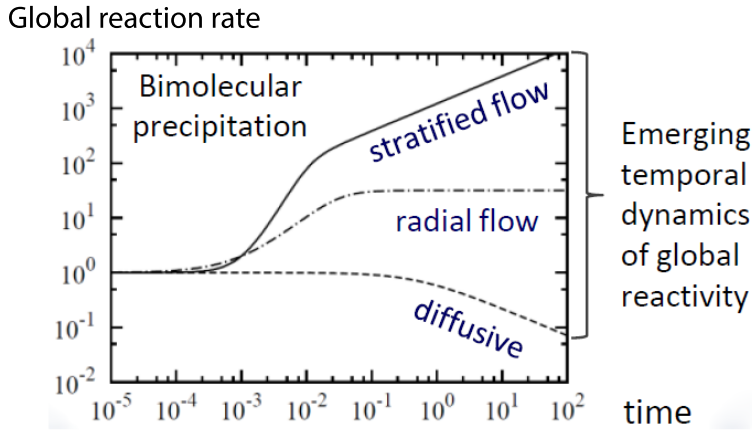


Figure 14: Global reaction rates for (solid) linear shear flow, (dashed-dotted) radial flow, and (dashed) uniform flow. The reaction rates are normalized by $Ls_0\Delta c_0\mathcal{A}/\tau_D$, from (Le Borgne et al., 2014).

conditions we set $c(-\infty, \tau) = c_d$ and $c(\infty, \tau) = c_r$. Under these conditions, the scalar distribution and the scalar gradient across the front have the scaling form

$$c(\tilde{n}, \tau) = \hat{c}(\tilde{n}/\tilde{s}), \quad \frac{\partial c}{\partial \tilde{n}} = \frac{1}{\tilde{s}} \left. \frac{\partial \hat{c}(a)}{\partial a} \right|_{a=\tilde{n}/\tilde{s}}, \quad (32)$$

where we defined the non-dimensional interface width $\tilde{s} = \sqrt{1 + 2\tau}$. The scaling function here is simply given by $\hat{c}(\tilde{n}) = c(\tilde{n}, 0)$. Using the scaling forms (32) in (30), we obtain for the global reaction rate (27) on a single lamella the expression

$$R_\ell = \frac{\ell_0 s_0 \Delta c_0 \mathcal{A} s_0 \rho^2}{\tau_D \sqrt{1 + 2\tau}}, \quad (33)$$

where the constant \mathcal{A} is given by

$$\mathcal{A} = \frac{1}{\Delta c_0} \int_{-\infty}^{\infty} da \frac{d^2 c_A}{d\hat{c}^2} \left(\frac{\partial \hat{c}}{\partial a} \right)^2. \quad (34)$$

The diffusion time τ_D over the initial interface width is given by $\tau_D = s_0^2/D$.

The solution (33) aligns clearly the terms contributing to the global reaction rate: diffusion quantified by D , lamella elongation and elongation history through warped time τ , see (24), and the speciation term encoded in \mathcal{A} , which represents the chemistry. The global reaction rate is obtained from the sum of the contributions of individual lamellae and thus integrates the heterogeneous distribution of velocity gradients into large scale reactivity. We use this approach to analyze simplified yet fundamental reactive flow scenarios characterized by distinct topological features (figure 14). We demonstrate that the upscaled reaction rate (per 33) depends explicitly on the history of lamella deformation and on the equilibrium point of the reaction. Through the study of the lamella dynamics, the temporal evolution of the global reaction rates is related to the distribution of local velocity gradients. **The effective reaction rates are shown to follow distinct temporal scaling laws, which are determined by the flow topology and the distribution of local velocity gradients. This implies that they differ by orders of magnitude from their homogeneous flow field equivalents.** This approach allows for the systematic evaluation of the temporal evolution of equilibrium reaction rates, and establishes a direct link between the reaction efficiency and the spatial characteristics of the underlying flow field as quantified by the deformation of material fluid elements.

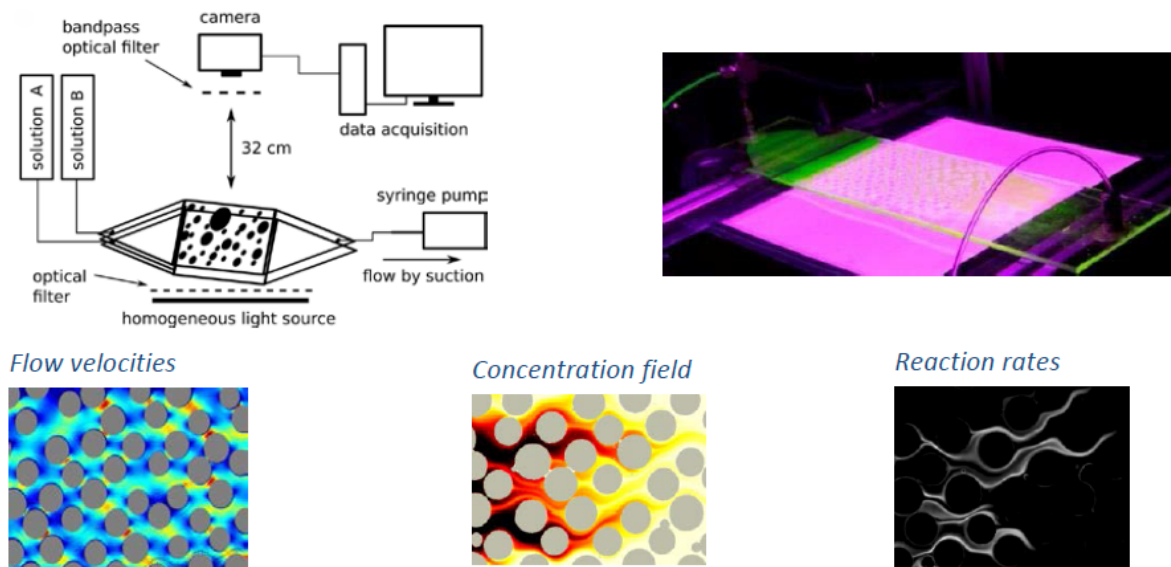


Figure 15: Above: technical sketch and photo of our millifluidic experimental setup for imaging flow distribution, mixing and reactions in a 2D micromodel (de Anna et al., 2014b). Bottom: three images of laboratory experiments in a milli-fluidic cell representing a porous medium (the grey disks are solid grains with an average pore size ranging from 500 μm to 7 μm , depending on the applications) Bottom left: velocity field measured from tracking the spatial position of micro-spheres of diameter 1 μm . Bottom center: the concentration field of an incoming solute, measured using a fluorescent solute. Bottom right: spatial distribution of the light emitted by a chemiluminescent reaction at the front between two reactants.

4.4.3 Imaging and modeling reactive front dynamics

In parallel to this theoretical work, I have been promoting the development of a new milli-microfluidic lab in Rennes, in collaboration with Y. Méheust (Geosciences Rennes) and Hervé Tabuteau (IPR), to study the coupling between flow, mixing and chemical reactions at the microscale. The experimental setup, based on soft lithography techniques, allows imaging the pore scale distribution of flow, concentrations and reaction rates in 2D (figure 15). In the context of porous media, we have been the first group to use of chemiluminescent reactions (Jonsson and Irgum, 1999) that emit a photon upon reacting. Hence, the spatial distribution of light produced by the reaction maps directly to the spatial distribution of reaction rates (de Anna et al., 2014b). This characteristic, which makes the experimental approach unique compared to other existing setup, provides an entirely new vision of the intimate fluid stretching reactivity interaction (figure 16). Based on this new method, we have shown that the measured global kinetics is controlled by the evolution of the spatial organization of the reactants in lamellae-like structures which are elongated by the local flow and merged by diffusion (de Anna et al., 2014b,a). This experimental setup will be largely developed in the next years within the ERC project ReactiveFronts as discussed in the perspective section of this manuscript.

4.4.4 In situ characterization of reactive transport processes

The lab experimental models presented above provide key information about fundamental processes and their coupling, however they cannot capture all the relevant features of natural environments. Thus, I am developing experimental methods to investigate field scale reactivity under heterogeneous conditions. Running controlled in situ reactive transport experiments is technically very challenging, specially when biological components are involved. As a consequence, data on mixing and effective reaction rates collected in the field are still relatively scarce compared to the vast amount of data on

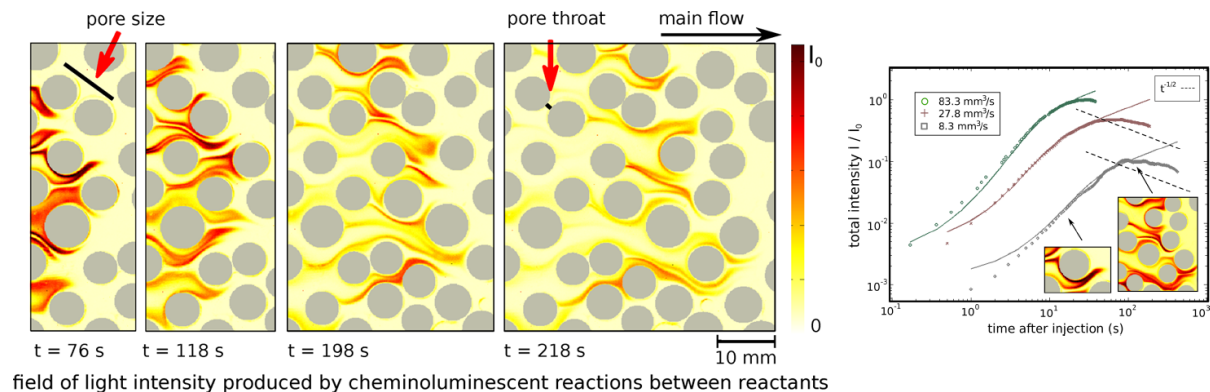


Figure 16: Spatial distribution of the light intensity produced by chemiluminescent reactions, measured experimentally at different times as the reactive front progresses from left to right in a 2D porous medium. Hotspots of chemical reactivity are found to be localized in strongly stretched regions of the front, corresponding to the steepest concentration gradients. Right: Temporal evolution of the global rate of product formation for three imposed flows. Due to stretching enhanced mixing, the observed temporal behavior is different from that expected from a classical macro-dispersion model. From de Anna et al. (2014b).

laboratory batch experiments. While these experiments provide useful insights on reaction mechanisms, they are not representative of the complex mixing conditions in the field.

Large scale field infrastructures have been developed over the last ten years, including the H+ observatory (<http://hplus.ore.fr/>), which is a network of hydro-geological observatories providing both long term monitoring data and focused experiments. After the phase of setup and basic field characterization, a range of new data about reactivity is currently being produced, including detailed biological and chemical characterizations (either long chronicles or high resolution spatial characterization) and controlled reactive tracers test experiments. The latter will be particularly developed in the next years through the equipment project CRITEX. In particular, a mobile laboratory (an equipped truck) is currently developed within this project with the objective of bringing in the field sites the measuring instruments normally used in the laboratory, including chromatographs, to measure different chemical and microbiological components with high temporal resolution during the experiments.

In this context, I have been developing new field experimental methods in recent years to quantify in situ coupled mixing and biochemical reaction rates. Biofilms play a major role in controlling the fluxes and reactivity of chemical species transported in hydrological systems (e.g. Golfier et al., 2009). Their development can have either positive impacts on groundwater quality (e.g. attenuation of contaminants under natural or stimulated conditions), or possible negative effects on subsurface operations (e.g. bio-clogging of geothermal dipoles or artificial recharge systems). Micro-organisms require both electron donors and electron acceptors for cellular growth, proliferation and maintenance of their metabolic functions. The mechanisms controlling these reactions derive from the interactions occurring at the micro-scale that depend on mineral compositions, the biota of subsurface environment, but also fluid mixing, which determines the local concentrations of nutrients, electron donors and electron acceptors. Hence, **mixing zones between oxygen and nutrient rich shallow groundwater and mineralized deep groundwater are often considered as potential hotspots of microbial activity, although relatively few field data document flow distributions, transport properties, chemical gradients and micro-organisms distributions across these mixing interfaces.**

During the PhD thesis of Alexandre Boisson (2007-2010), I collaborated in setting up a field tracer test experiment to characterize in situ denitrification processes mediated by micro-organisms (Boisson et al., 2013). A reactive pushpull tracer test was carried out in the fractured crystalline aquifer of Ploemeur (H+ network). The kinetics of nitrate consumption and by product formation (NO_2^- , N_2O)

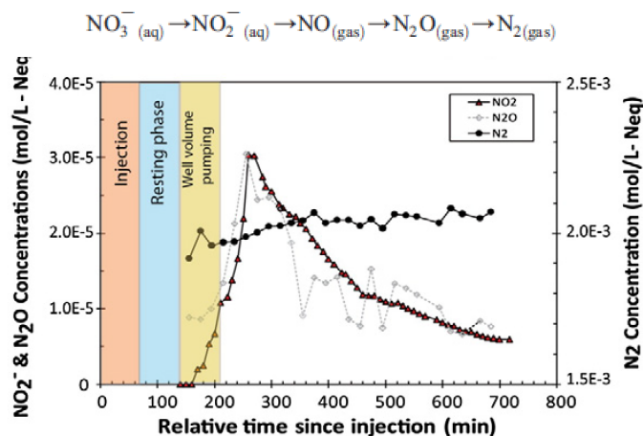


Figure 17: Results of the reactive pushpull test experiment: breakthrough curves for the reaction by-products NO_2^- , N_2O , and N_2 (H+ Ploemeur test site).

during autotrophic denitrification were quantified by using a reactive tracer (NO_3^-) and a non reactive tracer (Br^-). Comparison of Br^- and NO_3^- breakthrough curves showed that 10% of the injected NO_3^- molar mass was transformed during the 12 h experiment (2% into NO_2^- , 1% into N_2O and the rest into N_2 and NO), see figure 17. Field chemical rates were compared to batch experiments performed on rock and water samples from the site. This field experiment demonstrated the reliability of using pushpull tests to assess the autotrophic denitrification reaction including by-product formation. The NO_3^- reduction coefficient rates determined from laboratory experiments revealed lower coefficients than the field estimates. This study provided a first set of coefficients for the complete reaction kinetics which was not available previously. To interpret the push pull experiment, we extended the analytical solution developed by Haggerty et al. (1998) to model an entire 1st order reaction chain and estimate the kinetic parameters for each reaction step of the denitrification process.

In the PhD thesis of Olivier Bochet (2014-), we currently investigate the origin of a localized massive biofilm development observed in the fractured granite aquifer at the Ploemeur observatory (H+ network hplus.ore.fr). This biofilm composed of ferro-oxidating bacteria is observed in an 130m deep artesian well (figure 18). Borehole video logs show an important colonization of the well by the biofilm in the shallower part (0 to 60m), while it is inexistent in the deeper part (60 to 130m). As flow is localized in a few deep and shallow fractures, we presume that the spatial distribution of biofilm is controlled by mixing between shallow and deep groundwater. To verify this hypothesis we have conducted a field campaign with joint characterization of the flow and chemical composition of water flowing from the different fractures, as well as the microbiological composition of the biofilm at different depths, using pyrosequencing techniques. Interpretations are currently on-going. The objective in the next months is to design and perform in situ reactive tracer test experiments to characterize the response of this system to changes in flow and chemical conditions.

4.5 Hydrogeophysical imaging of flow structures and transport processes

The subsurface flow heterogeneity is at the root of the complex dispersion, mixing and reaction processes described in the previous sections. Since my doctorate, I have continuously been involved in field experimentation, which is particularly important for ensuring that the developed models and lab experiments are relevant for application to natural systems. **The characterization of underground structures, fluxes, chemical reactivity and biological activity in these flow systems demands the development of novel geophysical methods, innovative sensors and in situ experimental approaches.** A range of innovative technologies and methodologies have been developed in recent years, based on emergent interdisciplinary approaches integrating diverse methods

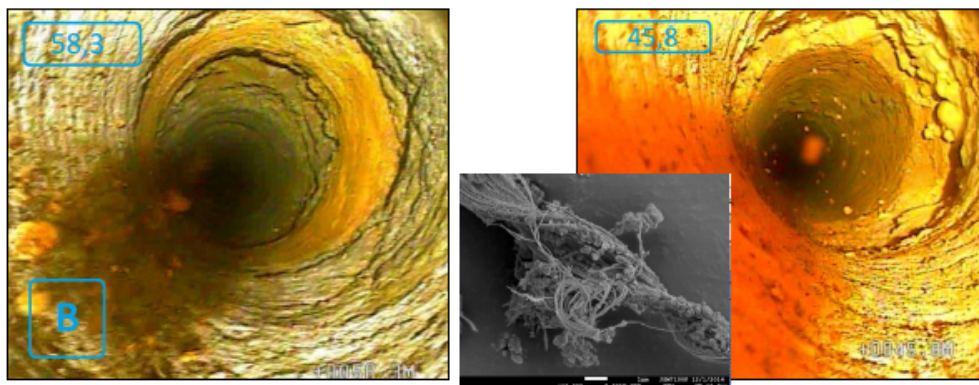


Figure 18: Borehole videos showing in PZ26 Borehole (H+ Ploemeur test site) showing the development of a large biofilm in a mixing zone at 45 m (right). At 58 m the biofilm is no longer observed (left). The microscope image suggest that the biofilm is formed by *Gallionella* bacteria .

from geophysics, hydrology, soil physics, geochemistry and biology. These innovative imaging methods represent a new opportunities for enhancing our knowledge of subsurface hydrological systems and monitor their evolutions, for understanding coupled hydro-thermo-chemical coupled processes and for using this knowledge and understanding to improve water resources management.

4.5.1 Context

Geophysics has played a prominent role in recent progress to (1) image hydrologically relevant subsurface structures, (2) estimate the spatial distribution of subsurface properties controlling flow and transport, and (3) monitor subsurface processes associated with natural or engineered in situ perturbations (National.Research.Council, 2012). Enhanced spatial resolution has been obtained from a more accurate physical description of the measurement processes such as in full waveform data inversion. Hydrogeophysical research has led to new strategies to combine hydrological and geophysical data to enhance resolution and reduce characterization uncertainty (Hubbard and Linde, 2011) (figure 19). Current research focuses on strategies that integrate multiple and disparate data types in ways that account for scale effects, error sources, inherent geological uncertainty and prior knowledge of subsurface properties, knowledge about the processes being monitored and their response to known boundary conditions and perturbations of the system, and appropriate rock physics relationships. These relationships are fundamental to link geophysical properties to those of primary interest for hydrology (Slater, 2007) (e.g., porosity, hydraulic conductivity, clay content, water content, salinity, contaminant concentrations, microbial activity...).

Important instrumental and methodological advances have also been achieved in hydraulic and tracer investigation techniques. In particular, tomographic approaches that employ repeated measurements using multiple hydrologic perturbations and monitoring points offer enhanced spatial resolution (Cardiff et al., 2013). The combined use of different tracers, including heat or reactive tracers is considered a promising approach to reduce characterization uncertainty of transport processes and conceptual models . Furthermore, the development of new sensor technologies has enabled the measurement of variables, fluxes and properties that were not achievable before. Fibre-optic distributed temperature sensing yields new opportunities for direct spatially distributed measurements of fluxes, in particular at interfaces between surface and subsurface hydrological systems. Spectral induced polarization methods open up new ways to map distributions of subsurface hydraulic properties and to monitor biogeochemical processes.

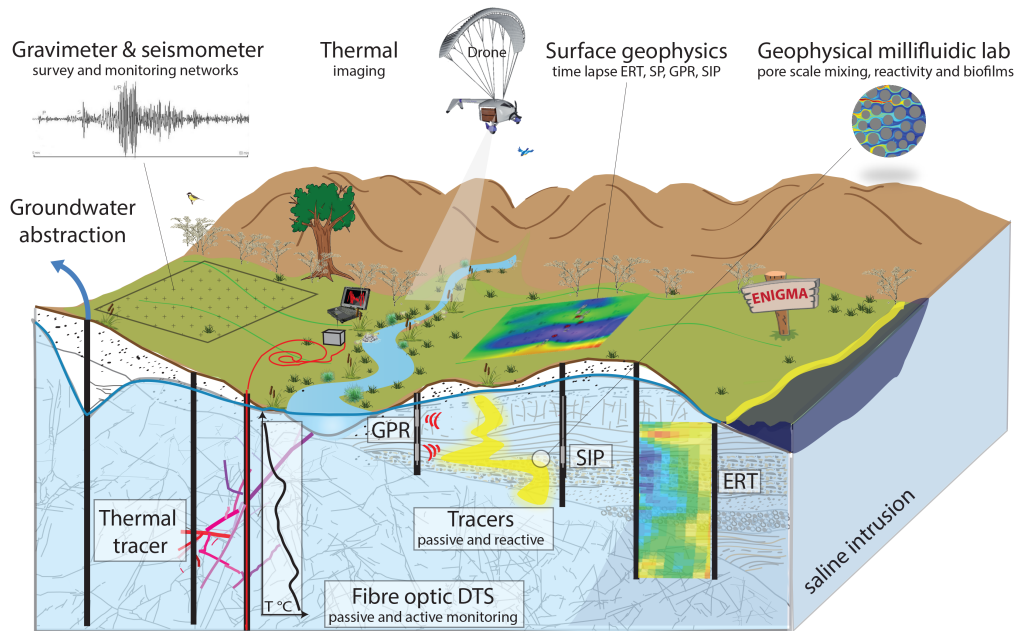


Figure 19: Co-location of different imaging techniques on densely monitored experimental sites to quantify subsurface spatial structures, fluxes, heat transfer and reactive transport phenomena (ENIGMA network proposal, see perspective section).

4.5.2 Inverting in situ flow measurements for fracture hydraulic properties and connectivity

The accurate characterization of the location, hydraulic properties, and connectivity of major fracture zones is essential to model flow and solute transport in fractured media. Cross-borehole flowmeter tests, which consist of measuring changes in vertical borehole flows when pumping a neighboring borehole (figure 20), were shown to be an efficient technique to provide information on the properties of the flow zones that connect borehole pairs (e.g. Le Borgne et al., 2006, 2007). The interpretation of such experiments may, however, be quite uncertain when multiple connections exist. In the PhD thesis of Maria Klepikova (2009-2013), **we have developed a flow tomography tomography approach (i.e., sequential cross-borehole flowmeter tests) for characterizing aquifer heterogeneity** (Klepikova et al., 2013). We have proposed a framework for inverting flow and drawdown data to infer fracture connectivity and transmissivities. In particular, we have demonstrated that successively exchanging the roles of pumping and observation boreholes improves the quality of available information and reduces the under-determination of the problem. The inverse method was validated for several synthetic flow scenarios. It is shown to provide a good estimation of connectivity patterns and transmissivities of main flow paths. It also allows the estimation of the transmissivity of fractures that connect the flow paths but do not cross the boreholes, although the associated uncertainty may be high for some geometries.

We then further developed the method to passive temperature tomography experiments in which borehole temperature profiles are measured under different pumping conditions by changing successively the pumping and observation boreholes (figure 20). To interpret these temperature-depth profiles, we propose a three step inversion-based framework (Klepikova et al., 2014). We consider first an inverse model that allows for automatic permeable fracture detection from borehole temperature profiles under pumping conditions. Then we apply a borehole-scale flow and temperature model to produce flowmeter profiles by inversion of temperature profiles. This second step uses inversion to characterize the relationship between temperature variations with depth and borehole flow velocities

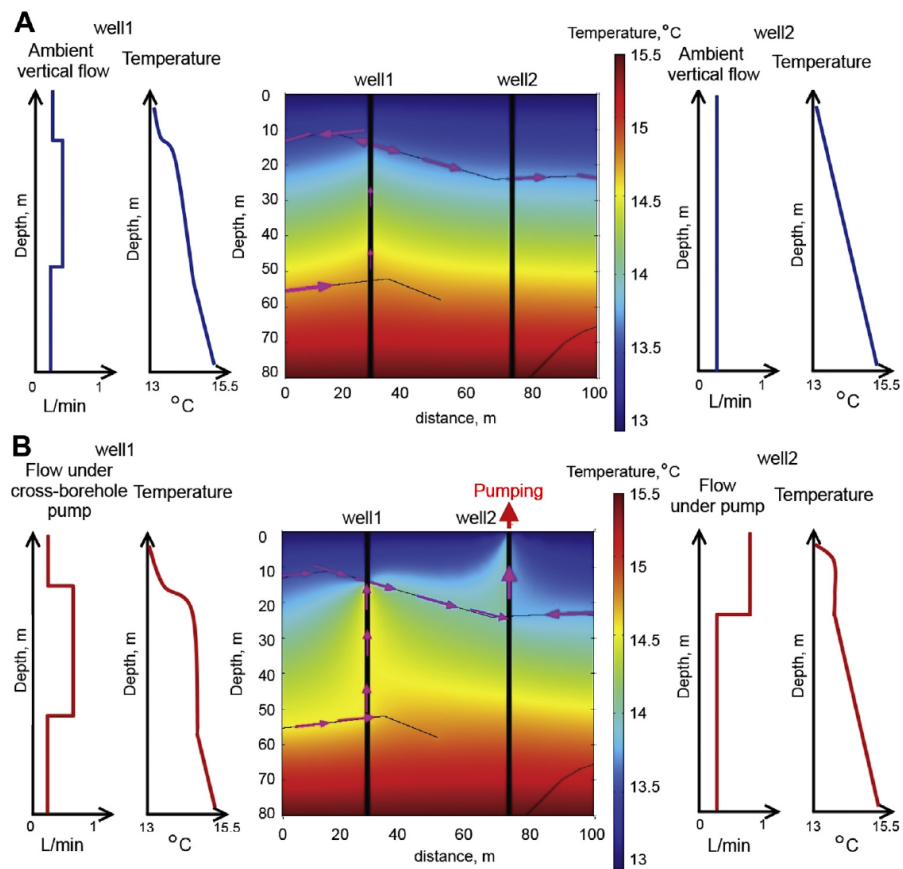


Figure 20: Illustration of a typical groundwater flow and temperature fields for a pair of boreholes connected by one main flow path and intersected by one disconnected fracture in each borehole under ambient (A) and pumping (B) flow conditions. The velocity field and temperature field are computed using a 2D model (after Klepikova et al. (2014)).

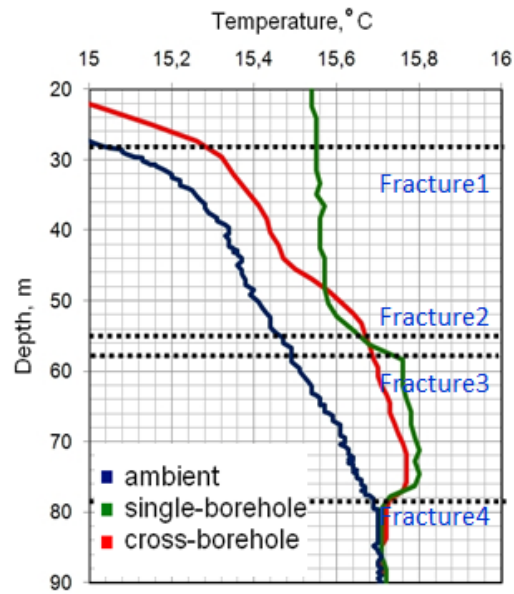


Figure 21: (A) Temperature profiles in B2 (H+ Ploemeur test site) measured under different flow conditions. The blue curve presents temperature profile under ambient flow. The green curve was collected while pumping with pumping at the top of B2 with a pumping rate $Q = 125$ l/min. The red curve corresponds to the cross-hole pumping test while pumping was turned on in B3 with a pumping rate $Q = 145$ l/min.

(Klepikova et al., 2011), see figure 21. The third inverse step, which exploits cross-borehole flowmeter tests, is aimed at inferring inter-borehole fracture connectivity and transmissivities. This multi-step inverse framework provides a means of including temperature profiles to image fracture hydraulic properties and connectivity. We tested the proposed approach with field data obtained from the H+ Ploemeur fractured rock aquifer, where the full temperature tomography experiment was carried out between three 100 m depth boreholes 10 m apart. We identified several transmissive fractures and their connectivity which correspond to known fractures and corroborate well with independent information, including available borehole flowmeter tests and geophysical data. Hence, although indirect, temperature tomography appears to be a promising approach for characterizing connectivity patterns and transmissivities of the main flow paths in fractured rock.

4.5.3 Thermal imaging of fractured media with distributed temperature sensing fibre optic

The passive temperature tomography methodology presented above has shown the interest of temperature as a tracer of heterogeneous flow distributions in the subsurface. **This motivated a broader use of temperature for detecting and quantifying flow in heterogeneous media** through a new collaboration developed with John Selker (Oregon State University) and Victor Bense (East Anglia university UK) based on fully distributed space-time measurements with Fiber-Optic Distributed Temperature Sensing (FO-DTS). Heat injection experiments were combined with temperature measurements along fiber-optic cables installed in boreholes. Thermal dilution tests were shown to enable detection of cross-flowing fractures and quantification of the cross flow rate. A cross borehole thermal tracer test was then analyzed to identify fracture zones that are in hydraulic connection between boreholes and to estimate spatially distributed temperature breakthrough in each fracture zone (figure 22). This technique provides a significant improvement compared to classical tracer tests, for which concentration data are usually integrated over the whole abstraction borehole (Read et al., 2013).

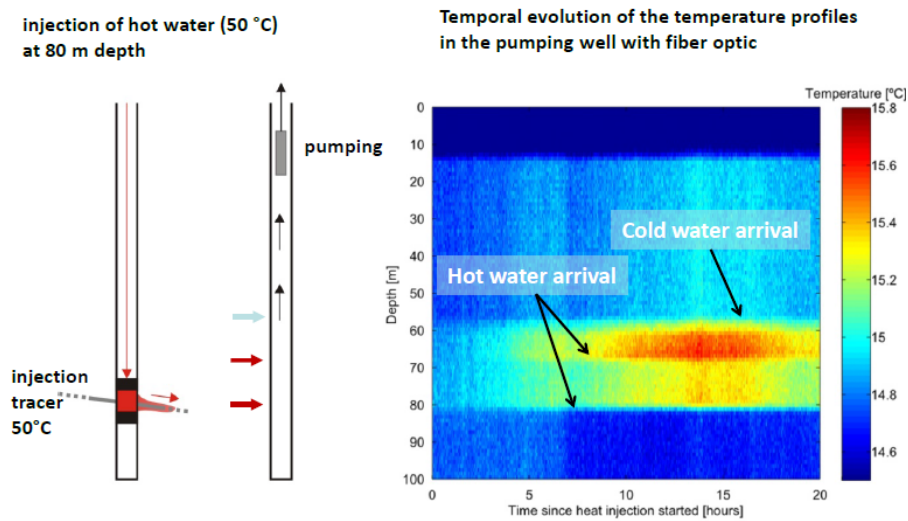


Figure 22: Fiber optic DTS measured temperature monitoring of a thermal tracer test from B1 to B2 (H+ Ploemeur test site).

All the above applications involve temperature monitoring with non-heated fiber optic (passive mode). Alternatively, DTS can be deployed in an active mode, which we call Active-DTS (A-DTS), defined as the distributed measurement of temperature along a FO cable with a distributed heat source incorporated into or in contact with the same cable, where the temperature data collected while actively heating are of primary interest. These temperature data reflect the combined efficiency of heat dissipation from the cable and the surrounding medium, so that spatially distributed estimates of the surrounding physical properties or fluid fluxes are possible. **We thus showed how a distributed borehole flowmeter can be created from armored Fiber Optic cables with the Active-Distributed Temperature Sensing (A-DTS) method.** The principle is that in a flowing fluid, the difference in temperature between a heated and unheated cable is a function of the fluid velocity. We have outlined the physical basis of the methodology and report on the deployment of a prototype A-DTS flowmeter in a fractured rock aquifer (Read et al., 2014). With this design, an increase in flow velocity from 0.01 to 0.3m/s elicited a 2.5C cooling effect.

4.5.4 Radar imaging of transport in fractured media

Spatially distributed temperature sensing is expanding significantly our capacity to image the spatial distribution of flow in the subsurface. Although indirect information on large scale flowpath permeability and connectivity can be derived with this technique, direct flow measurements are still limited to boreholes. **New techniques based on time lapse geophysical monitoring of tracer experiments have recently emerged in recent years for exploring flow and transport processes outside boreholes.** Through a collaboration with Niklas Linde (University of Lausanne), we have demonstrated that saline tracer experiments combined with single hole ground penetrating radar (GPR) reflection imaging can be used to monitor saline tracer movement within *mm* aperture fractures (PhD thesis of Caroline Dorn).

A dipole tracer test was performed in the H+ Ploemeur granitic aquifer by injecting a saline solution in a known fracture, while repeatedly acquiring single hole GPR sections in the pumping borehole located 6 m away. The final depth migrated difference sections make it possible to identify consistent temporal changes at locations corresponding to fractures previously imaged in GPR sections acquired under natural flow and tracer free conditions (Dorn et al., 2011). The experiment allows determining the dominant flow paths of the injected tracer and the velocity (0.4 to 0.7m/min) of the tracer front. Based on this novel dataset Caroline Dorn was able to stochastically generate three-

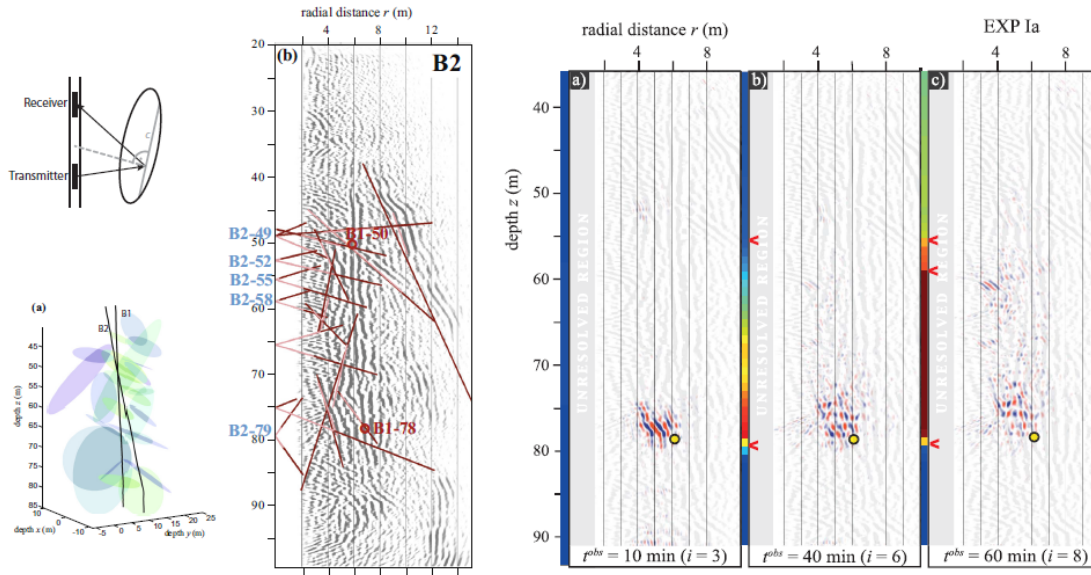


Figure 23: Radar imaging of transport in fracture media. Left: principle of reflection imaging with borehole Ground Penetrating Radar and stochastically generated discrete fracture network conditioned on radar data. Middle: imaging of conductive fractures up to 100 meters depth and 14 meters radial distance from the borehole. Right: Time lapse images of a saline tracer injected at 80 meters depth.

dimensional discrete networks of connected fractures conditioned to hydrological and geophysical data (Dorn et al., 2013). We analyzed a set of 230 posterior realizations that reproduce all data given their uncertainties assuming the same uniform transmissivity in all fractures. The posterior models provide valuable statistics on length scales and density of connected fractures, as well as their connectivity. In an additional analysis, effective transmissivity estimates of the posterior realizations indicated a strong influence of the DFN structure, in that it induces large variations of equivalent transmissivities between realizations.

4.5.5 Large scale signature of flow heterogeneity

The multi-scale heterogeneity implies a potential scale dependency of effective flow and transport properties. To investigate the impact of flow heterogeneity at larger scale in fractured media, we have analyzed the hydraulic response to recharge of a fractured aquifer, using a frequency domain approach (Jimenez-Martinez et al., 2013), see figure 24. Transfer functions were calculated in a range of temporal scales from 1 day up to a few years, for the H+ Ploemeur fractured crystalline-rock aquifer, using recharge and groundwater level fluctuations as input and output respectively. The spatial variability of the response to recharge (characteristic response time, amplitude, temporal scaling) was analyzed for 10 wells sampling the different compartments of the aquifer. Some of the transfer functions follow the linear reservoir model behavior. On the contrary, others display a temporal scaling at high frequency that cannot be represented by classic models. Large-scale hydraulic parameters, estimated from the low-frequency response, were compared with those estimated from hydraulic tests at different scales (figure 25). The variability of transmissivity and storage coefficient was found to decrease with scale, and the average estimates converge toward the highest values at large scale. The small-scale variability of diffusivities, which implies the existence of a range of characteristic temporal scales associated with different pathways, is suggested to be at the origin of the unconventional temporal scaling of the hydraulic response to recharge at high frequency.

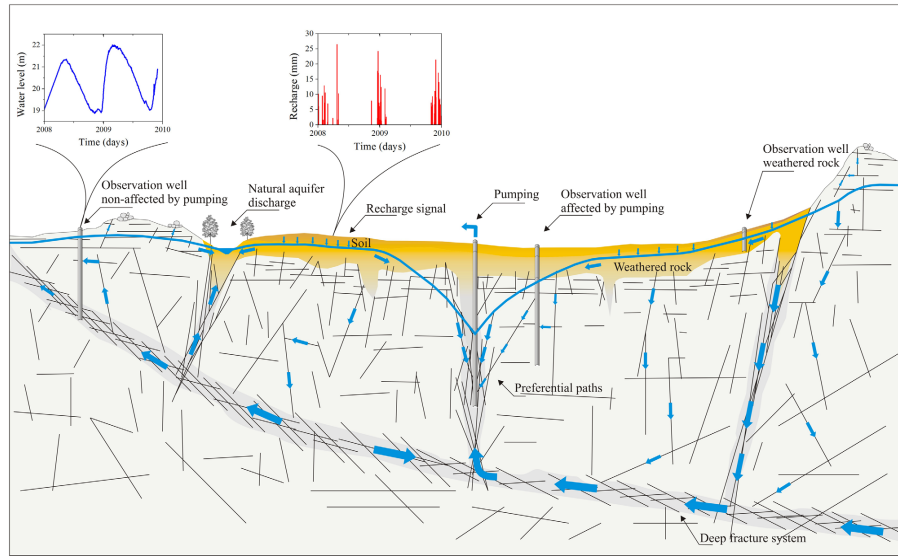


Figure 24: Conceptual scheme of a fractured aquifer. Fracture networks are characterized by a multiscale heterogeneity. Arrow size represents the relative contribution to the flow of the different structures (from Jimenez-Martinez et al. (2013)).

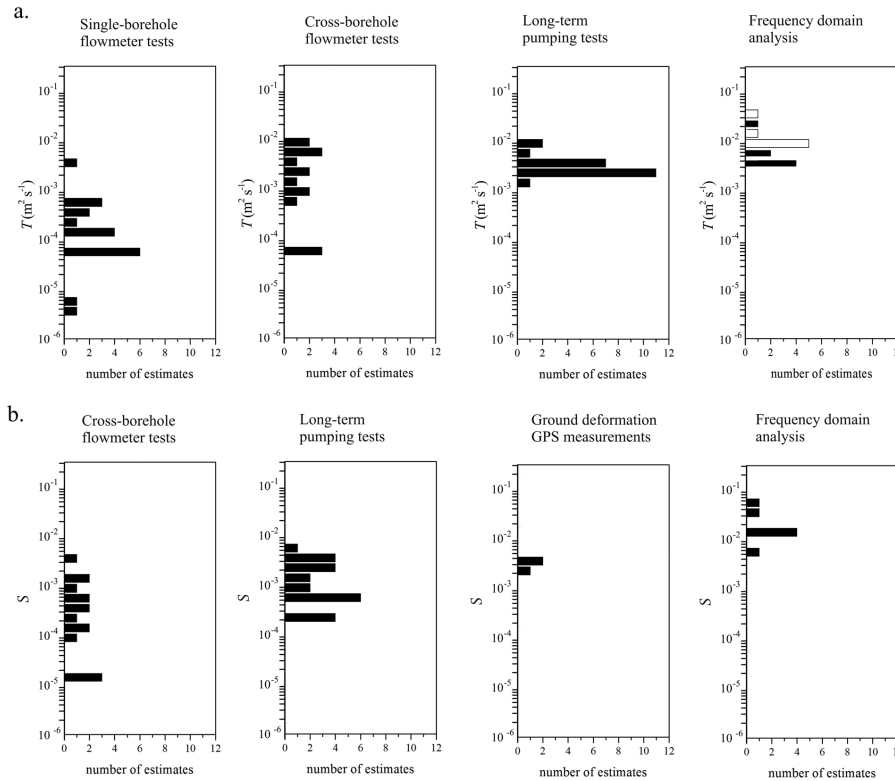


Figure 25: Storage coefficient (a) and transmissivity (b) estimates from field techniques (single-borehole flowmeter, cross-borehole flowmeter and long-term pumping tests, from ground deformation by GPS measurements, and frequency domain analysis). Plots are organized according to increasing observation scale from left to right. Two different aquifer lengths L are used to compute transmissivity values from the frequency domain analysis (equation (10)): 2000 m (black bars) ; 3000 m (white bars), (from Jimenez-Martinez et al. (2013)).

4.6 Conclusions

My research has been evolving during the last ten years from the study of subsurface flow distributions and their consequences for upscaled dispersion properties, to the analysis of mixing processes that determine concentration distributions and subsequent chemical reactions. I have developed this research through continuous exchanges between theoretical modeling, numerical simulations and experimentation in the field and in the lab. This has led to a number of scientific progresses on the development and validation of new models that capture the impact of flow heterogeneity on subsurface transport processes, as well as innovative instruments to image and monitor these processes in situ. Transfer to applications has been developed more specifically during the last years as closer exchanges and projects have been established with industrial partners, including Antea group (international consulting company on environment, energy and water), ADEME (the french environmental and energy agency) and TOTAL.

The results presented here have been obtained through close collaborations with colleagues in France and abroad including:

Marco Dentz, CSIC research centre, Barcelona, Spain modeling of transport processes in heterogeneous media,

Niklas Linde, University of Lausanne, Switzerland geophysical imaging of transport in fractured media,

Pietro de Anna, Peter Kang, Ruben Juanes, MIT, USA experimental characterization and modeling of transport processes in heterogeneous media

Emmanuel Villiermaux, University of Aix-Marseille, France modeling of mixing in porous media, IRPHE Marseille,

Diogo Bolster, Notre Dame University, USA modeling of transport processes in heterogeneous media,

Victor Bense, Tom Read, University of East Anglia, UK in situ measurement of flow velocities from distributed fiber optic sensing,

John Selker, Oregon State University, USA in situ measurement of flow velocities from distributed fiber optic sensing,

Tim Ginn, University of California at Davis, USA modeling reactive transport in heterogeneous media,

Olivier Bour, Yves Méheust, Philippe Davy, Jean-Raynald de Dreuzy, Luc Aquilina, Laurent Longuevergne, Géosciences Rennes, CNRS, University of Rennes 1, France Field and lab experimentation, and numerical modeling of flow and transport processes in heterogeneous media.

5 Scientific challenges and perspectives

In the next years, I will focus my research on the study of reactive transport processes, which are largely controlled by the temporal dynamics and spatial distribution of solute concentrations as discussed in the previous section. This research will be mostly funded by the ERC project ReactiveFronts (2015-2020).

5.1 Context

Reactive processes occurring in flow through porous materials have recently received increasing attention because they play a key role in a number of important applications, including CO₂ sequestration (Jha et al., 2011; Szulczewski et al., 2012; Chaudhary et al., 2012), fracture patterns formation and reaction-enhanced permeability (Malthe-Sorensen and Meakin, 2006; Jamtveit et al., 2008) and the degradation of pollutants at the fringes of contaminated plumes, either in natural conditions or during remediation operations. Reactive processes are commonly involved in engineering activities that involve the mixing of oxygen-rich surface water and mineralized groundwater. The latter creates highly reactive fronts which may generate drastic permeability reduction due to clogging and dramatically impact the efficiency of injection processes. This represents a major issue for instance in artificial recharge operations, unconventional irrigation, or geothermal doublets where the extracted groundwater is re-injected after heat extraction. **While much progress has been made to characterize and model flow and transport processes in porous media, their coupling with biochemical reactions remains a largely open question.**

In reactive systems, biochemical transformation rates depend on the probability of chemical species, either dissolved or in solid phase, to meet and react. Thus, the large-scale reactive behavior results from the microscale distribution of chemical gradients, which are often strongest at mixing interfaces between different water bodies (e.g. McClain, 2003). In this context, large parts of subsurface water bodies may be viewed as in equilibrium with the host aquifer and characterized by relatively low reactivity compared to the mixing interfaces between these different water bodies. Typically, due to the non-linearity of the mass action law, the mixture of two waters, both at equilibrium with the host rock, creates disequilibrium and generates precipitation or dissolution processes (e.g. de Simoni et al., 2007). Hence, the assumption that mixing front reactivity is the main contribution to the large scale effective reaction rates constitute a novel paradigm that is worth being tested.

5.2 A paradigm shift from dispersion to mixing

Classical macro dispersion transport theories are known to be poorly predictive for modeling chemical reactions in these systems (Kapoor et al., 1997; Kapoor and Kitanidis, 1998; Gramling et al., 2002; Cirpka et al., 2008a; Tartakovsky et al., 2009; Battiato et al., 2009; de Anna P. et al., 2011). The main reason is that they assume that chemical species are well mixed at the relevant support scale and therefore focus on the potential reactive volume rather than on the actual reactive volume localized along mixing interfaces (Le Borgne et al., 2011b). Let me demonstrate the problem with the example of subsurface remediation operations. Reactants and/or biochemical catalysts are injected to remediate a solute contaminant plume. The injected solution pushes the plume before it. Therefore the reaction between the target plume contaminant and the injected solutes occurs primarily along the interface between the two solutions. Transport modeling has focused historically on the plume itself and not on the interface, and calculation of the plume motion has had primary focus on the spatial moments of the plume, and more recently on the tailing behavior of the plume, resulting in various nonlocal transport upscaling models (e.g. Berkowitz et al., 2006; Neuman and Tartakovsky, 2009). Although these theories provide useful predictive models for the motion of non-reactive solutes, they do not accommodate well in general the nonlinearities of biogeochemical reactions (Dentz et al., 2011).

Recently, hydrogeologists have recognized that the typical measures of plume spreading do not represent the actual mixing between displacing and displaced solutions, and that understanding actual mixing is the key to quantifying biogeochemical reactions. Intensive research efforts over the last decades have led to the definition of hybrid' models that deliver the mean behavior of the species concentration on the one hand and information on local concentrations on the other hand (Dentz et al., 2011). These models include the multicontinuum approach (e.g. Lichtner and Kang, 2007; Donado et al., 2009), the stochastic-convective approach (e.g. Cirpka and Kitanidis, 2000; Ginn, 2001; Seboonruang and Ginn, 2006) and reactive particles approaches (Benson and Meerschaert, 2008; Ederly

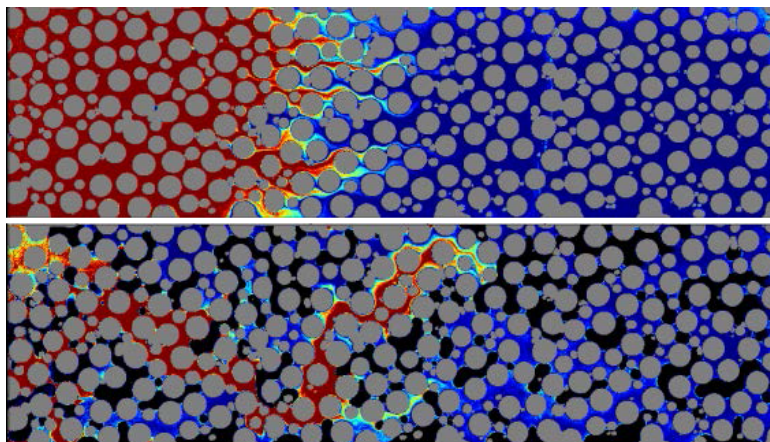


Figure 26: Conservative mixing front experiments. On the top the concentration field of a passive tracer front injected from left to right in a saturated porous medium (tracer concentration from red to yellow, water in blue and solid grains in grey). On the bottom the concentration field of the same passive tracer injected in unsaturated conditions: the dark zones represent air clusters (from Jiménez-Martnez, under review).

et al., 2009). The main issue with these conceptual models is that their parameters cannot be generally related to the basic properties of the structural heterogeneity (variability, spatial organization) or to the fluid dynamics, and thus their predictive capacity is highly debated.

5.3 Major open scientific questions and key experimental challenges

In the context of reactive fronts, the lack of a solid conceptual framework to quantify the coupling between flow heterogeneities and biochemical processes represents a major gap of knowledge which is addressed in this proposal. I list three major scientific questions (S1-S3) and two key experimental issues (E1-E2) related to this challenge:

S1 The impact of flow dynamics on reaction kinetics in porous media While the importance of mixing interface deformation in the control of effective reaction kinetics has been largely recognized in the context of turbulent and chaotic flows (Ranz, 1979; Ottino, 1989; Jimenez and Martel, 1991; Tel et al., 2005), this coupling remains largely unexplored in porous media flows because of the difficulty to observe reactive flow structures in these opaque systems. Yet, while the porous media structure does not deform in general, the flow heterogeneity at different scales is expected to generate similar folding and stretching as in open flows (Le Borgne et al., 2013). Figure 26 displays a 2D experiment of mixing front displacement in porous media (Jimenez-Martinez et al., under review). The mixing front, initially oriented perpendicular to the main flow direction, distorts into a brush made of a collection of strips, aligned on average with the direction of the mean flow, thus forming a lamella-like topology (Ottino, 1989). This stretching process, generated by the action of spatial velocity gradients, strongly enhances diffusive mass transfer across the interface by steepening the chemical gradients and elongating the surface of contact between the different solutes. The same experiment performed in unsaturated conditions shows a much more complex mixing pattern with the coexistence of fast preferential flow paths and stagnation zones that develop in between the air clusters (Figure 26). This demonstrates the expected strong control of medium heterogeneity on mixing processes. The deformation of mixing fronts by the flow heterogeneity is expected to strongly affect effective reaction kinetics, although a quantitative framework is currently critically lacking for formalizing the fluid deformation reactivity coupling in porous media. The lamellar representation of fluid mixing in porous media flows that I have recently proposed (Le Borgne et al., 2013) may be a key to quantify this interaction and its impact on upscaled reactivity. This will be investigated in the present project.

S2 The coupling between fluid dynamics and biological activity and its impact of re-

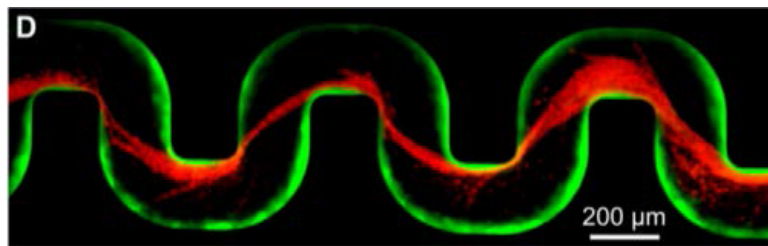


Figure 27: Experimentation investigation of the development of a biofilm streamer in channel. Biofilm streamers are exclusively composed of red cells, whereas very few red cells attach to the resident green biofilm on the wall, indicating that streamers consist of cells that were transported to the eventual clogging site by flow (from Drescher and Stone (2013)).

activity In many reactive front systems, microorganisms play a major role in triggering chemical reactions, producing catalysts or degrading pollutants. Mixing fronts generally provide particularly favorable conditions for micro-organism development as fluid mixtures provide them access to the main elements for the maintenance of their metabolic functions, that may otherwise be spatially segregated. Hence reactive fronts constitute favorable habitats for microorganism proliferation. Indeed, during microbial growth, the production of biomass can dramatically impact flow properties by clogging pores, or increasing grain surface roughness and surface area. Different microorganisms species coexist, cooperating or competing for space and nutrients which are not homogeneously distributed at the microscale (e.g. Sturman et al., 1994; Stewart et al., 1997; Castelle et al., 2014). Some bacteria may exploit chemical gradients by swimming toward zones highly concentrated in nutrient, whereas others survive in uniform background conditions (e.g. Or D. and Friedman, 2007). As in question S1, the control of flow dynamics, determining the spatial distribution of chemical gradients, on the motion and development of micro-organism is a largely open question. This issue is made even complex by the feedbacks of biofilm growth on flow dynamics, through the clogging of areas receiving most nutrients. This induces preferential flow paths between biofilm paths that may deviate the transport of nutrients and thus limit biofilm growth (e.g. Seymour et al., 2004; Durham et al., 2012). Moreover, the flow dynamics can also profoundly modify the morphology of biofilms through the formation of elongated biofilm streamers, creating a sieve-like network that captures cells and other biomass, as recently discovered by Drescher and Stone (2013), see Figure 27. The investigation of these micro-scale interactions and their effect on the large scale sets formidable theoretical and experimental challenges. Yet, the current scientific conjuncture is particularly favorable to foresee great advances in this domain, with fluid mixing models (see scientific question S1) and bio-microfluidic techniques (see experimental challenge E1) both reaching maturity at the same time.

S3 The upscaling of micro-scale fluid-bio-reactive processes to scales relevant to applications - The key challenge when attempting to make quantitative predictions is the wide scale gap between the scale of basic biochemical processes and the scale of field applications. The corresponding upscaling problem is particularly difficult as it involves flow heterogeneities inducing complex reactive structures and a multiscale variability physical and biochemical properties. Together with the development of models that couple flow heterogeneity and biochemical reactions, recent advances in both laboratory imaging and field investigation (see key experimental challenges below) provide new opportunities for establishing a quantitative framework of chemical reactivity upscaling in heterogeneous porous media.

E1 The microscale imaging of flow, mixing and biochemical kinetics - A major issue in porous media studies is the limited accessibility to the spatial organization of flow, concentration fields, reactive interfaces and micro-organism interactions. Traditional experiments rely on column studies where reactive components concentration may be measured at the outlet of the system and at best at some discrete points. New experimental methods and capacities based on Hele-Shaw experiments (Willingham et al., 2008; Rolle et al., 2009; de Anna et al., 2014b) are currently profoundly changing

our vision of coupled flow reaction processes at the pore scale, in 2D. A few groups have recently developed 3D experiments to investigate the distribution of pore-scale velocities or the spatial distribution of biofilm using confocal microscopy or micro-tomography (e.g. Davit et al., 2011). However, to our knowledge no experiments have successfully imaged the spatial distribution of reaction rates in 3D porous media. Building on recent technological breakthroughs (de Anna et al., 2014b) and interdisciplinary collaborations (H. Tabuteau, Physics department, A. Dufresne, Ecology department), the team assembled at OSUR has a strong potential to obtain significant advances and form a leading group in this domain.

E2 The in situ characterization of reactive transport at field scale - While synthetic experimental models can provide much information about basic processes and their coupling, the heterogeneity of a synthetic model built in a laboratory cannot capture all the relevant features of natural environments. How to characterize and model chemical reactivity in the field is a long standing issue. A range of new in situ experimental methodologies have recently been developed for measuring biochemical reaction rates from reactive tracer tests in the field (e.g. Istok, 2013). Furthermore, measureable geophysical signatures have been observed to be produced by biological activity, although it is still difficult to distinguish between the multiple origins of the measured signals (Atekwana and Slater, 2009). Biogeophysics may be a promising avenue for mapping the spatial distribution of biological activity in reaction fronts. Strong investments have been made over recent years for setting up highly instrumented field observatories (e.g. H+ network and CRITEX project in France, TERENO project in Germany, CZO network in USA), which is presage a fast pace of progresses over coming years.

5.4 Methodology that will be developed in the ERC project ReactiveFronts

5.4.1 The reactive lamella approach for upscaling the impact flow dynamics on chemical reactions in porous media

In order to describe and quantify mixing processes in heterogeneous subsurface environments, I propose to integrate biogeochemical transformation processes into a new modeling approach of reactive transport based on a kinematics of mixing that focuses on the deformation of the interface between displacing and displaced fluids. In this framework, reactive fronts will be represented as an ensemble of stretched material lines, called lamellae, composing the backbone of the mixing interfaces deformed by the action of heterogeneous advection (Figures 7, 13). In preliminary studies, I have quantified the lamella deformation process and the statistics of interaction of neighboring lamellae, termed diffusive coalescence. These processes control the local concentration gradients and thus the evolution of the concentration mixture through stretching-enhanced diffusion. This novel theoretical framework provides an accurate prediction of the conservative concentration probability distributions (Le Borgne et al., 2013). As reaction rates are controlled by the distribution of species concentrations, we expect that it will be particularly relevant to predicting reactive transport in heterogeneous porous media. While this framework has been shown to successfully predict conservative mixing, it needs to be adapted so as to include biochemical reactions.

Elementary lamella scale reactivity - In order to solve the reaction-diffusion problem at the lamella scale (figure 28) we will use an appropriate change of variable, which allows converting the deformation-diffusion-reaction equation into a simple diffusion-reaction equation (Ranz, 1979; Meunier and Villiermaux, 2010). In case of reactions that are fast compared to transport processes, reactive species concentrations can be expressed as functions of the concentrations of conservative components (de Simoni et al., 2007). Hence, the results obtained for the concentration distribution in conservative mixing systems can be used to predict the reaction kinetics. A simple example demonstrates this idea (Le Borgne et al., 2014): for a linear shear flow, the reaction rates are expected to increase with time t as $\nabla v \sqrt{Dt}$, where D is the diffusion coefficient and ∇v is the velocity gradient causing the shear deformation (figure 14). This is due to the fact that concentration gradients are steepened by the

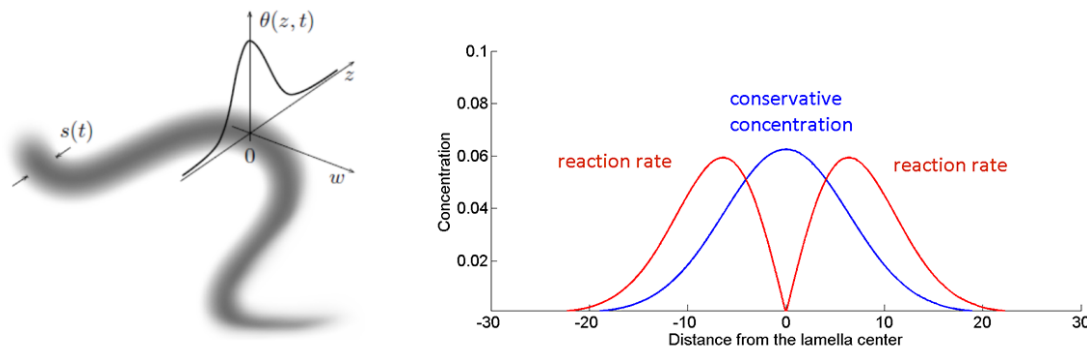


Figure 28: Lamellar representation of mixing and reactive transport. In the direction transverse to the lamella, the concentration field around a lamella, evolving under stretching and diffusion, can be approximated by a Gaussian distribution (left) that is fully parametrized by the lamella deformation history. For fast chemical reactions, local reaction rates can be estimated from the spatial distribution of the conservative component. The reaction rates are maximal where the concentration gradients are steepest (right).

lamella deformation and that the surface area available for diffusive mass transfer increases constantly with time. This result is in contrast with the purely diffusive case, for which the reaction rate decays as $1/\sqrt{Dt}$, since concentration gradients are smeared out in time by diffusion. This simple example shows that flow heterogeneity is expected to have a strong impact on effective reaction rates. We will investigate this phenomenon for heterogeneous flows existing in porous media using the lamellar representation of fluid mixing (Le Borgne et al., 2013). We will further investigate the impact of the ratio of advective to diffusive time scales (Péclet number) and the ratio of transport time scales to chemical reaction time scales (Damkhler number). We will study complex multispecies reaction by coupling the fluid deformation-diffusion problem with chemical reactions modeled using the widely used code Phreeqc that can handle complex chemical reactions.

Upscaling and collective lamellae behavior In the lamellar representation of mixing and reaction, the upscaling procedure consists in analyzing the collective behavior of an ensemble of lamellae, stretched by the flow field, diffusing, reacting and merging. Since reaction rates depend non-linearly on the concentrations, the global behavior does not result in general from a simple additive effect of reactions at each lamella. Different collective behaviors are expected to arise under different flow and reaction regimes (characterized by the Péclet and Damkhler numbers) which control the geometry of the mixing front and the distribution of concentrations within it. These behaviors will be analyzed in a first step by considering fast chemical reactions, for which the reaction rates can be derived explicitly from conservative concentration distributions. The study will then be extended to a range of reaction kinetics. Using this approach, we will establish constitutive laws to describe the impact of heterogeneity on upscaled reaction rates.

5.4.2 Millimicro fluidics to open a new window on micro-scale flow-mixing-reaction interactions

Exploring a range of structural heterogeneities, reaction rates and flow conditions relevant for porous media systems The versatility of the experimental system will be exploited to investigate different grain geometries and size distributions, that can be constructed from the lithography technique, different Damkhler numbers (representing the ratio of chemical to mixing time scales), that can be created by tuning the chemiluminescent reaction by modifying combination of the catalysts, different flow conditions, including parallel injections, sequential injections or point injections of the two reactive solutes. Keeping the diffusion coefficient constant, we will vary the flow rate in order to analyse mixing and reactions under a broad range of flow and transport conditions (i.e for a large range of

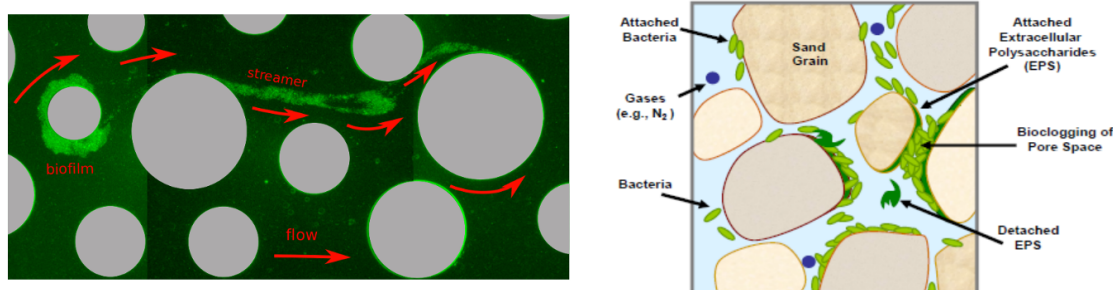


Figure 29: Left: microfluidic imaging of biofilm dynamics in porous media (image provided by P. de Anna, MIT). The transport of nutrients regulates the growth rate of biofilm structures which can trigger the formation of preferential flow channels by pore clogging. This channeling of the flow conveys the transport of nutrients by the flow around biofilm patches, limiting their growth rate. On the other hand, biofilm streamers are created by the flow field, increasing drastically the surface area available for nutrient intake. Right: schematic of main processes involved in bacteria motion and development (from Atekwana, biogeophysics lecture, Cargese summer school 2010).

Péclet numbers). Furthermore, in this setup the grain can be coated with reactive layers such as metal elements, which will allow studying fluid-solid reactions, which play a key role in many geochemical processes. Finally, the experimental setup will be adapted to explore effective reaction kinetics of multiphase flows, already operational for non-reactive mixing (figure 26).

5.4.3 Uncovering the coupling of fluid dynamics and biological activity in porous media flows

Fluid deformation is known to be a key factor in controlling the spatial distribution of micro-organisms in heterogeneous flows, as recently highlighted for oceanic flows (Stocker, 2012; Durham et al., 2013; Rusconi et al., 2014b). This relationship is unknown for porous media flow since these interactions are generally inaccessible due to the opacity of the solid grains. The objective is i) to quantify how fluid stretching in porous media shapes the distribution of micro-organisms by controlling the spatial gradients of chemical element and nutrient concentrations, and ii) to investigate the feedback mechanisms of biofilm growth on the flow distribution, through bioclogging processes.

Bio-microfluidics - The coupling between flow dynamics and bacteria activity will be studied from high resolution microfluidic experiments (e.g. Rusconi et al., 2014a) allowing to resolve at the same time the position of individual bacteria, biofilm growth patterns, flow structures and changes in permeability induced by clogging (Figure 29). Experiments will be run using selected bacterial strains, with the objective of imaging the flow and concentration fields over time scales ranging from the second to the week. The joint imaging of flow, concentration and micro-organisms will represent a major technological breakthrough which is expected to provide new insights in the coupling between flow dynamics, mixing processes and biological activity. These results will be interpreted in the reactive lamella framework, which will need to be adapted for this purpose.

5.4.4 3D flow topologies and the role of chaotic mixing in reactivity enhancement

This research line is motivated by the recent theoretical conjecture of our collaborator Daniel Lester from CSIRO Melbourne (Lester et al., 2013), which suggests that the fluid deformation properties in 3D may differ significantly from their 2D counterparts due to the additional degree of freedom. In this work, Daniel Lester and his collaborators argue that the growth of material interfaces due to fluid stretching is much faster in 3D (exponentially fast) leading to chaotic fluid mixing processes. If verified this conjecture would have a profound impact on reactive transport representations as chaotic

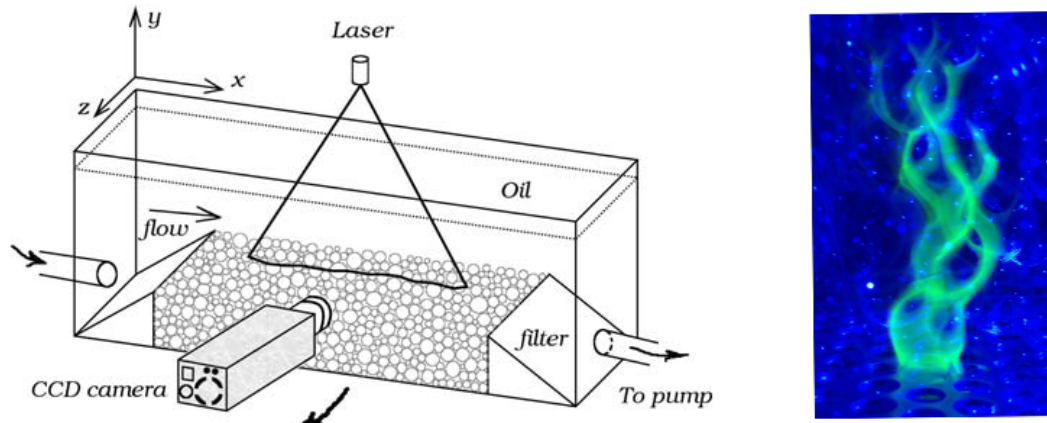


Figure 30: Illustration of the 3D milli-fluidic experimental set up under construction for conservative mixing (PhD thesis R. Turuban). Left: schematics of the measurement principle (from Morad and Khalili (2009)). Right: preliminary results obtained for concentration field imaging.

mixing processes are known to strongly enhance effective upscaled reaction kinetics. For instance, chaotic mixing in oceanic flows is suggested to explain the coexistence of different types of competing planktonic species, while they would not coexist in fully mixed flows (Tel et al., 2005), one of them dominating the others. Chaotic mixing may also be forced and controlled by designing appropriated pumping and injection protocols (Trefry et al., 2012). Complex patterns may be generated by alternating simple dipole flows, which are commonly created by pumping and injection wells in the field. The resulting drastic increase of the mixing interface length is expected to significantly enhance effective reaction rates, which is a possible avenue for designing more efficient remediation strategies.

A new prototype for imaging three dimensional reaction rates - A new milli-fluidic experimental set up is currently developed in Rennes (PhD thesis Régis Turuban) to investigate flow kinematics and mixing properties of conservative solutes in 3D heterogeneous porous media, using laser sheets and synchronized cameras to measure the concentration distribution in indexed-matched porous materials. Based on this principle, we propose to develop the first experimental set up able to image the spatial distribution of reactive tracers in a 3D porous medium (figure 30). We will pack transparent solid grains distributed in size, such as plastic or glass beads, into analogous medium. In order to image the spatial distribution of concentration products in 3D, we will test chemical reactions involving a fluorescent product, a technique recently developed by C. Almarcha (IRPHE laboratory). Furthermore, we will take advantage of the confocal microscope available at IPR to test the imaging of concentration within microscale 3D porous media, which offers access to small scale features (colloids, bacteria) and have some practical advantages (injection control, production of 3D porous material, increasing the statistics through a larger number of grains).

Modeling reaction kinetics in 3D and chaotic flows - In order to model chemical reactions under chaotic mixing conditions, the theoretical framework developed above will be extended to exponential stretching behaviors. Furthermore, we propose to extend this conceptual model to 3D by considering 2D stretched sheets instead of lamellae. In this framework, the mixing surfaces in 3D will be decomposed in a series of elementary surfaces (sheets) that are deformed by the flow field and carry concentration fields that evolve under the combined action of stretching and diffusion.

5.4.5 In situ imaging of fluid mixing and biochemical processes

In situ processes are much more complex and difficult to characterize than in the lab since natural systems are characterized by strong physical, chemical and microbiological heterogeneities and can be accessed directly only through boreholes. Yet field validation is in my view an essential step for the completion of conceptual developments towards operational tools. My objective is to identify and

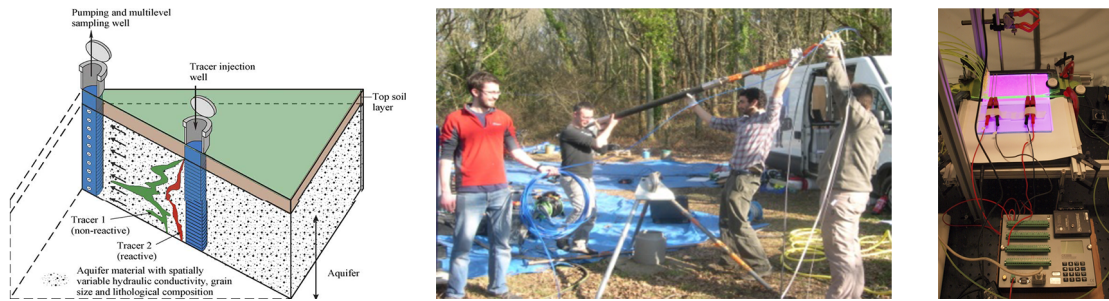


Figure 31: Left: illustration of the reactive tracer test principle (Ptak et al., 2004; Istok, 2013). Center: photo of field operation during 2012 tracer test campaign on H+ site. Reactive and non reactive tracers are simultaneously injected in the medium. Their concentration, evolving through dispersion, mixing and reaction, can be measured in a neighboring borehole or in the injection borehole after reversal of the flow. Right: geophysical millifluidic prototype currently developed in Rennes to investigate the potential for monitoring mixing and reactive transport processes with geophysical measurements such as Electrical Resistivity, Spontaneous Potential and Spectral Induced Polarization (collaboration J. Jimenez-Martinez, D. Jougnot, N. Linde).

characterize the salient field scale properties that are controlled by small scale mixing processes, such as the dependence of reaction rates on the flow conditions or on the scale of investigation. In particular, the dependence of the effective measured reaction rate on the characteristic spatial experiment scale should be directly dependent on the surface of the mixing front (green area in figure 31) as quantified in the modeling concept described above. I will take advantage of the synergy with on-going field activities in the Rennes group and H+ network to test the applicability of the new modeling concepts in natural media. For this, the interpretation framework will be based on intermediate scale models containing the basic ingredients observed and modelled at the pore scale.

Innovative in situ methodologies and smart tracers - A range of new field methodologies have recently been developed for measuring biochemical reaction rates in the field (e.g. Istok 2013). When a reactive and a non-reactive tracer are simultaneously injected in the medium, their concentrations can be simultaneously detected at the monitoring well. The difference between the concentrations of the two tracers provides a quantification of effective reaction rates. The tracers can be measured in neighbouring boreholes (dipole-multipole configuration) or in the same injection borehole after reversal of the flow (push-pull configuration). Using this methodology, we have recently successfully performed and interpreted such tests to estimate denitrification rates under bacteria mediated biochemical reactions using a calibrated reactive transport models (Boisson et al., 2013). This methodology will be extended to a range of (bio)chemical reactions, such as oxydo-reduction reactions, aerobic and anaerobic transformations or sorption-desorption processes. A mobile chemical laboratory (an equipped truck) is currently being developed within the CRITEX project with the objective of bringing in the field sites the measuring instruments normally used in the laboratory, including chromatographs, to measure the different chemical and microbiological components with high temporal resolution during the experiments. We will explore the use of smart tracers that become fluorescent when exposed to biochemical reactions. For example Resazurin is a compound that degrades to Resorufin in the presence of living bacteria. As Resorufin is fluorescent it can be detected continuously in time using field spectrometers (Haggerty et al., 2009).

Biogeophysics Biogeophysics may be a promising avenue for mapping the spatial distribution of biological activity in reaction fronts (Atekwana and Slater, 2009). Before being tested in the field, the potential for geophysical monitoring of biological activity will be explored first by integrating electrodes in the 2D millifluidic setup presented above (figure 31). We have recently tested this approach for non-reactive tracers in collaboration with D. Jougnot and N. Linde (Univ. of Lausanne). These geophysical milli-fluidic experiments are particularly promising in that they allow addressing

the key question of the impact of subresolution processes on geophysical signals. Hence, geophysical signatures of biofilm will be studied in the laboratory using concurrent geophysical measurements (electrical conductivity, self potential and induced polarization) and controlled high-resolution camera images that will track the evolution of the local concentration field and biofilm spatial distribution in time.

Impact of flow dynamics on reaction kinetics - To investigate the impact of flow dynamics on reaction rates, we will analyze and model reactive tracers tests carried out under different flow conditions. The flow rate can be varied in order to change the ratio of transport rates to reaction rates (Damkehler number), which is expected to impact the chemical reactivity, although this has never been tested directly in the field. Based on the analysis of the impact of chaotic mixing on chemical reactions, chaotic mixing protocols will be tested on the field. This recently patented concept (Trefry et al., 2012) has not been tested in field conditions yet. If successful, this approach may represent a great potential to improve the efficiency of contaminated site treatment. In order to document the scale dependence of effective reaction rates reactive tracer tests will be performed at different scales: i) push-pull experiments with different duration of push phase, allowing for tracer exploration of a larger area; ii) dipole test with different distances between wells.

5.5 Perspective in field experimentation: the ENIGMA network proposal

In the next years, my objective, as a coordinator of the H+ network of experimental sites, is to develop collaborations and exchanges in Europe between teams that develop experimental field infrastructures, innovative sensors, hydrogeophysical inversion methods and subsurface models. A significant step in this direction has been achieved by submitting the Marie Curie International Training Network proposal ENIGMA: the European Training Network in Innovative Imaging Methods for Heterogeneous Aquifers (figure 32). The term imaging denotes herein the spatial representation of subsurface heterogeneity, fluxes, chemical reactivity and microbial activity, through the integration of interdisciplinary approaches from geophysics, hydrology, soil physics, geochemistry and microbiology. The teams that take part in this proposal are: CNRS and the H+ network, the Julich Research Center (Germany), the CSIC Barcelona research center (Spain), the University of Liege (Belgium), the UFZ Leipzig research center (Germany), the University of Tübingen (Germany), the University of Lausanne (Switzerland), the University of Neuchâtel (Switzerland), the University of Copenhagen (Denemark), the Oregon State University (USA) and Stanford University (USA). It also includes a number of closely involved industrial partners.

ENIGMA thus regroups leading academic and industrial partners in hydrogeophysical imaging, field experimentation, and heterogeneous porous and fractured media modeling, to train young scientists around three main Research Objectives (figure 19):

1. Develop innovative technologies and methodologies for imaging of subsurface systems,
2. Test, compare and validate these novel methods in highly instrumented experimental research sites, where the new results, data and open source codes will be made available to academia and industry through a common on-line database,
3. Integrate the produced datasets into predictive simulation tools to enhance process understanding and improve operational simulations for subsurface operations.

5.6 Conclusions

My research program for the coming year will promote the development of a new research line at OSUR for the experimental characterization and modeling of the dynamics of reactive mixing fronts in heterogeneous media (ERC project ReactiveFronts). This project will foster interdisciplinary collaborations in France (Geosciences Rennes lab, ECOBIO lab in Rennes, Rennes Physics Institute,

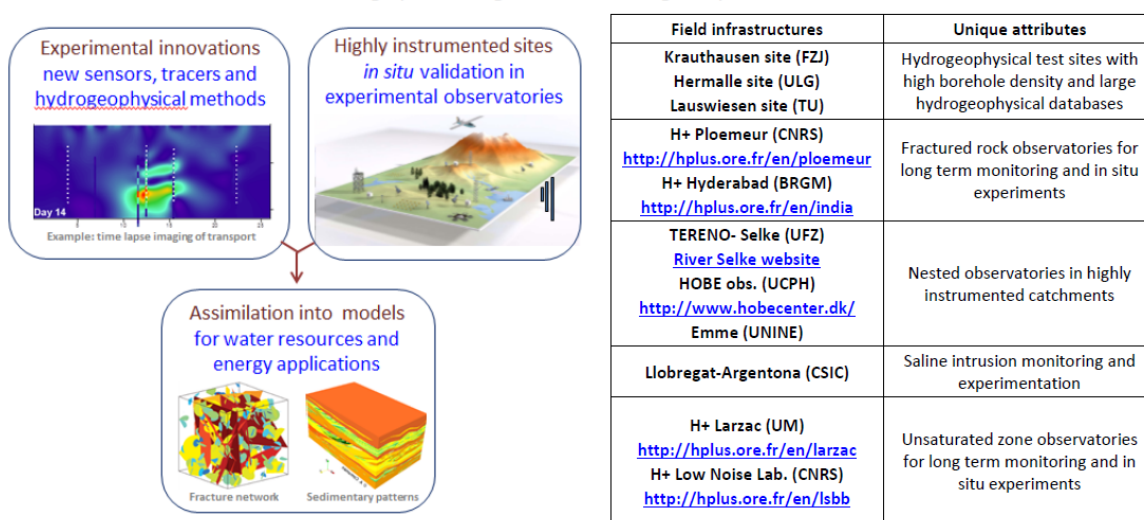


Figure 32: Left: Illustration of ENIGMA research and training strategy, Right: The most advanced European infrastructures for in situ hydrogeological investigations will form the basis of ENIGMA collaborative field campaigns for testing and comparing imaging methods in a range of environments.

IRPHE lab in Marseille) and internationally (CSIC Barcelona, CSIRO Melbourne, UC Davis). Possible new collaborations are currently being discussed with Kate Maher (Stanford) on the modeling of large scale fluid-solid geochemical reactions and with Sylvie Lorthois (CNRS IMFT Toulouse) on the modeling of transport processes in blood micro-circulation in the brain, which illustrates the wide spectrum of possible applications of these investigations.

6 Curriculum Vitae

6.1 Identification

6.1.1 Etat civil

Tanguy Le Borgne,

date de naissance : 13/08/1978,

NUMEN : 14S0700006HAV, section CNU : 35

6.1.2 Coursus académique

Thèse de doctorat effectuée au laboratoire Géosciences Rennes sous la direction de O. Bour et P. Davy (Géosciences Rennes) 2001-2004,

Master of Science in hydrology, Imperial College, London 2000-2001,

Ecole des Mines de Nancy 1998-2001

6.1.3 Carrière professionnelle

Physicien adjoint du Corps National des Astronomes et Physiciens (CNAP) depuis 2007,

Post-doctorat (bourse Marie Curie IEF) à l'Université Polytechnique de Catalogne, Barcelone 2006-2007,

Post-doctorat au laboratoire de Tectonophysique de Montpellier 2005-2006

6.2 Projets de recherché financés

Projet ERC consolidator ReactiveFronts (2015-2020) PI Tanguy Le Borgne, budget 2 million €,

Projet ANR jeune chercheur Subsurface mixing and reaction (2014-2018) PI Tanguy Le Borgne, budget 300 000 €,

Projet ADEME geoclogging (2015-2018), PI Tanguy Le Borgne, budget 250 000€, Etude des risques de colmatage et optimisation des procédés de traitement des doublets géothermiques superficiels, en partenariat avec l'entreprise ANTEA groupe,

Projet equipex CRITEX (2012-2019), PI Jerome Gaillardet (IPGP), budget 7 millions €, responsable de deux work packages, titre: Challenging equipment for the temporal and spatial exploration of the Critical Zone at the catchment scale,

Marie Curie initial training European network IMVUL (2008-2012), PI Noelle Odling (Leeds), coordinateur pour le CNRS, budget pour le CNRS: 500000€, titre: Towards improved ground-water vulnerability assessment (<http://www.see.leeds.ac.uk/imvul/index.htm>),

European INTERREG IV project CLIMAWAT (2009-2012) : <http://www.climawat.info/>, budget pour le CNRS et l'université de Rennes: 500000€,

Service national d'observation H+ (2002-présent), hplus.ore.fr, budget annuel : 120000€,

6.3 Organisation de conférences (école d'été et sessions dans des conférences internationales)

Director of the international summer school on Flow and Transport in porous and fractured media, 16-28 August 2010, Cargese institute, France,

Chairman AGU session Mixing and Reaction in Hydrological Systems: From Experiment to Theory and Back. AGU Fall Meeting, San Francisco, 2013,

Chairman Goldschmidt session Mixing, chemical reactions and biological activity in porous media, Florence, 2013,

Chairman SIAM Geosciences session The Complex Dynamics of Mixing and Chemical Reactions in Porous Media Padova, 2013,

Chairman AGU session Anomalous transport, mixing and reaction in hydrological systems. AGU Fall Meeting, San Francisco, 2012,

Chairman AGU session Multiscale Nature of Mixing and Reaction in Heterogeneous Media: Advances in Experiment and Theory. AGU Fall Meeting, San Francisco, 2011,

Chairman AGU session Mixing and Reactive Transport: From Pore to Field Scale. AGU Fall Meeting, San Francisco, 2010,

Chairman AGU session Mixing and Reactive Transport: From Pore to Field Scale. AGU Fall Meeting, San Francisco, 2010,

Chairman AGU session Hydrogeological Research Sites and Observatories. AGU Fall Meeting, San Francisco, 2008,

Chairman AGU session Flow and Reactive Transport in Heterogeneous Media: New Insights Obtained From the Interaction Between Experiment and Theory. AGU Fall Meeting, San Francisco, 2008,

Chairman AGU session: Flow and Transport in Heterogeneous Media: New Experimental and Modeling Approaches AGU Fall Meeting, San Francisco, 2007,

6.4 Conférences invitées

Le Borgne T., M. Dentz, E. Villermanx (2014) Stretching, mixing and coalescence in porous media, Turbulent mixing and beyond, International Centre for Theoretical Physics, Trieste, August 2014 (invited),

Le Borgne T., M. Dentz, P. de Anna, E. Villermanx (2014) The impact of hydrologic mixing processes on concentration distributions and associated reaction kinetics, 10th international symposium Geochemistry of the Earth's surface (GES-10) Institut de Physique du Globe de Paris, August 18-22 2014 (invited),

Le Borgne T., P. de Anna, M. Dentz, A. Tartakovsky (2012) Effective mixing and reaction front kinetics in porous media, Goldschmidt conférence, Montreal, keynote presentation (invited),

Le Borgne T., M. Dentz, P. Davy, D. Bolster, J. Carrera, J.-R. de Dreuzy, and O. Bour (1) (2012) Persistence of incomplete mixing in heterogeneous porous media, Computational Methods in Water Resources, University of Illinois Urbana-Champaign (invited),

Le Borgne T., M. Dentz, D. Bolster, and J. Carrera, J.R. de Dreuzy (2009), scaling of mixing and spreading in heterogeneous porous media, American Geophysical Union meeting, San Francisco (invited),

6.5 Séminaires invités

MIT, Boston, USA, December 2013, Mixing in porous and fractured media in situ observations, experimental imaging and theoretical upscaling, T. Le Borgne,

Physics of Geological Processes, Oslo, Norway, June 2013, Stretching, coalescence and mixing in porous media, T. Le Borgne,

Hydrogeological society of Chile, Santiago, Chile, April 2013, Mixing in hydrogeological systems, T. Le Borgne,

CSIRO Melbourne, Australia, March 2013, Mixing in heterogeneous porous media, T. Le Borgne,

Institute of Physics, Rennes, France, January 2013, Mixing and concentration PDF in porous media, T. Le Borgne,

NGRI Hyderabad, India, November 2012, Transport in fractured aquifers, T. Le Borgne,

ETH Zurich, Switzerland, November 2011, Upscaling dispersion and Mixing in Heterogeneous Porous Media", T. Le Borgne,

University of Lausanne, Switzerland, 2011, Persistence of incomplete mixing in heterogeneous flows: a key to model transport and reactivity in the subsurface, T. Le Borgne,

University of Bochum, Germany, 2011, Persistence of incomplete mixing in heterogeneous flows: a key to model transport and reactivity in the subsurface, T. Le Borgne,

Institut de recherche sur les phénomènes hors équilibre, Marseille, 2011, "Dispersion and Mixing in Heterogeneous Porous Media", T. Le Borgne.

6.6 Lien avec la formation à la recherche, capacité d'encadrement et prise de responsabilités collectives

Taches d'enseignement

18h ETD Modélisation hydrogéologique, master 2 "Hydrogéologie, hydrobiogéochimie, hydrogéologie"

12h ETD Transport en milieu poreux, master 2 "Hydrogéologie, hydrobiogéochimie, hydrogéologie"
et master 2 "Systèmes complexes naturels et industriels"

6h ETD stage terrain M2 "Hydrogéologie, hydrobiogéochimie, hydrogéologie"

30h ETD stage terrain M1 "Hydrogéologie, hydrobiogéochimie, hydrogéologie"

Responsabilités de module d'enseignement de master 2

Responsable du module "Modélisation hydrogéologique", niveau master 2 "Hydrogéologie, hydrobiogéochimie, hydrogéologie" de l'Université de Rennes 1.

Responsable du module "Transport en milieu poreux", niveau master 2 mutualisé entre les master 2 "Hydrogéologie, hydrobiogéochimie, hydrogéologie", module commun avec le master "Systèmes complexes naturels et industriels" de l'Université de Rennes 1.

Encadrement doctoral

Olivier Bochet (implication 50%), Université Rennes 1, 2013-2016, Caractérisation in situ de la dynamique des biofilms en milieu fracturé.

Regis Turuban (implication 50%), Université Rennes 1, 2012-2015, dispersion et mélange dans les milieux poreux non saturés.

Nicolas Guiheneuf (implication 25%), Université de Rennes 1, 2010-2013, caractérisation des écoulements et du transport dans les aquifères de socle: application à la gestion des ressources en eaux dans le sud de l'Inde, actuellement ATER à l'université de Rennes 1.

Peter Kang (implication 25%), 2010-2013, MIT, USA, caractérisation expérimentale et modélisation du transport dans les milieux fracturés, actuellement postdoctorant au MIT, USA.

Maria Klepikova (implication 50%), Université Rennes 1, 2009-2013, traçage thermique de l'hétérogénéité des écoulements dans les eaux souterraines, actuellement postdoctorante à l'ETH Zurich, Suisse.

Anna Russian (implication 25%), 2009-2013, UPC Barcelone, Espagne, théories multi-continuum pour la modélisation des aquifères hétérogènes, actuellement post-doctorante à l'université de Montpellier.

Caroline Dorn (implication 25%), 2009-2013, Université de Lausanne, Suisse, imagerie radar du transport dans les milieux fracturés, actuellement postdoctorante à l'université de Bern, Suisse.

Pietro de Anna (implication 50%), Université Rennes 1, 2009-2012, mélange et réactions en milieu poreux, actuellement postdoctorant au MIT, USA.

Encadrement de postdocs

Joaquin Jimenez-Martinez (implication 50%), 2010-2014, étude des processus de transport en milieu non-saturé, actuellement postdoctorant au Los Alamos National Lab, USA.

Pascal Goderniaux (implication 25%), 2010-2012, étude de l'impact du changement climatique sur la recharge des aquifères, actuellement professeur à l'université de Mons, Belgique.

Activités éditoriales

Reviewer pour *Geophysical Review Letters*, *Journal of Fluid Mechanics*, *Water Resources Research*, *Physical Review E*, *PLOS One*, *Advances in Water Resources*, *Journal of Hydrology*, *Journal of Contaminant Hydrology*, *Environmental Science and Technology*, *Transport in Porous Media*

Invited associated editor for a special issue of the *Journal of Contaminant Hydrology* on "Reactive Transport in the Subsurface: Mixing, Spreading and Reaction in Heterogeneous Media", Vol. 120-121, pages 1-236 (March 2011)

6.7 Liste complète de publications

2015

52. Le Borgne T., M. Dentz and E. Villermanx (in press) The lamellar representation of mixing in porous media, *J. of Fluid Mech.*
51. Ferrari A., J. Jimenez-Martinez, T. Le Borgne, Y. Meheust, I. Lunati (in press) Challenges in modeling unstable two-phase flow experiments in porous micromodels, *Water Resour. Res.*
50. Kang P. K., T. Le Borgne, M. Dentz, O. Bour, and R. Juanes (in press) Impact of velocity correlation and distribution on transport in fractured media : field evidence and theoretical model, *Water Resour. Res.*

2014

49. Le Borgne T., T. Ginn and M. Dentz (2014) Impact of Fluid Deformation on Mixing-Induced Chemical Reactions in Heterogeneous Flows, *Geophys. Res. Lett.*, Vol. 41, Issue 22, 78987906
48. de Anna, P., M. Dentz, A. Tartakovsky, and T. Le Borgne (2014) The filamentary structure of mixing fronts and its control on reaction kinetics in porousmedia flows, *Geophys. Res. Lett.*, Vol. 41, 4586-4593
47. Read, T., O. Bour, J. Selker, V. Bense, T. Le Borgne, R. Hochreutener, N. Lavenant (2014) Active-Distributed Temperature Sensing to continuously quantify vertical flow in boreholes, *Water Resour. Res.*, Vol. 50, 3706-3713
46. Bolster D., Y. Meheust, T. Le Borgne, J. Bouquain, P. Davy (2014) Modeling preasymptotic transport in flows with significant inertial and trapping effects - the importance of correlation and a spatial Markov modeling approach, *Adv. In Water Resour.*, Vol. 70, 89-103
45. de Anna, P., J. Jimenez-Martinez, H. Tabuteau, R. Turuban, T. Le Borgne, M. Derrien, and Y. Méheust (2014) Mixing and reaction kinetics in porous media : an experimental pore scale quantification, *Environ. Sci. Technol.* 48 (1), 508516
44. Leray S., de Dreuzy J. R., Aquilina L., Vergnaud-Ayraud V., Labasque T., Bour O., Le Borgne T. (2014) Temporal evolution of age data under transient pumping conditions, *J. of Hydrol.*, Vol. 511, 555566
43. Roques, C., O. Bour, L. Aquilina, B. Dewandel, S. Leray, J.H. Schroetter, L. Longuevergne, T. Le Borgne, R. Hochreutener, T. Labasque, N. Lavenant, V. Vergnaud-Ayraud (2014) Hydrological behavior of a deep sub-vertical fault in crystalline basement and relationships with surrounding reservoirs, *J. of Hydrol.* 509 (2014) 4254

2013

42. Le Borgne, T., M. Dentz, E. Villermaux (2013) Stretching, coalescence and mixing in porous media, *Phys. Rev. Lett.*, 110, 204501
41. de Anna, P., T. Le Borgne, M. Dentz, A. M. Tartakovsky, D. Bolster, P. Davy (2013) Flow Intermittency, Dispersion and Correlated Continuous Time Random Walks in Porous Media, *Phys. Rev. Lett.*, 110, 184502
40. Read, T. O. Bour, V. Bense, T. Le Borgne, P. Goderniaux, M.V., Klepikova, R. Hochreutener, N. Lavenant, and V. Boschero (2013) Characterizing groundwater flow and heat transport in fractured rock using Fiber-Optic Distributed Temperature Sensing, *Geophys. Res. Lett.*, VOL. 40, 15
39. Russian, A., M. Dentz, T. Le Borgne, J. Carrera and J. Jimenez-Martinez Temporal Scaling of Groundwater Discharge in Dual and Multi-Continuum Catchment Models, *Water Resour. Res.* Vol. 49, 8552-8564
38. Dorn, C., Linde, N., Le Borgne, T., Bour, O., de Dreuzy, J. R. (2013) Conditioning of stochastic 3-D fracture networks to hydrological and geophysical data, *Adv. in Water Resour.*, Vol. 62, Part A, 7989
37. Klepikova, M. V., Le Borgne, T., Bour, O., de Dreuzy J. R (2013), Inverse modeling of flow tomography experiments in fractured media, *Water Resour. Res.*, Vol. 49, Issue 11, 72557265
36. Jiménez-Martnez, J., L. Longuevergne, T. Le Borgne, P. Davy, A. Russian, O. Bour (2013) Temporal and spatial scaling of hydraulic response to recharge in fractured aquifers : insights from a frequency domain analysis, *Water Resour. Res.*, VOL. 49, 117
35. Goderniaux, P., P. Davy, E. Bresciani, J.-R. de Dreuzy, T. Le Borgne (2013) Partitioning a regional groundwater flow system into shallow local and deep regional flow compartments, *Water Resour. Res.*, VOL. 49, 113
34. Boisson, A., P. de Anna, O. Bour, T. Le Borgne, T. Labasque, L. Aquilina (2013) Reaction chain modeling of denitrification reactions during a pushpull test. *J. of Contam. Hydrol.*, 148, 111

2012

33. Dorn, C., Linde, N., Le Borgne, T., Bour, O. and Klepikova, M. (2012) Inferring transport characteristics in a fractured rock aquifer by combining single-hole GPR reflection monitoring and tracer test data, *Water Resour. Res.*, Vol. 48, W11521
32. J.-R. de Dreuzy, J. Carrera, M. Dentz, and T. Le Borgne (2012) Time evolution of mixing in heterogeneous porous media, *Water Resour. Res.* Vol. 48, W06511
31. Dorn, C., Linde, N., Doetsch, J., Le Borgne, T., Bour, O. (2012) Fracture imaging within a granitic rock aquifer using multiple-offset single-hole and cross-hole GPR reflection data, *Journal of Applied Geophysics*, 78, 123-132
30. Tartakovsky, A. M.; de Anna, P.; Le Borgne, T.; Balter, A.; Bolster, D. (2012) Effect of spatial concentration fluctuations on effective kinetics in diffusion-reaction systems, *Water Resour. Res.*, 48, W02526
29. de Dreuzy, J.-R.; Carrera, J.; Dentz, M.; Le Borgne, T. (2012) Asymptotic dispersion for two-dimensional highly heterogeneous permeability fields under temporally fluctuating flow, *Water Resour. Res.*, 48, W01532

2011

28. Le Borgne, T. D. Bolster, M. Dentz, P. de Anna, and A. Tartakovsky (2011) Effective pore-scale dispersion upscaling with a correlated continuous time random walk approach. *Water Resour. Res.*; Vol. 47, W12538
27. Le Borgne T., Dentz M., Davy P., Bolster D., de Dreuzy, J. R. and Bour O. (2011) Persistence of incomplete mixing : A key to anomalous transport *Phys. Rev. E*, 84, 1
26. Kang P., M. Dentz, T. Le Borgne and R. Juanes (2011) Spatial Markov model of anomalous transport through random lattice networks. *Phys. Rev. Lett.* 107, 180602
25. Dorn C., Linde N., Le Borgne T., O. Bour and L. Baron (2011) Single-hole GPR reflection imaging of solute transport in a granitic aquifer *Geophys. Res. Lett.* Vol.38, L08401
24. de Anna P., T. Le Borgne, M. Dentz, D. Bolster and P. Davy (2011) Anomalous kinetics in diffusion limited reactions linked to non-Gaussian concentration probability distribution function. *J. of Chem. Phys.* 135, 174104
23. Klepikova M., T. Le Borgne, O. Bour and P. Davy (2011), Single and cross-borehole temperature profiles for estimating fracture zone hydraulic properties, *J. of Hydrol.* 407, 145152
22. Dentz M., T. Le Borgne, A. Englert, B. Bijeljic (2011) Mixing, spreading and reaction in heterogeneous media : A brief review, Review Article *Journal of Contaminant Hydrology*, 120-121, 117.
21. Bolster D., Valdés-Parada, F. J., Le Borgne, T., Dentz, M., Carrera, J. (2011) Mixing in confined stratified aquifers, *J. Contam. Hydrol.* , Volumes 120-121, 1 March 2011, 198-212
20. Bolster D., M. Dentz and T. Le Borgne (2011) Hypermixing in linear shear flow, *Water Resour. Res.*, 47, W09602

2010

19. Le Borgne T., M. Dentz, D. Bolster, J. Carrera, J.-R. de Dreuzy, P. Davy (2010) Non-Fickian mixing : Temporal evolution of the scalar dissipation rate in porous media, *Advances in Water Resources*, Volume 33, Issue 12, 1468-1475,
18. Bolster D., D.A. Benson, T. Le Borgne, M. dentz (2010) Anomalous mixing and reaction induced by superdiffusive nonlocal transport, *Phys. Rev. E*, 82, 2.

2009

17. Dentz M, Bolster D, Le Borgne T. (2009) Concentration statistics for transport in random media, *Physical Review E*, 80, 1, 010101, Part 1
16. Dentz M, Carrera J, Bolster D, Le Borgne T. (2009) Multipoint concentration statistics for transport in stratified random velocity fields, *Phys. Rev. E*, 80, 3, 036306, Part 2
15. Bolster D., Dentz M., Le Borgne T. (2009) Solute dispersion in channels with periodically varying apertures. *Physics of Fluids* 21, 056601.
14. Pezard PA, Gautier S, Le Borgne T, et al. (2009) MuSET : A multiparameter and high precision sensor for downhole spontaneous electrical potential measurements *Comptes Rendus Geoscience*, 341, 10-11, 957-964

13. Gouze P, Leprovost R, Poidras T, Le Borgne T., Lods G., Pezard, P. A. (2009) CoFIS and TELog : New downhole tools for characterizing dispersion processes in aquifers by single-well injection-withdrawal tracer tests, *Comptes Rendus Geoscience*, 341, 10-11, 965-975

2008

12. Le Borgne T., Dentz M., and Carrera J. (2008) Lagrangian Statistical Model for Transport in Highly Heterogeneous Velocity Fields. *Phys. Rev. Lett.* 101, 090601.
11. Le Borgne T., Dentz M., and Carrera J. (2008). Spatial Markov processes for modeling Lagrangian particle dynamics in heterogeneous porous media. *Phys. Rev. E* 78, 026308.
10. Dentz M., Le Borgne T., and Carrera J. (2008) Effective transport in random shear flows. *Phys. Rev. E* 77, 020101 Rapid Communication.
9. Gouze P., T. Le Borgne, R. Leprovost, G. Lods, T. Poidras, P. Pezard (2008), Non-Fickian dispersion in porous media : 1. Multiscale measurements using single-well injection withdrawal tracer tests, *Water Resour. Res.*, 44, W06426
8. Le Borgne T., P. Gouze (2008), Non-Fickian dispersion in porous media : 2. Model validation from measurements at different scales, *Water Resour. Res.*, 44, W06427
7. Gouze, P., Y. Melean, T. Le Borgne, M. Dentz, and J. Carrera (2008), Non-Fickian dispersion in porous media explained by heterogeneous microscale matrix diffusion, *Water Resour. Res.*, 44, W11416

2007

6. Le Borgne T., Bour O, Riley MS, Gouze P, Pezard PA, Belghoul A, Lods G, Le Provost R, Greswell RB, Ellis PA, Isakov E, Last BJ (2007). Comparison of alternative methodologies for identifying and characterizing preferential flow paths in heterogeneous aquifers. *J. of hydrology*. 345 (3-4) : 134-148.
5. Le Borgne, T., J.-R. de Dreuzy, P. Davy, and O. Bour (2007), Characterization of the velocity field organization in heterogeneous media by conditional correlation, *Water Resour. Res.*, 43, W02419.

2006

4. Le Borgne T., Bour O., Paillet F.L. and Caudal J-P. (2006). Assessment of preferential flow path connectivity and hydraulic properties at single-borehole and cross-borehole scales in a fractured aquifer. *Journal of Hydrology*, Volume 328, Issues 1-2, 30 August 2006, 347-359.
3. Le Borgne, T., F. Paillet, L. O. Bour and Caudal J-P. (2006). Cross borehole flowmeter tests for transient heads in heterogeneous aquifers. Volume 44, Issue 3, 444-452, *Ground Water*.
2. Le Borgne T., O Bour., J-R. De Dreuzy, P. Davy (2006) Characterizing flow in natural fracture networks : Comparison of the discrete and continuous descriptions. *IAH-SP Volume groundwater in fractured rocks*.

2004

1. Le Borgne T., O Bour., J-R. De Dreuzy, P. Davy, F. Touchard (2004) Equivalent mean flow models relevant for fractured aquifers : Insights from a pumping tests scaling interpretation, *Water Resour. Res.*, 40, W05112, doi:10.1029/2003WR002436.

References

- Adams, E. E. and Gelhar, L. W. (1992). Field study of dispersion in a heterogeneous aquifer, 2. Spatial moment analysis. *Water Resour. Res.*, 28(12):3293–3308.
- Atekwana, E. A. and Slater, L. D. (2009). Biogeophysics: A new frontier in earth science research. reviews of geophysics. 47:RG4004.
- Battiato, I., Tartakovsky, D. M., Tartakovsky, A. M., and Scheibe, T. (2009). On breakdown of macroscopic models of mixing-controlled heterogeneous reactions in porous media. *Adv. Water Resour.*, 32:1664–1673.
- Bear, J. (1972). *Dynamics of fluids in porous media*. American Elsevier, New York.
- Bellin, A. and Tonina, D. (2007). Probability density function of non-reactive solute concentration in heterogeneous porous formations. *J. of Cont. Hydrol.*, 94:109–125.
- Benson, D., Schumer, R., Wheatcraft, S., and and, M. M. (2001). Fractional dispersion, levy motion, and the made tracer tests. *Transport in Porous Media*, 42:211–240.
- Benson, D., wheatcraft, S., and Meerschaert, M. (2000). The fractional-order governing equation of levy motion. *Water Resources Research*, 36:1413–1423.
- Benson, D. A. and Meerschaert, M. M. (2008). Simulation of chemical reaction via particle tracking: Diffusion-limited versus thermodynamic rate-limited regimes. *Water Resour. Res.*, 44:W12201.
- Berkowitz, B., Cortis, A., Dentz, M., and Scher, H. (2006). Modeling non-fickian transport in geological formations as a continuous time random walk. *Rev. Geophys.*, 44:RG2003.
- Bijeljic, B. and Blunt, M. J. (2006). Pore-scale modeling and continuous time random walk analysis of dispersion in porous media. *Water Resour. Res.*, 42:W01202.
- Boisson, A., de Anna, P. a. B. O., Le Borgne, T., Labasque, T., and Aquilina, L. (2013). Reaction chain modeling of denitrification reactions during a pushpull test. *J. of Contam. Hydrol.*, 148:1–11.
- Bolster, D., Meheust, Y., Le Borgne, T., Bouquain, J., and Davy, P. (2014). Modeling preasymptotic transport in flows with significant inertial and trapping effects - the importance of correlation and a spatial markov modeling approach. *Adv. In Water Resour.*, 70:89–103.
- Bolster, D., Valdes-Parada, F. J., Le Borgne, T., Dentz, M., and Carrera, J. (2011). Mixing in confined stratified aquifers. *J. of Cont. Hydrol.*, 120-121:198212.
- Bouchaud, J. P. and Georges, A. (1990). Anomalous diffusion in disordered media: Statistical mechanisms, models and physical applications. *Phys. Rep.*, 195(4,5):127–293.
- Brenner, H. (1980). Dispersion resulting from flow through spatially periodic porous media. *Proc. Roy. Soc. A*, 297:81–133.
- Brenner, H. and Adler, P. (1980). Dispersion resulting from flow through spatially periodic porous media ii surface and intraparticle transport. *Proc. Roy. Soc. A*, 307:149–200.
- Brenner, H. and Edwards, D. (1993). *Macrotransport Processes*. Butterworth-Heinemann, MA, USA.
- Cardiff, M., Barrash, W., and Kitanidis, P. K. (2013). Hydraulic conductivity imaging from 3-d transient hydraulic tomography at several pumping/observation densities. *Water Resour. Res.*, 49:7311–7326.

- Carrera, J., Sanchez-Vila, X., Benet, I., Medina, A., Galarza, G., and Guimera, J. (1998). On matrix diffusion: formulations, solution methods and qualitative effects. *Hydrogeology Journal*, 6:178–190.
- Castelle, L., Hug, A., Wrighton, K. C., Thomas, B. C., Williams, K. H., Wu, D., Tringe, S. G., Singer, S., Eisen, J., and Banfield, J. F. (2014). Extraordinary phylogenetic diversity and metabolic versatility in aquifer sediment. *Nat. Commun.*, 4:2120.
- Chastanet, J. and Wood, B. D. (2008). The mass transfer process in a two-region medium. *Water Resour. Res.*, 44:W05413.
- Chaudhary, K., M., C., Wolfe, W., Maisano, J., Ketcham, R., and Bennett, P. (2012). Pore-scale trapping of supercritical co2 and the role of grain wettability and shape. *Geophys. Res. Lett.*, 40.
- Chechkin, A. V., Hofmann, M., and Sokolov, I. M. (2009). Continuous time random walks with correlated waiting times. *Phys. Rev. E*, 80:031112.
- Chen, H. D., Chen, S. Y., and Kraichnan, R. H. (1989). Probability distribution of a stochastically advected scalar field. *Phys. Rev. Lett.*, 63(24):2657–2660.
- Cherblanc, F., Ahmadi, A., and Quintard, M. (2007). Two-domain description of solute transport in heterogeneous porous media: Comparison between theoretical predictions and numerical experiments. *Advances in Water Resources*, 20:1127–1143.
- Chiogna, G., Hochstetler, D., Bellin, A., Kitanidis, P., and Rolle, M. (2012). Mixing, entropy and reactive solute transport. *Geophys. Res. Lett.*, 30:L20405.
- Cirpka, O. A. and Kitanidis, P. K. (2000). An advective-dispersive streamtube approach for the transfer of conservative tracer data to reactive transport. *Water Resour. Res.*, 36:1209–1220.
- Cirpka, O. A., Schwede, R., Luo, J., and Dentz, M. (2008a). Concentration statistics of reactive constituents in random heterogeneous media. *J. Cont. Hydrol.*, 98:61–74.
- Cirpka, O. A., Schwede, R. L., Luo, J., and M., D. (2008b). Concentration statistics for mixing-controlled reactive transport in random heterogeneous media. *J. Cont. Hydrol.*, 98:61–74.
- Cirpka, O. A. and Valocchi, A. J. (2007). Two-dimensional concentration distribution for mixing-controlled bioreactive transport in steady-state. *Adv. in Water Resour.*, 30:1668–1679.
- Cushman, J. and Ginn, T. (1993). Nonlocal dispersion in media with continuously evolving scales of heterogeneity. *Transport in Porous Media*, 13:123–138.
- Cushman, J. and Ginn, T. (1994). Nonequilibrium statistical mechanics of preasymptotic dispersion. *Journal of Statistical Physics*, 75:859–878.
- Cushman, J. H. and Ginn, T. R. (2000). The fractional advection-dispersion equation is a classical mass balance with convolution-fickian flux. *Water Resour. Res.*, 36:3763–3766.
- Davit, Y., Iltis, G., Debenest, G., Veran-Tissoires, S., Wildenschild, D., Gerino, M., and Quintard, M. (2011). Imaging biofilm in porous media using x-ray computed microtomography. *Journal of microscopy*, 242:15–25.
- de Anna, P., Dentz, M., Tartakovsky, A., and Le Borgne, T. (2014a). The filamentary structure of mixing fronts and its control on reaction kinetics in porous media flows. *Geophys. Res. Lett.*, 41:45864593.
- de Anna, P., Jimenez-Martinez, J., Tabuteau, H., Turuban, R., Le Borgne, T., Derrien, M., and Méheust, Y. (2014b). Mixing and reaction kinetics in porous media: An experimental pore scale quantification. *Environ. Sci. Technol.*, 48(508-516):508516.

- de Anna, P., Le Borgne, T., Dentz, M., Tartakovsky, A. M., Bolster, D., and Davy, P. (2013). Flow intermittency, dispersion, and correlated continuous time random walks in porous media. *Phys. Rev. Lett.*, 110:184502.
- de Anna P., Le Borgne, T., Dentz, M., Bolster, D., , and Davy, P. (2011). Anomalous kinetics in diffusion limited reactions linked to non-gaussian concentration probability distribution function. *J. of Chem. Phys.*, 135:174104.
- de Barros, F., Dentz, M., Koch, J., and Nowak, W. (2012). Flow topology and scalar mixing in spatially heterogeneous flow fields. *Geophys. Res. Lett.*, 39:L08404.
- de Dreuzy, J. R., Carrera, J., Dentz, M., and Le Borgne, T. (2012). Time evolution of mixing in heterogeneous porous media. *Water Resour. Res.*, 48:W06511.
- de Simoni, M., Carrera, J., Sánchez-Vila, X., and Guadagnini, A. (2005). A procedure for the solution of multicomponent reactive transport problems. *Water Resour. Res.*, 41:2005WR004056.
- de Simoni, M., Sánchez-Vila, X., Carrera, J., and Saaltink, M. W. (2007). A mixing ratios-based formulation for multicomponent reactive transport. *Water Resour. Res.*, 43:W07419.
- Deng, F.-W., Cushman, J. H., and Delleur, J. W. (1993). A fast fourier transform stochastic analysis of the contaminant transport problem. *Water Resour. Res.*, 29:3241–3247.
- Dentz, M. (2012). Concentration statistics for transport in heterogeneous media due to stochastic fluctuations of the center of mass velocity. *Adv. Water Resour.*, 36.
- Dentz, M. and Berkowitz, B. (2005). Exact effective transport dynamics in a one-dimensional random environment. *Phys. Rev. E*, 72(3):031110.
- Dentz, M., Kinzelbach, H., Attinger, S., and Kinzelbach, W. (2000). Temporal behavior of a solute cloud in a heterogeneous porous medium, 1, point-like injection. *Water Resour. Res.*, 36(12):3591–3604.
- Dentz, M., LeBorgne, T., Englert, A., and Bijeljic, B. (2011). Mixing, spreading and reaction in heterogeneous media: A brief review. *J. Cont. Hydrol.*, 120-121:1–17.
- Dentz, M. and Tartakovsky, D. M. (2010). Probability density functions for passive scalars dispersed in random velocity fields. *Geophys. Res. Lett.*, 37:L24406.
- Donado, L. D., Sanchez-Vila, X., Dentz, M., Carrera, J., and Bolster, D. (2009). Multi-component reactive transport in multi-continuum media. *Water Resour. Res.*, 45:W11402.
- Dorn, C., Linde, N., Doetsch, J., Le Borgne, T., and Bour, O. (2012a). Fracture imaging within a granitic rock aquifer using multiple-offset single-hole and cross-hole gpr reflection data. *J. of Applied Geophysics*, 78:123–132.
- Dorn, C., Linde, N., Le Borgne, T., Bour, O., and Baron, L. (2011). Single-hole gpr reflection imaging of solute transport in a granitic aquifer. *Geophys. Res. Lett.*, 38:L08401.
- Dorn, C., Linde, N., Le Borgne, T., Bour, O., and de Dreuzy, J. R. (2013). Conditioning of stochastic 3-d fracture networks to hydrological and geophysical data. *Adv. in Water Resour.*, 62:7989.
- Dorn, C., Linde, N., Le Borgne, T., Bour, O., and Klepikova, M. (2012b). Inferring transport characteristics in a fractured rock aquifer by combining single-hole gpr reflection monitoring and tracer test data. *Water Resour. Res.*, 48:W11521.

- Drescher, K., Y. S. B. L. B. and Stone, H. A. (2013). Biofilm streamers cause catastrophic disruption of flow with consequences for environmental and medical systems. *Proc. Natl. Acad. Sci.*, 110:4345-4350.
- Duplat, J., Innocenti, C., and Villermaux, E. (2010). A nonsequential turbulent mixing process. *Phys. Fluids*, 22:035104.
- Duplat, J. and Villermaux, E. (2008). Mixing by random stirring in confined mixtures. *J. Fluid Mech.*, 617:51–86.
- Durham, W., Clement, E., Barry, M., De Lillo, F., Boffetta, G., Cencini, M., and Stocker, R. (2013). Turbulence drives microscale patches of motile phytoplankton. *Nature Communications*, 4:2148.
- Durham, W. M., Tranzer, O., Leombruni, A., and Stocker, R. (2012). Division by fluid incision: Biofilm patch development in porous media. *Phys. of Fluids*, 24.
- Ederly, Y., Scher, H., and Berkowitz, B. (2009). Modeling bimolecular reactions and transport in porous media. *Geophysical Research Letters*, 36(2):1–5.
- Fedotov, S., Ihme, M., and Pitsch, H. (2005). Stochastic mixing model with power law decay of variance. *Phys. Rev. E*, 71(1):016310.
- Fiori, A. (2001). The lagrangian concentration approach for determining dilution in aquifer transport: Theoretical analysis and comparison with field experiments. *Water Resour. Res.*, 37:3105–3114.
- Fiori, A. and Dagan, G. (2000). Concentration fluctuations in aquifer transport: a rigorous first-order solution and applications. *J. of Cont. Hydrol.*, 45(1-2):139–163.
- Fiorotto, V. and Caroni, E. (2002). Concentration statistics in heterogeneous aquifers for finite peclet values. *Transp. in Porous Media*, 48.
- Fox, R. O. (2004). *Computational Models for Turbulent Reacting Flows*. Cambridge University Press.
- Gelhar, L. W., Welty, C., and Rehfeldt, K. R. (1992). A critical review of data on field-scale dispersion in aquifers. *Water Resour. Res.*, 28(7):1955–1974.
- Ginn, T. R. (2001). Stochastic-convective transport with nonlinear reactions and mixing: finite stream-tube ensemble formulation for multicomponent reaction systems with intra-streamtube dispersion. *J. Contam. Hydrol.*, 47(1-2):1–28.
- Golfier, F., Wood, B. D., Orgogozo, L., Quintard, M., and Bues, M. (2009). Biofilms in porous media: Development of macroscopic transport equations via volume averaging with closure for local mass equilibrium conditions. *Adv. In Water Resour.*, 32:463–485.
- Gouze, P., Le Borgne, T., Leprovost, R., Lods, G., Poidras, T., and Pezard, P. (2008a). Non-Fickian dispersion in porous media: 1. multi-scale measurements using single well injection withdrawal tracer tests at the ses sitjoles/aliance test site (spain). *Water Resources Research*, 44:W06426.
- Gouze, P., Melean, Z., Le Borgne, T., Dentz, M., and Carrera, J. (2008b). Non-fickian dispersion in porous media explained by heterogeneous microscale matrix diffusion. *Water Resour. Res.*, 44:W11416.
- Gramling, C. M., Harvey, C. F., and Meigs, L. C. (2002). Reactive transport in porous media: A comparison of model prediction with laboratory visualization. *Environ. Sci. Technol.*, 36:2508 – 2514.
- Haggerty, R. and Gorelick, S. (1995). Multiple-rate mass transfer for modeling diffusion and surface reactions in media with porescale heterogeneity. *Water Resources Research*, 31:2383–2400.

- Haggerty, R., Mart, E., Argerich, A., von Schiller, D., and Grimm, N. B. (2009). Resazurin as a smart tracer for quantifying metabolically active transient storage in stream ecosystems. , (114): G03014. *J. of Geophys. Res.*, 114:G03014.
- Haggerty, R., Schroth, M., and Istok, J. (1998). Simplified method of pushpull test data analysis for determining in situ reaction rate coefficients. *Ground Water*, 36:314324.
- Hochstetler, D. L. and Kitanidis, P. K. (2013). The behavior of effective reaction rate constants for bimolecular reaction under physical equilibrium. *J. Contam. Hydrol.*, 144:88–98.
- Hubbard, S. and Linde, N. (2011). Hydrogeophysics, in s. uhlenbrook (ed.) , ch. 2.15, elsevier. *Treatise on Water*, 2:402–434.
- Istok, J. (2013). *Push pull tests for site characterization, lecture notes in earth system science*. Springer.
- Jamtveit, B., Malthe-Sorensen, A., and Kostenko, O. (2008). Reaction enhanced permeability during retrogressive metamorphism. *Earth and Planetary Sci. Lett.*, 267:620–627.
- Jha, B., Cueto-Felgueroso, L., and Juanes, R. (2011). Fluid mixing from viscous fingering, 301 phys. rev. lett., 106, 194,502. *Phys. Rev. Lett.*, 106:194,502.
- Jimenez, J. and Martel, C. (1991). Fractal interfaces and product generation in the two dimensional mixing layer. *Phys. of Fluids A*, 3:1261–1268.
- Jimenez-Martnez, J., Longuevergne, L., Le Borgne, T., Davy, P., Russian, A., and Bour, O. (2013). Temporal and spatial scaling of hydraulic response to recharge in fractured aquifers: Insights from a frequency domain analysis. *Water Resour. Res.*, 49:1–17.
- Kang, P. K., Dentz, M., Le Borgne, T., and Juanes, R. (2011). Spatial Markov model of anomalous transport through random lattice networks. 107:180602.
- Kang, P. K., Le Borgne, T., Dentz, M., Bour, O., and Juanes, R. (2015). Impact of velocity correlation and distribution on transport in fractured media : field evidence and theoretical model. *Water Resour. Res.*, in press.
- Kapoor, V. and Anmala, J. (1998). Lower bounds on scalar dissipation in bounded reactilinear flows. *Flow, turbulence and combustion*, 60:125–156.
- Kapoor, V., Gelhar, L., and Miralles-Wilhelm, F. (1997). Bimolecular second-order reactions in spatially varying flows: Segregation induced scale-dependent transformation rates. *Water Resour. Res.*, 33:527–536.
- Kapoor, V. and Kitanidis, P. K. (1998). Concentration fluctuations and dilution in aquifers. *Water Resour. Res.*, 34:1181–1193.
- Kitanidis, P. K. (1994). The concept of the dilution index. *Water Resour. Res.*, 30(7):2011–2026.
- Klepikova, M., Le Borgne, T., Bour, O., and Davy, P. (2011). Single and cross-borehole temperature profiles for estimating fracture zone hydraulic properties. *J. of Hydrol.*, 407:145152.
- Klepikova, M. V., Le Borgne, T., Bour, O., and de Dreuzy, J. R. (2013). Inverse modelling of flow tomography experiments in fractured media. *Water Resour. Res.*, 49:11.
- Klepikova, M. V., Le Borgne, T., Bour, O., Gallagher, K., Hochreutener, R., and Lavenant, N. (2014). Passive temperature tomography experiments to characterize transmissivity and connectivity of preferential flow paths in fractured media. *J. of Hydrol.*, 512:549562.

- Le Borgne, T., Bolster, D., Dentz, M., de Anna, P., and Tartakovsky, A. (2011a). Effective pore-scale dispersion upscaling with a correlated continuous time random walk approach. *Water Resour. Res.*, 47:W12538.
- Le Borgne, T., Bour, O., and Paillet, F.L. and Caudal, J.-P. (2006). Assessment of preferential flow path connectivity and hydraulic properties at single-borehole and cross-borehole scales in a fractured aquifer. *J. of Hydrol.*, 328:347–359.
- Le Borgne, T., de Dreuzy, J. R., Davy, P., and Bour, O. (2007). Characterization of the velocity field organization in heterogeneous media by conditional correlation. *Water Resour. Res.*, 43:2006WR004875.
- Le Borgne, T., Dentz, M., Bolster, D., Carrera, J., de Dreuzy, J. R., and Davy, P. (2010). Non-fickian mixing: Temporal evolution of the scalar dissipation rate in heterogeneous porous media. *Adv. in Water Resour.*, 33.
- Le Borgne, T., Dentz, M., and Carrera, J. (2008a). A Lagrangian statistical model for transport in highly heterogeneous velocity fields. *Phys. Rev. Lett.*, 101:090601.
- Le Borgne, T., Dentz, M., and Carrera, J. (2008b). Spatial markov processes for modeling lagrangian particle dynamics in heterogeneous porous media. *Phys. Rev. E*, 78:041110.
- Le Borgne, T., Dentz, M., Davy, P., Bolster, D., Carrera, J., de Dreuzy, J.-R., and Bour, O. (2011b). Persistence of incomplete mixing: A key to anomalous transport. *Phys. Rev. E*, 84:015301(R).
- Le Borgne, T., Dentz, M., and Villermaux, E. (2013). Stretching, coalescence and mixing in porous media. *Phys. Rev. Lett.*, 110:204501.
- Le Borgne, T., Dentz, M., and Villermaux, E. (2015). The lamellar representation of mixing in porous media. *J. of Fluid. Mech.*, in press.
- Le Borgne, T., Ginn, T., and Dentz, M. (2014). Impact of fluid deformation on mixing-induced chemical reactions in heterogeneous flows. *Geophys. Res. Lett.*, 41:78987906.
- Le Borgne, T. and Gouze, P. (2007). Non-fickian dispersion in porous media: 2. model validation from measurements at different scales. *Water Resour. Res.*, 44:W06427.
- Lester, D. R., Metcalfe, G., and Trefry, M. (2013). Is chaotic advection inherent to porous media flow ? *Phys. Rev. Lett.*, 111:174101.
- Lichtner, P. C. and Kang, Q. (2007). Upscaling pore-scale reactive transport equations using a multiscale continuum formulation. *Water Resour. Res.*, 43:W12S15.
- Luo, J., Dentz, M., Carrera, J., and P., K. (2008). Effective reaction parameters for mixing controlled reactions in heterogeneous media. *Water Resour. Res.*, 44:W02416.
- Magdziarz, M., Metzler, R., Szczotka, R., and Zebrowski, P. (2012). Correlated continuous-time random walk scaling limits and langevin picture. *J. Stat. Mech.*, 04:P04010.
- Maher, K. and Chamberlain, C. P. (2014). Hydrologic regulation of chemical weathering and the geologic carbon cycle. *Science*, 343:1502–1504.
- Malthe-Sorensen, A. and Jamtveit, B. and Meakin, P. (2006). Fracture patterns generated by diffusion controlled volume changing reactions. *Phys. Rev. Lett.*, 96:245,501.
- Matheron, M. and de Marsily, G. (1980). Is transport in porous media always diffusive? *Water Resour. Res.*, 16:901–917.

- Mays, D. and Neupauer, M. (2012). Plume spreading in groundwater by stretching and folding. *Water Resour. Res.*, 48:W07501.
- McClain (2003). Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems*, 6:301312.
- Meerschaert, M. M., Nane, E., and Xiao, Y. (2009). Correlated continuous time random walks. *Statistics and Probability Letters*, 79:1194–1202.
- Metcalf, G., Lester, D., Ord, A., Kulkarni, P., Trefry, M., Hobbs, B. E., Regenaur-Lieb, K., and Morris, J. (2010). A partially open porous media flow with chaotic advection: towards a model of coupled fields. *Phil. Trans. R. Soc. A*, 368:217–230.
- Metzler, R. and Klafter, J. (2000). The random walk’s guide to anomalous diffusion: a fractional dynamics approach. *Phys. Rep.*, 339(1):1–77.
- Meunier, P. and Villiermaux, E. (2010). The diffusive strip method for scalar mixing in two dimensions. *J. Fluid Mech.*, 662:134–172.
- Meyer, D. W. and Tchelep, H. (2010). Particle based transport model with markovian velocity processes for tracer dispersion in highly heterogeneous porous media. *Water Resour. Res.*, 46:W11552.
- Montero, M. and Masoliver, J. (2007). Nonindependent continuous-time random walks. *Phys. Rev. E*, 76:061115.
- Montroll, E. W. and Weiss, G. H. (1965). Random walks on lattices, 2. *J. Math. Phys.*, 6(2):167.
- Morad, M. R. and Khalili, A. (2009). Transition layer thickness in a fluid-porous medium of multi-sized spherical beads. *Exp. Fluids*, 46:323330.
- Morales-Casique, E., Neuman, S., and A., A. G. (2006). Nonlocal and localized analyses of nonreactive solute transport in bounded randomly heterogeneous porous media: theoretical framework. *Advances in Water Resources*, 29:1238–1255.
- Moroni, M., Kleinfelder, N., and Cushman, J. (2007). Analysis of dispersion in porous media via matched-index particle tracking velocimetry experiments,” *adv water resour*, vol. 30, pp. 1-15, 2007. *Advances in Water Resources research*, 30:1–15.
- National Research Council (2012). *Challenges and Opportunities in the Hydrologic Sciences*. The National Academies Press, Washington.
- Neufeld, Z. and Hernandez-Garica, E. (2010). *Chemical and Biological Processes in Fluid Flows: A dynamical System Approach*. Imperial College Press, London.
- Neuman, S. (1993). Eulerian-lagrangian theory of transport in spacetime nonstationary velocity fields: Exact nonlocal formalism by conditional moments and weak approximation. *Water Resources Research*, 29:633–645.
- Neuman, S. and Tartakovsky, D. (2009). Perspective on theories of anomalous transport in heterogeneous media. *Advances in Water Resources*, 32:670–680.
- Or D., B. F. Smets, J. M. W. A. D. and Friedman, S. P. (2007). Physical constraints affecting bacterial habitats and activity in unsaturated porous media - a review. *Adv. Wat. Res.*, 30:15051527.
- Ottino, J. (1989). *The Kinematics of Mixing: Stretching, Chaos, and Transport*. Cambridge University Press.

- Pope, S. B. (2000). *Tubulent Flows*. Cambridge University Press.
- Ptak, T., Piepenbrink, M., and Martac, E. (2004). Tracer tests for the investigation of heterogeneous porous media and stochastic modelling of flow and transport a review of some recent developments. *J. of Hydrol.*, 294:122–163.
- Quintard, M. and Whitaker, S. (1994). transport in ordered and disordered porous media: 2. generalized volume averaging. *Transp. in Porous Media*, 14:179–206.
- Ranz, W. E. (1979). Application of a stretch model to mixing, diffusion and reaction in laminar and turbulent flows. *AIChE Journal*, 25(1):41–47.
- Read, T., Bour, O., Bense, V., Le Borgne, T., Goderniaux, P., Klepikova, M.V. and Hochreutener, R., Lavenant, N., and Boschero, V. (2013). Characterizing groundwater flow and heat transport in fractured rock using fiber-optic distributed temperature sensing. *Geophys. Res. Lett.*, 40:15.
- Read, T., Bour, O., Selker, J., Bense, V., Le Borgne, T., Hochreutener, R., and Lavenant, N. (2014). Active-distributed temperature sensing to continuously quantify vertical flow in boreholes. *Water Resour. Res.*, 50:3706–3713.
- Risken, H. (1996). *The Fokker-Planck Equation*. Springer Heidelberg New York.
- Rolle, M., Eberhardt, C., Chiogna, G., Cirpka, O., and Grathwohl, P. (2009). Enhancement of dilution and transverse reactive mixing in porous media: experiments and model-based interpretation. *J. of Contam. Hydrol.*, 110:130–142.
- Rusconi, R., Garren, M., and Stocker, R. (2014a). Microfluidics expanding the frontiers of microbial ecology. *Annual Review of Biophysics*, 43:2.1–2.27.
- Rusconi, R., Guasto, J., and Stocker, R. (2014b). Bacterial transport suppressed by fluid shear. *Nature Physics*, 10:212–217.
- Seeboonruang, U. and Ginn, T. R. (2006). Upscaling heterogeneity in aquifer reactivity via exposure-time concept: Forward model. *J. Cont. Hydrol.*, 84:127–154.
- Seymour, J. D., Gage, J. P., Codd, S. L., and Gerlach, R. (2004). Anomalous fluid transport in porous media induced by biofilm growth. *Phys. Rev. Lett.*, 93:198103.
- Silliman, S., Konikow, L., and Voss, C. (1987). Laboratory experiment of longitudinal dispersion in anisotropic porous media. *Water Resources Research*, 23:2145–2154.
- Slater, L. (2007). Near surface electrical characterization of hydraulic conductivity: From petrophysical properties to aquifer geometries - a review. *Surveys in Geophysics*, 28:169–197.
- Stewart, P. S., Camper, A. K., Handran, S. D., Huang, C. T., and Warnecke, M. (1997). Spatial distribution and coexistence of *klebsiellapneumoniae* and *pseudomonas aeruginosa* in biofilms. *Microbial Ecology*, 33:210.
- Stocker, R. (2012). Marine microbes see a sea of gradients. *Science*, 338:628–633.
- Sturman, P. J., Jones, W. L., and Characklis, W. G. (1994). Interspecies competition in colonized porous pellets. *wat. res.*, 28:. *Wat. Res.*, 28:831839.
- Szulczewski, M. L., MacMinn, C. W., Herzog, H. J., and Juanes, R. (2012). Lifetime of carbon capture and storage as a climate-change mitigation technology. *Proc. Natl. Acad. Sci.*, 109:5185–5189.

- Tartakovsky, A. M., Redden, G., Lichtner, P. C., Scheibe, T. D., and Meakin, P. (2008a). Mixing-induced precipitation: Experimental study and multiscale numerical analysis. *Water Resour. Res.*, 44:W06S04.
- Tartakovsky, A. M., Tartakovsky, D. M., and Meakin, P. (2008b). Stochastic langevin model for flow and transport in porous media. *Phys. Rev. Lett.*, 101:044502.
- Tartakovsky, A. M., Tartakovsky, G. D., and Scheibe, T. D. (2009). Effects of incomplete mixing on multicomponent reactive transport. *Adv. Water Resour.*, 32:1674–1679.
- Taylor, G. I. (1953). Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc. R. Soc. Lond. A*, 219:186–203.
- Tejedor, V. and Metzler, R. (2010). Anomalous diffusion in correlated continuous time random walks. *J. Phys. A: Math. Theor.*, 43:082002.
- Tel, T., Demoura, A., Grebogi, C., and Karolyi, G. (2005). Chemical and biological activity in open flows: A dynamical system approach. *Physics Reports*, 413(2-3):91–196.
- Tonina, D. and Bellin, A. (2008). Effects of pore-scale dispersion, degree of heterogeneity, sampling size, and source volume on the concentration moments of conservative solutes in heterogeneous formations. *Adv. Water Resour.*, 31.
- Trefry, M., Lester, D. R., Metcalfe, G., Ord, A., and Regenauer-Lieb, K. (2012). Toward enhanced subsurface intervention methods using chaotic advection. *J. of Contam. Hydrol.*, 127:1529.
- Valiño, L. and Dopazo, C. (1991). A binomial Langevin model for turbulent mixing. *Phys. Fluids*, 3:3034–3037.
- Villermaux, E. (2012). Mixing by porous media. *C. R. Mécanique*, 340:933–943.
- Villermaux, E. and Duplat, J. (2003). Mixing as an aggregation process. *Phys. Rev. Lett.*, 91:18.
- Warhaft, Z. (2000). Passive scalars in turbulent flows. *Ann. Rev. Fluid Mech*, 32(1):203–240.
- Weiss, J. and Provenzale, A. (2008). *Transport and Mixing in Geophysical Flows*. Number 744. Springer Verlag.
- Whitaker, S. (1999). *The Method of Volume Averaging*. Kluwer Academic Publishers.
- Willingham, T., Werth, C., and Valocchi, A. (2008). Evaluation of the effects of porous media structure on mixing-controlled reactions using porescale modeling and micromodel experiments. *Environ. Sci. Technol.*, 42:3185–3193.