Thanks to the experimentalists we can now test mixing theories more broadly.

Molz, F. J., and M. A. Widdowson, **1988**
Internal inconsistencies in dispersion-dominated models that incorporate chemical and microbial kinetics, *WRR*, 24(4), 615-619.

Tim R. Ginn and Sabrina Volponi
Civil and Environmental Engineering
Washington State University USA

Kapoor, V., L. W. Gelhar, and F. Miralles-Wilhelm **1997** Bimolecular second-order reactions in spatially varying flows…*WRR*, 33(4), 527–536.

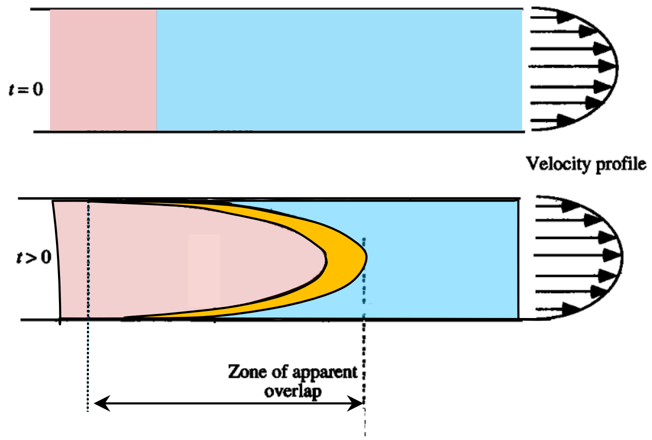


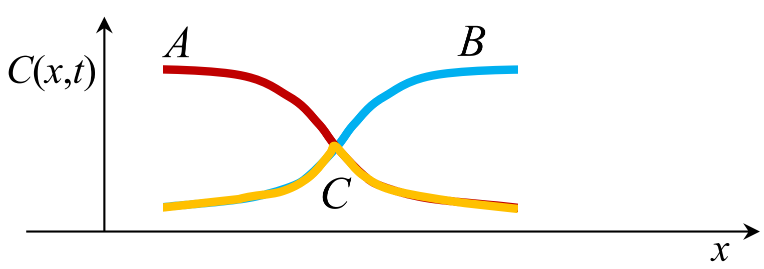
Figure 2. Illustration of the concept of segregation-induced scale dependence of transformation in laminar shear flow. Un-

Any material plane perpendicular to flow gets sheared and diffused.

This includes the one separating two interacting solutions.

Upscaled Spreading > Actual Mixing.

1-D Upscaled product concentration *C* is overestimated



C is created on the interface,
not on the zone of apparent overlap

Kapoor, V., L. W. Gelhar, and F. Miralles-Wilhelm **1997** Bimolecular second-order reactions in spatially varying flows…*WRR*, 33(4), 527–536.

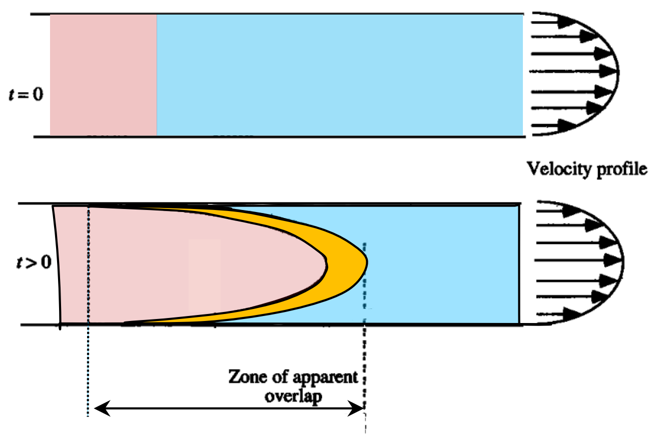
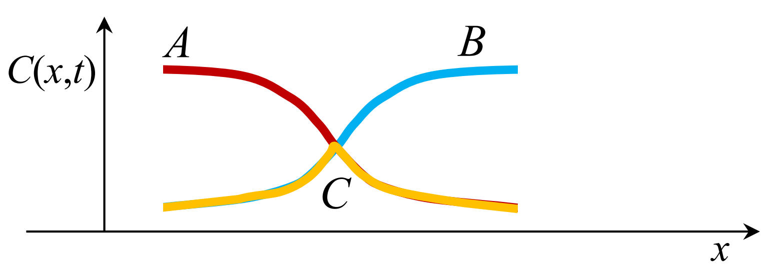


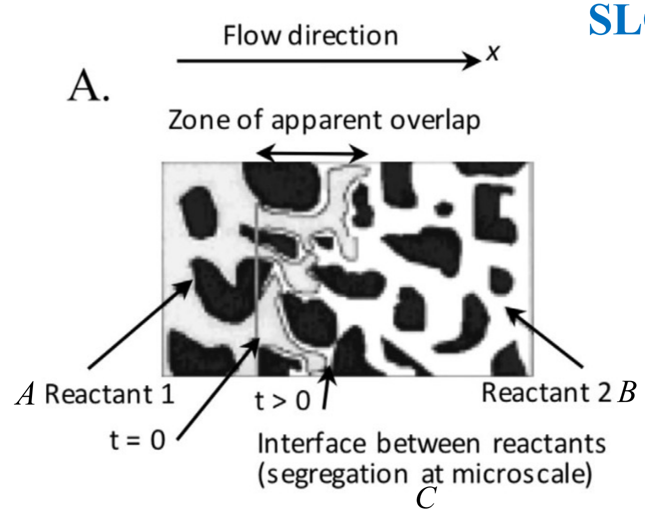
Figure 2. Illustration of the concept of segregation-induced scale dependence of transformation in laminar shear flow. Un-

1-D Upscaled product concentration is overestimated



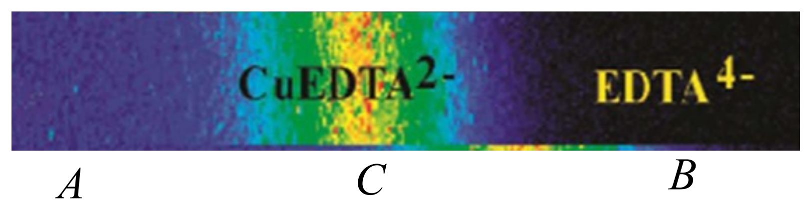
Raje & Kapoor **2000**.

RK00
SLOW



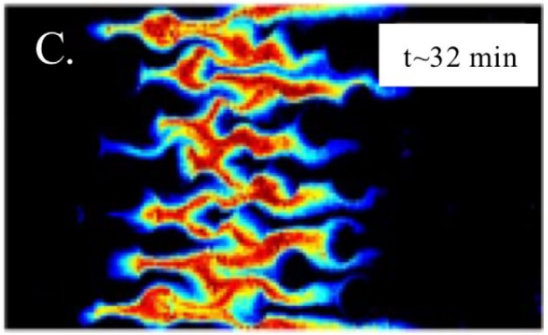
G02
FAST

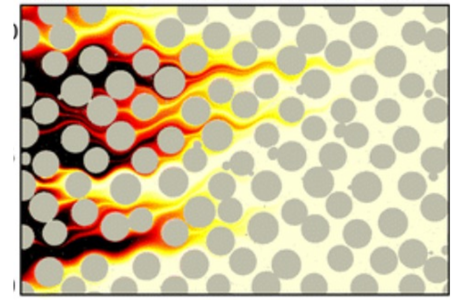
Gramling, Harvey & Meigs **2002**.



We can see the “segregation zones”

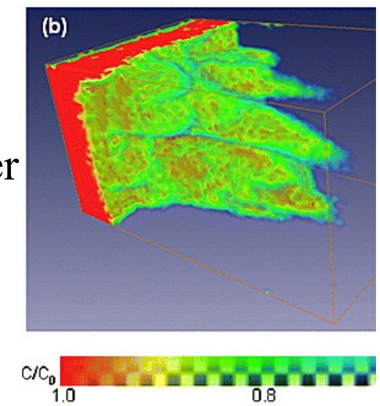
Oates & Harvey
2006 FAST (G02)
Bead pack

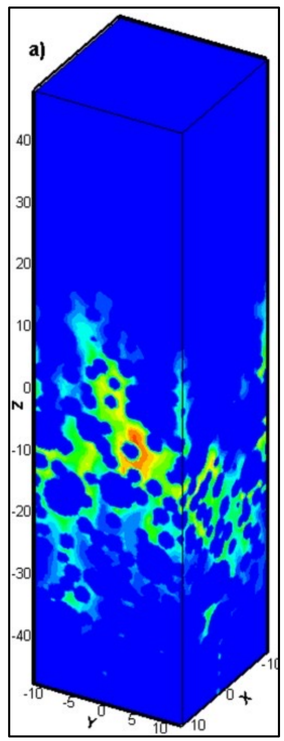




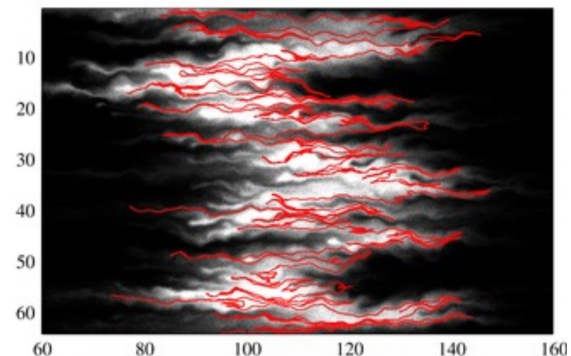
de Anna EST 2014

Yoon 2008
Passive tracer
$MgCl_2$
sandbox



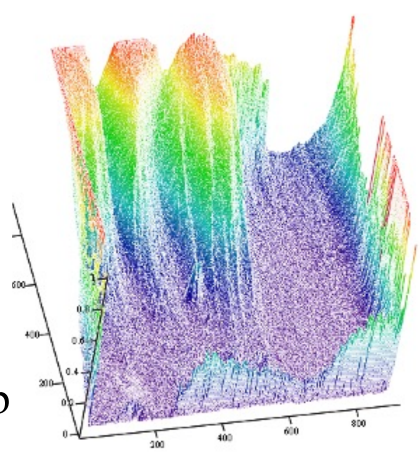


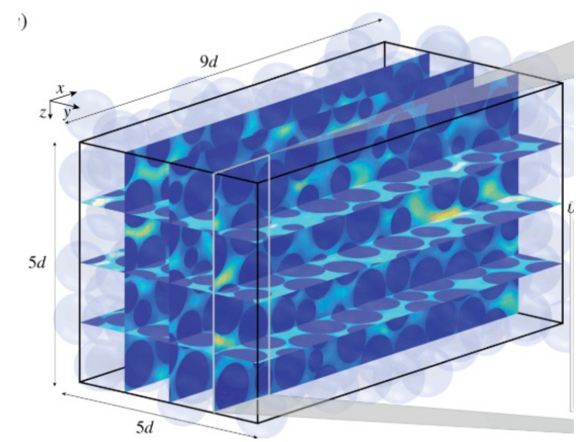
Scheibe 2013
In silico



Le Borgne 2017 Passive tracer

Klise 2008
KI(odine)
Massillon
Sandstone slab

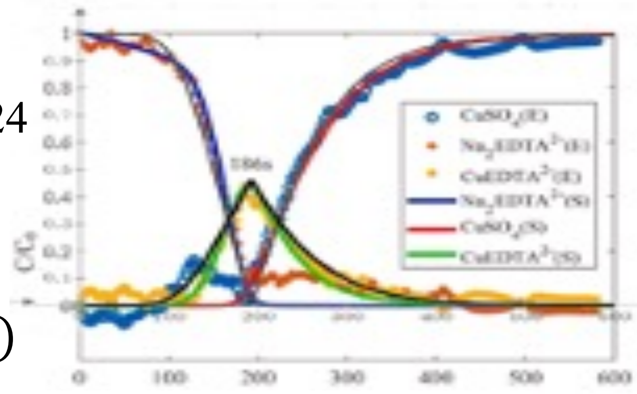




Souzy 2020 Passive tracer

The "Bimolecular reaction upscaling" game*

Xu 2024

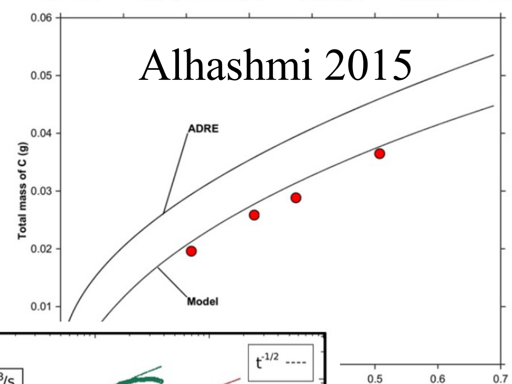


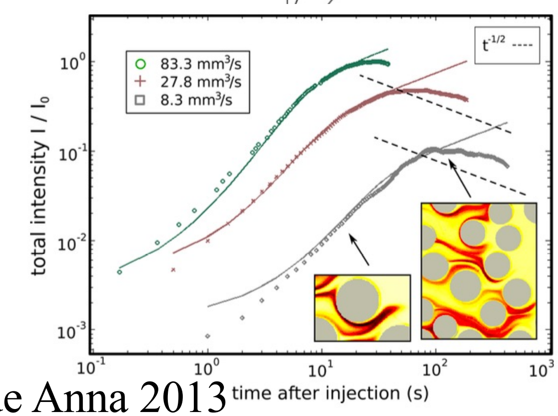
Target Metrics

$A, B, C(x,t)$

$C^{total}(t)$

$$\frac{dC^{total}}{dt}$$





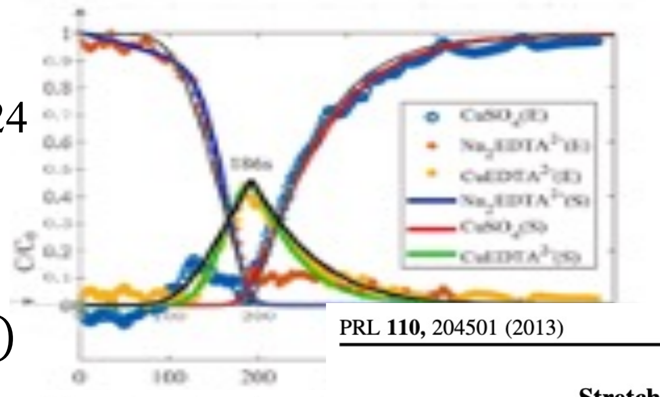
de Anna 2013

* A Parade of Modeling Innovations Wow !

The "Bimolecular reaction upscaling" game*

Interface (lamella) dynamics:
stretching
shrinking
diffusion

Xu 2024



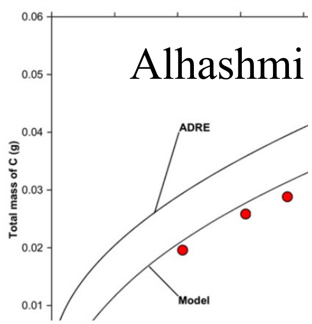
Target Metrics

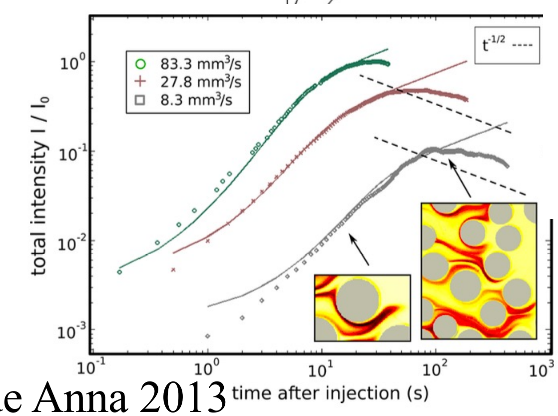
$$A, B, C(x,t)$$

$$C^{total}(t)$$

$$\frac{dC^{total}}{dt}$$

Alhashmi





de Anna 2013

PRL **110,** 204501 (2013) PHYSICAL REVIEW LETTERS week ending 17 MAY 2013

Stretching, Coalescence, and Mixing in Porous Media

Tanguy Le Borgne*
Geosciences Rennes, UMR 6118, Université de Rennes 1, CNRS, 35042 Rennes, France

Marco Dentz
Spanish National Research Council (IDAEA-CSIC), 08034 Barcelona, Spain

Emmanuel Villermaux†
Institut de Recherche sur les Phénomènes Hors Equilibre, Aix-Marseille Université, 13384 Marseille Cedex 13, France
(Received 18 February 2013; published 13 May 2013)

We study scalar mixing in heterogeneous conductivity fields, whose structural disorder varies from weak to strong. A range of stretching regimes is observed, depending on the level of structural heterogeneity, measured by the log-conductivity field variance. We propose a unified framework to quantify the overall concentration distribution predicting its shape and rate of deformation as it progresses toward uniformity in the medium. The scalar mixture is represented by a set of stretched lamellae whose rate of diffusive smoothing is locally enhanced by kinematic stretching. Overlap between the lamellae is enforced by confinement of the scalar line support within the dispersion area. Based on these elementary processes, we derive analytical expressions for the concentration distribution, resulting from the interplay between stretching, diffusion, and random overlaps, holding for all field heterogeneities, residence times, and Péclet numbers.

PHYSICAL REVIEW FLUIDS **10,** 024501 (2025)

Linking mixing interface deformation to concentration gradients in porous media

Saif Farhat and Diogo Bolster
Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana 46556, USA

Guillem Sole-Mari
Geosciences Rennes, University of Rennes, Rennes 35042, France

* A Parade of Modeling Innovations Wow !

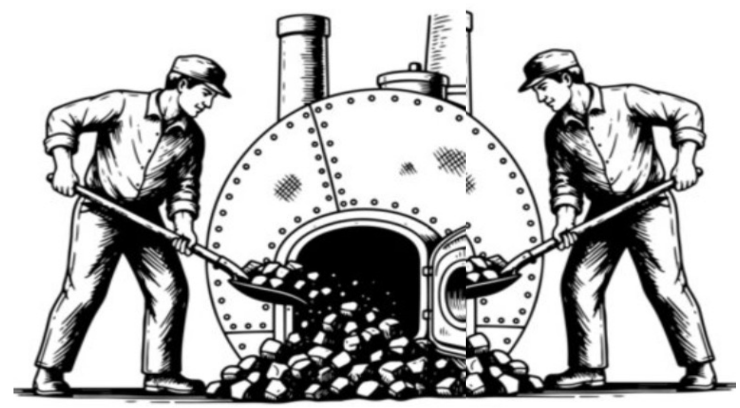
Our approach*

Both adjacent unmixed solutions deliver solute to the mixed zone via 1st-order mobile-mobile mass transfer with rate coeff.

$$k(\omega) = \frac{\gamma}{\sqrt{\omega}}$$

this rate coeff. originated with Sanchez-Vila et al. 2010 *WRR* who used it for the reaction itself, not mass xfer and put it in *t* not age.

$$A^{unmixed} \overset{k(\omega)}{\rightarrow} A^{mixed}, B^{mixed} \overset{k(\omega)}{\leftarrow} B^{unmixed}$$



* Le Borgne et al. @ Geos. Rennes. Ginn, *WRR* 2018. Gurung and Ginn, *WRR* 2023

Our approach

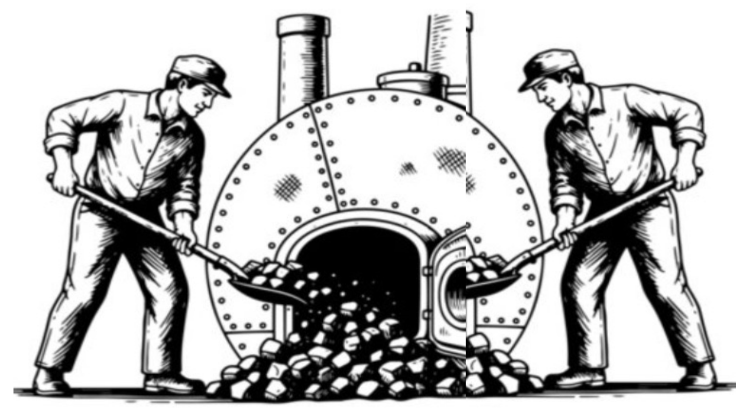
$$k(\omega) = \frac{\gamma}{\sqrt{\omega}}$$

Buckingham Π

If $k(\omega) = \frac{\gamma}{\sqrt{\omega}}$ then what is γ ?

If γ depends on:	Then:
α, v	$\gamma \propto \sqrt{\frac{v}{\alpha}}$
D_m, α, v	$\gamma \propto \sqrt{\frac{v}{\alpha}}\, f\left(\frac{D_m}{\alpha v}\right)$
d_{50}, D_m, α, v	$\gamma \propto \sqrt{\frac{v}{d_{50}}}\, f\left(\frac{D_m}{d_{50} v}, \frac{\alpha}{d_{50}}\right)$

$$A^{unmixed} \overset{k(\omega)}{\rightarrow} A^{mixed}, B^{mixed} \overset{k(\omega)}{\leftarrow} B^{unmixed}$$



Ginn, *WRR* 2018. Gurung and Ginn, *WRR* 2023

Our approach

$$k(\omega) = \frac{\gamma}{\sqrt{\omega}}, \ \gamma = \sqrt{\frac{v}{160\alpha}}$$

based on analysis of RK00, G02, and Alhashmi 2015 data

Buckingham Π

If $k(\omega) = \frac{\gamma}{\sqrt{\omega}}$ then what is γ ?

If γ depends on:	Then:
α, v	$\gamma \propto \sqrt{\frac{v}{\alpha}}$
D_m, α, v	$\gamma \propto \sqrt{\frac{v}{\alpha}} f\left(\frac{D_m}{\alpha v}\right)$
d_{50}, D_m, α, v	$\gamma \propto \sqrt{\frac{v}{d_{50}}} f\left(\frac{D_m}{d_{50} v}, \frac{\alpha}{d_{50}}\right)$*

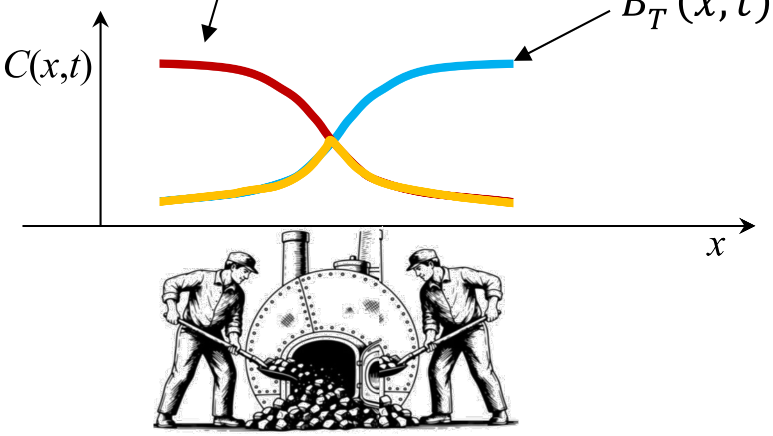
Ginn, *WRR* 2018. Gurung and Ginn, *WRR* 2023

Simple results

$$k(\omega) = \frac{\gamma}{\sqrt{\omega}}, \ \gamma = \sqrt{\frac{v}{160\alpha}}$$

$$A_T^{\mu}(x,t) = \int_0^t A_{in}(t-\omega)\left[1 - e^{-\mathrm{K}(\omega)}\right] \frac{1}{\sqrt{4\pi\tau(\omega)}} \exp\left(-\frac{(x - \mathrm{v}\omega)^2}{4\tau(\omega)}\right) d\omega$$

$$B_T^{\mu}(x,t) = \left[1 - e^{-\mathrm{K}(\omega)}\right] \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-u^2} B_o\left(x - vt + u\sqrt{4\tau(t)}\right) du$$



Exploits irreversibility of mixing

Classical endmember solutions, now with Hydraulic 'activity coefficient' $\left[1 - e^{-\mathrm{K}(\omega)}\right]$

Remains linear

Closed-form solutions (*for fast rxn; easy finite differences for slow reactions*)

Separates transport & reaction (*thus works with nonlinear reaction networks*)

Raje, D., Kapoor, V., 2000. Experimental study of bimolecular reaction kinetics in porous media. ES&T, 34, 1234–1239.

Gramling, C. M., C. F. Harvey, L. C. Meigs, 2002. Reactive transport in porous media: a comparison of model prediction with laboratory visualization, ES&T., 36, 25082514.

Oates, P.M., Harvey, C.F., **2006**. A colorimetric reaction to quantify fluid mixing. Exp. Fluids, 41(5),673–683.

Alhashmi, Z., B.J. Blunt, B. Bijeljic, **2015.** Simulated G02 data via pore-scale particle tracking, include PAD, *J. Contam. Hydrol*. 179, 171–181.

---

de Anna, P., J. Jimenez-Martinez, H. Tabuteau, R. Turuban, T. Le Borgne, M. Derrien, Y. Méheust **2014** Mixing and reaction kinetics in porous media: an experimental pore scale quantification. *ES&T*. 48 (1), 508–516.

Xu, Y., J-P. Carlier, H-G. Sun, Y. Jia, J. Qian, Y. Liu, **2024** The bimolecular reactive transport in heterogeneous porous media: Sub-diffusion in interpretation of laboratory experiment, *Chemosphere*, Volume 362.

Liu, Y., Qian, J., Liu, Y., Li, F., Fang, Y., **2023**. *Chemosphere* 321, 138126. Liu et al., 2025, transient flow in fractures

Zhang, Y. **2023** Adjoint models with non-Fickian reactive transport to identify pollutant sources in water, J Hazardous Materials Advances, Volume 12, 100331.

Zhang,Y., Qian, J., Papelis, C., Sun, P., Yu, Z., **2014**. *WRR*. 50 (2),1704–1715. Yin et al., **2024** 2D w/ stagnant zones…

Sole-Mari, G., Bolster, D. & Fernàndez-Garcia, D. **2023**. A Closer Look: High-Resolution Pore-Scale Simulations of Solute Transport and Mixing Through Porous Media Columns. *Transp Porous Med* 146, 85–111.

Hallack, D. M. C., G. Sole-Mari, S. Farhat, D. Bolster, **2025.** ARC Geophys Research, 1, 2. Farhat, S. et al., PRF, **2025**

Largely Untouched

e.g., Zhang 2014 has 29 citations, none are other modelers

RK00.

G02.

Alhashmi, **2015.**

---

de Anna, **2014**

Xu, **2024**

Zhang, **2023**

Zhang, **2014**.

Sole-Mari, **2023**.

Hallack, **2025.**

Farhat, **2025**

	Rate of Reaction	Metrics	PAD
RK00.	Slow	BTCs	No
G02.	Fast	Profiles, $C^{total}(t)$*	No
Alhashmi, 2015	Fast (G02 redo)	Profiles, $C^{total}(t)$	Yes
de Anna, **2014**	Fast (adjustable)	$\frac{dC^{total}}{dt}$(light intensity)	Yes
Xu, **2024**	Fast G02	BTCs	No ?
Zhang, **2023**			
Zhang, **2014**	Slow RK00	BTCs	No
Sole-Mari, **2023**	Fast		
Hallack, **2025**	(approximated G02)	Profiles, $C^{total}(t)$	Yes
Farhat, **2025**			

* Wrong

RK00.

G02.

Alhashmi, 2015

de Anna, 2014

Xu, 2024

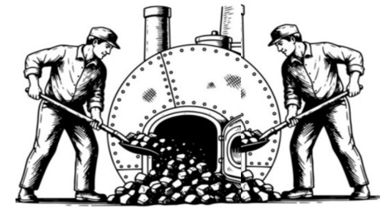
Zhang, 2023

Zhang, **2014**

Sole-Mari, 2023

Hallack, **2025**

Farhat, **2025**

Let’s simulate them all with the 

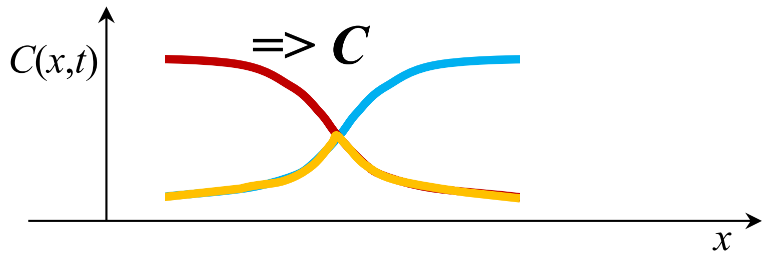
$k(\omega) = \frac{\gamma}{\sqrt{\omega}}$ approach, fit the

γ in each simulation,

and then see how well the obtained γ values match up with the

$\gamma = \sqrt{\frac{v}{160\alpha}}$ model !

Reactions *A* + *B* => *C*



SLOW: *Aniline* + *NQS* => *NQAB*

Colorimetric $C(x,t)$
RK00, Zhang 2014, BTCs.

FAST: $CuSO_4$ + Na_2EDTA^{-2} => $CuEDTA^{-2}$

Colorimetric $C(x,t)$**
G02, profiles; Xu 2024 BTCs

ADJUSTABLE/FAST:
DBU + Triazole**
+ H_2O_2 + *3-AFA* + *TCPO*
=> *Light*

Chemoluminescent dC/dt
de Anna 2014, rate of C total

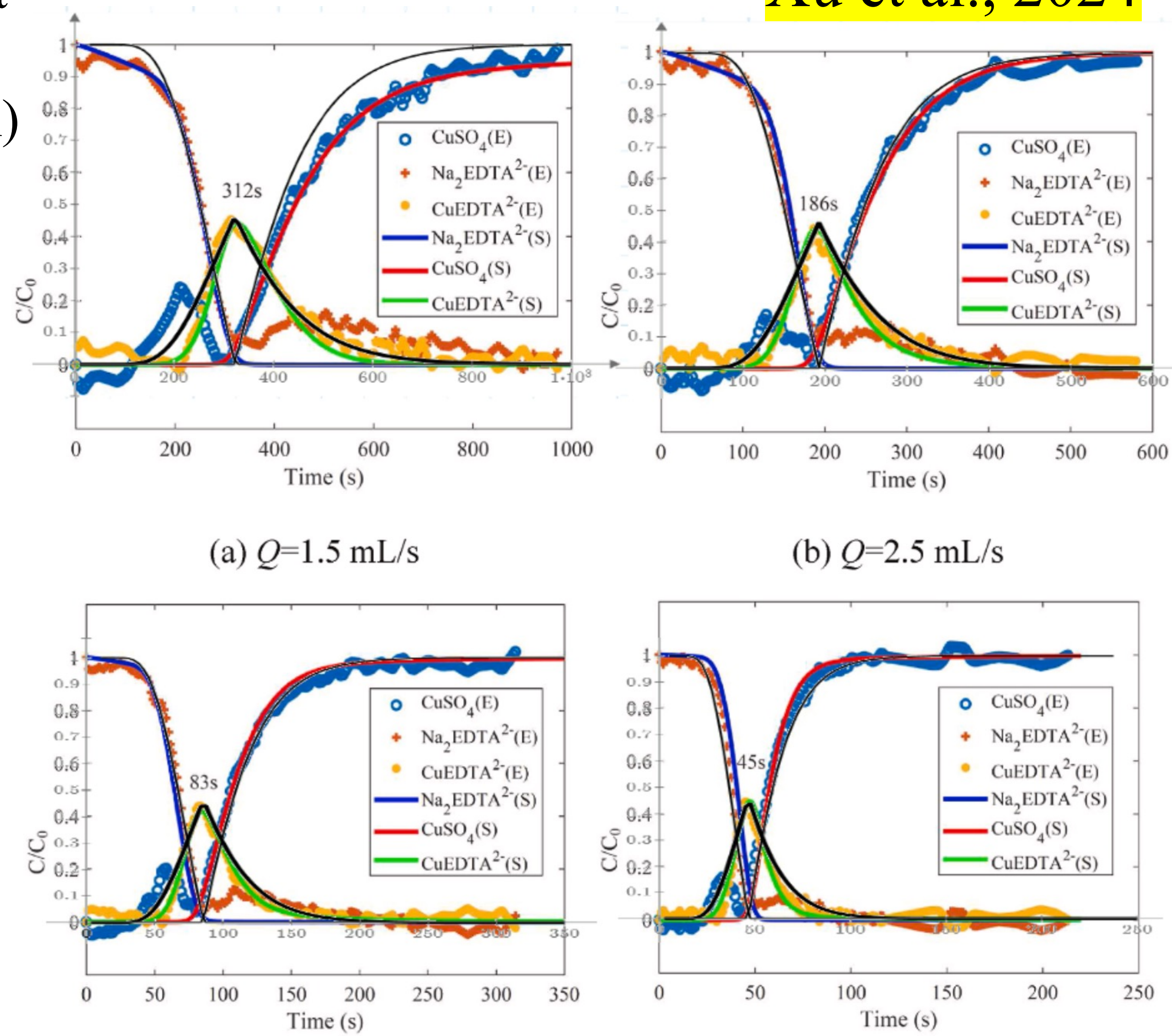
* catalysts

** simulated: Alhashmi 2015, Sole-Mari 2023

1 m long, 4 cm-square conduit glass bead pack in 4 mixtures of 4 sizes (2, 3, 4, and 5.5 mm)

Here we do ”pattern3”

Xu et al., 2024



(a) Q=1.5 mL/s

(b) Q=2.5 mL/s

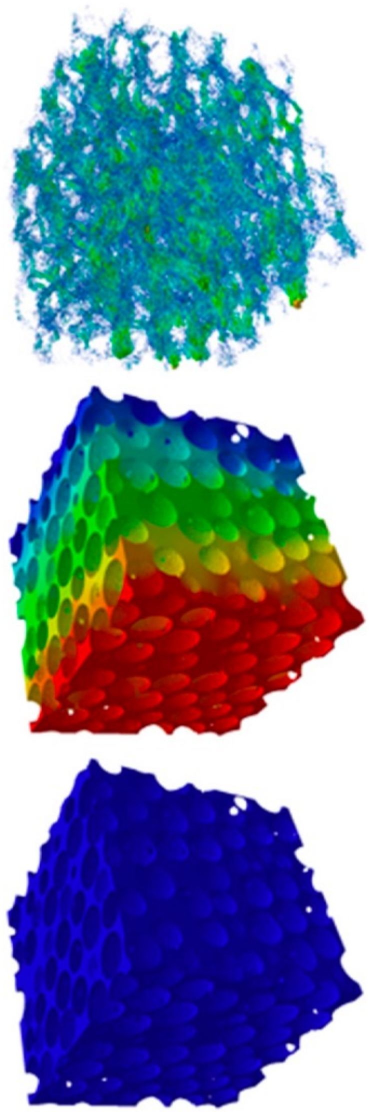
(c) Q=5.0 mL/s

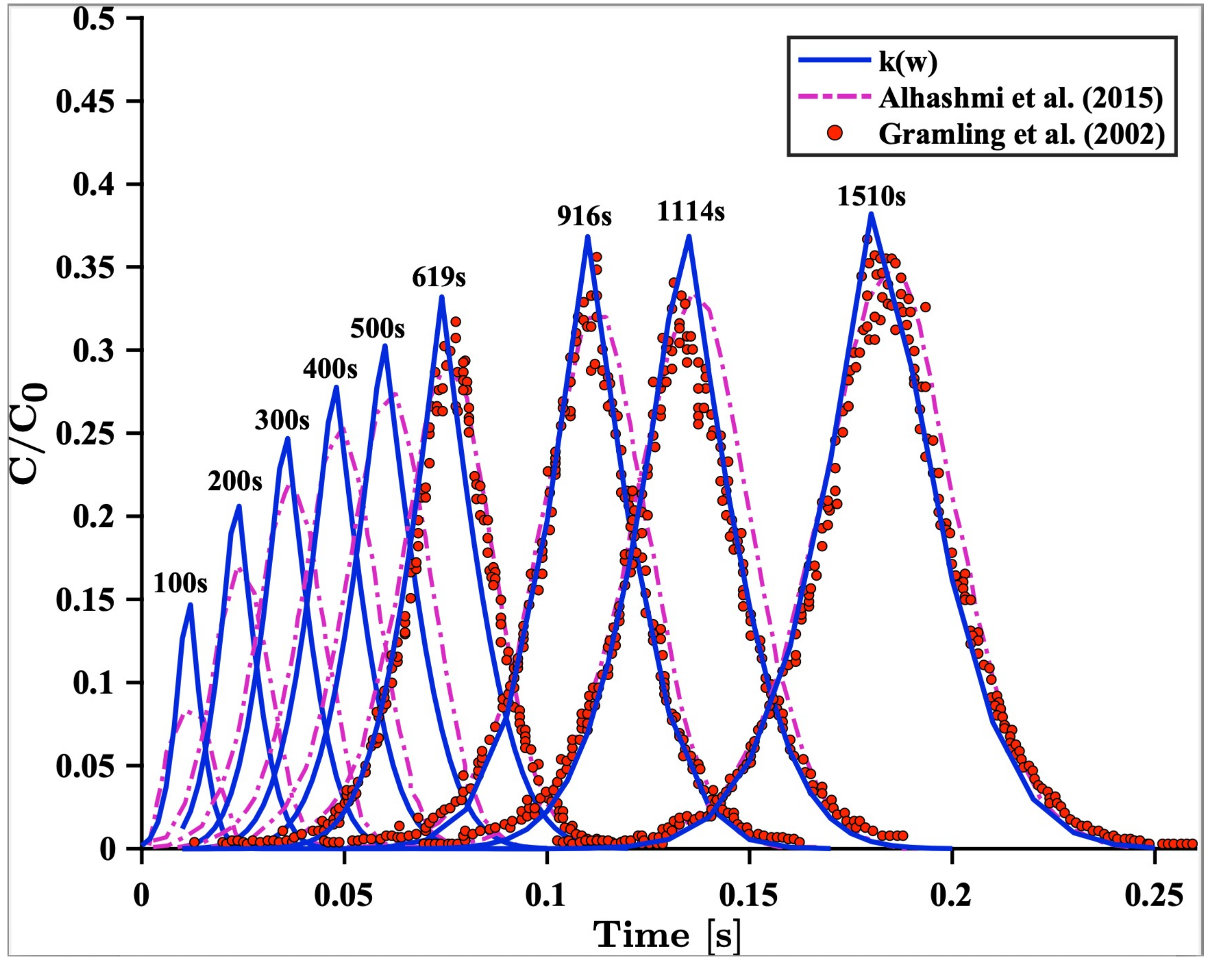
(d) Q=10.0 mL/s

All (yes, *All*) parameters refit per each experiment and each solute.
Also anomalies… look =>

Our new solutions are in **black** and involve fitting one dispersion coeff. (for all) and four insane γ values.

Alhashmi et al. 2015 Simulation, Particle tracking

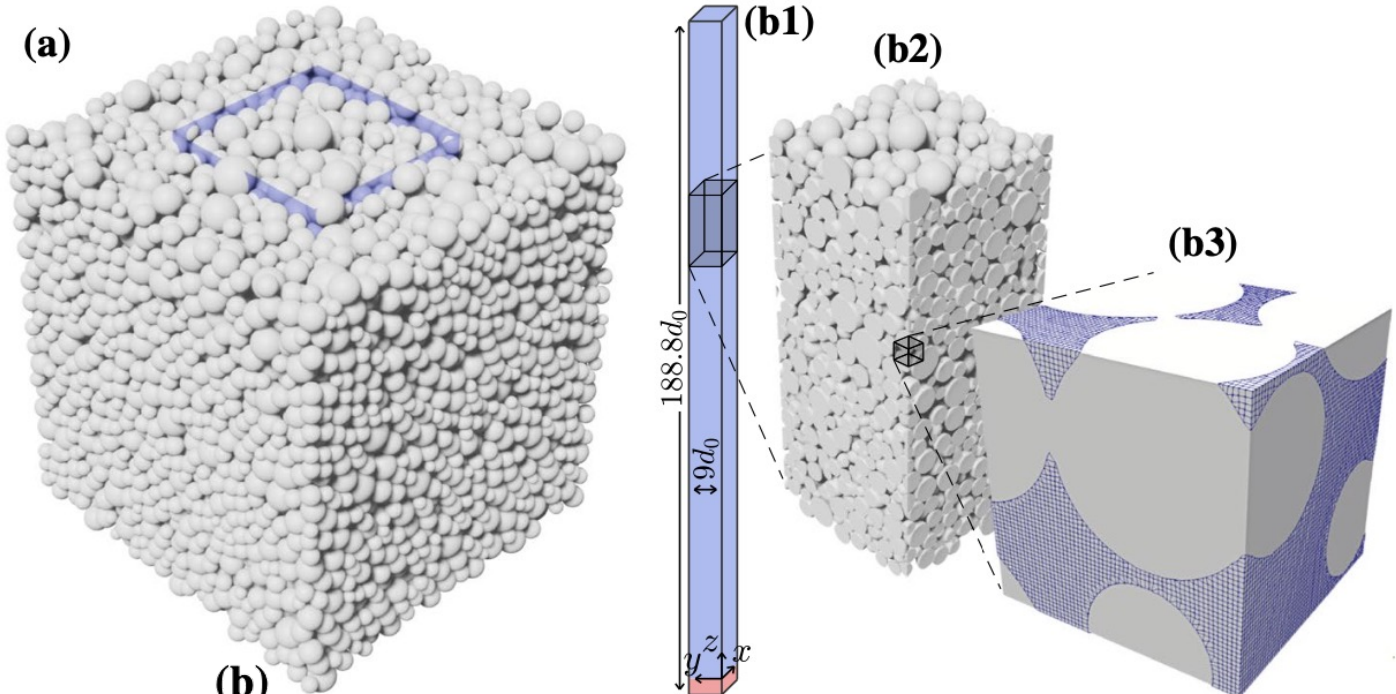


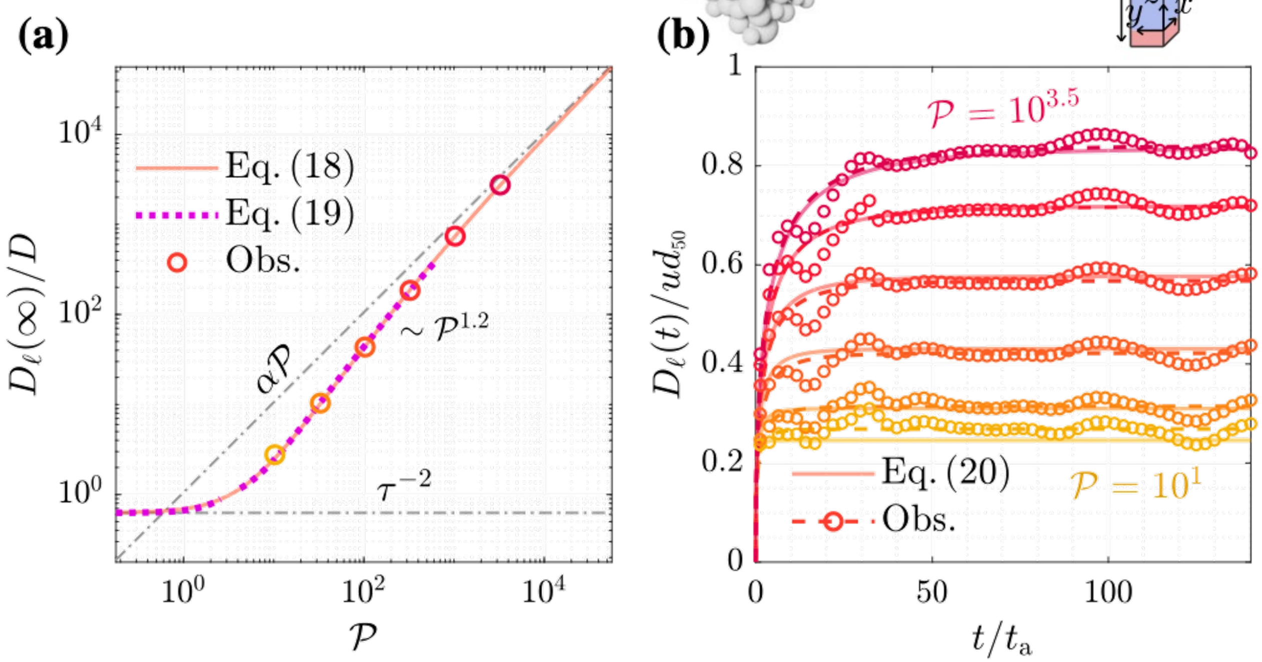


Replicated G02, including early time PAD is our solution in **blue**

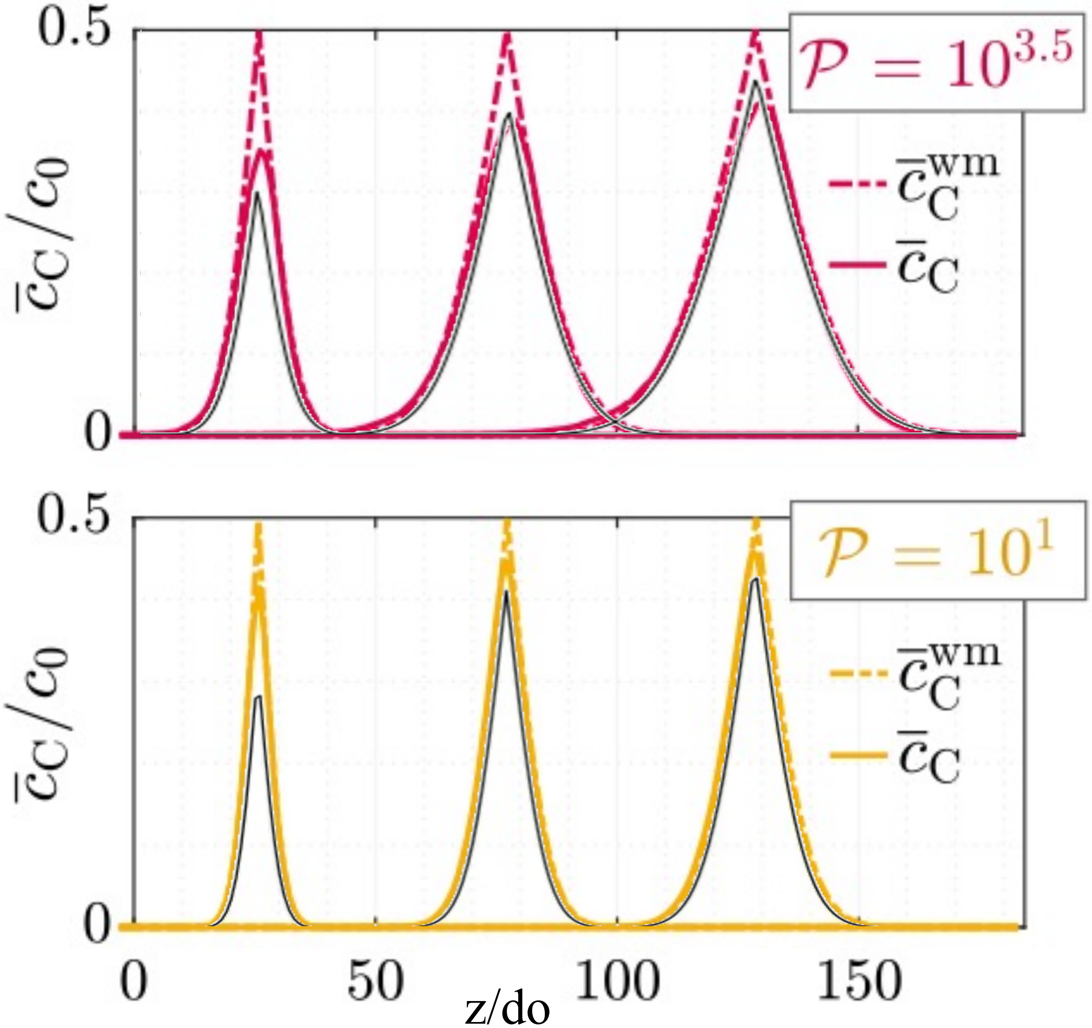
Ginn, *WRR* 2018. Gurung and Ginn, *WRR* 2023

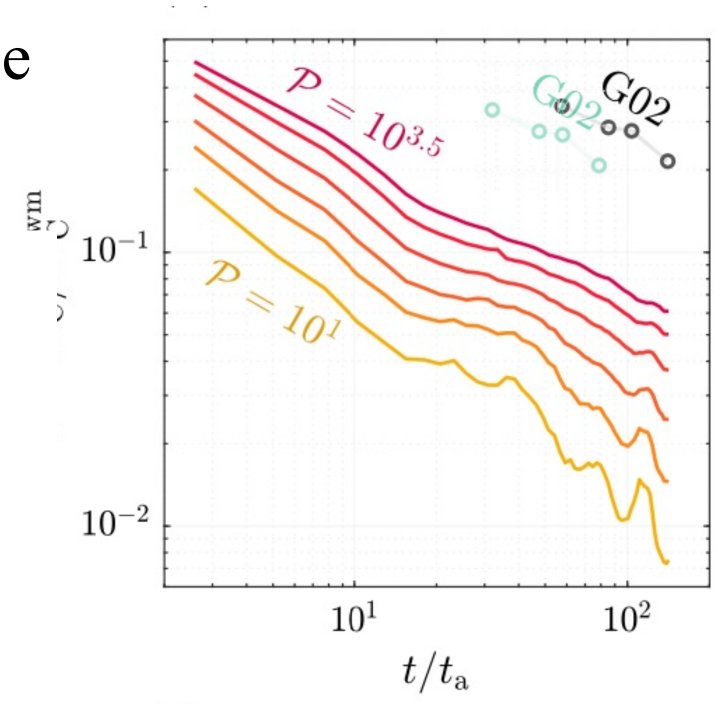
Sole-Mari et al., 2023 Simulation, Eulerian





Sole-Mari et al, 2023 Monodisperse case





	G02	S-M23
$\mathcal{P}$	$10^{3.35}$	$10^{3.5}$
do [mm]	1.3	2.0

Yet, a discrepancy in total mass (G02 dots remediated by Alhashmi et al 2015, who ID'd the trouble with total product mass in G02).

Our solution in **black**, fitted only γ. Only bracketing Peclet cases done so far.

Mathcad Code for our closed-form simulation of the Sole-Mari data.

$ORIGIN := 1$ $vw := 1$ units are mm and s $do := 2$ mm $L := 200 \cdot do$ $v := 0.103$ mm $ta := \frac{do}{v}$ $T1 := 25.7 \cdot ta$ $T2 := 77.2 \cdot ta$ $T3 := 128.7 \cdot ta$ $Pe := 10^{3.5}$ $Dm := \frac{v \cdot do}{Pe}$ $\alpha := 1.05$

$Pc := 228$ $\beta(P) := \frac{1}{1+\sqrt{\frac{Pc}{P}}}$ $tau := 1.263$ $\gamma what := 0.0275$ from figure 4c ? $tc := \gamma what \cdot \beta(Pe)^2 \cdot Pc \cdot ta$ $D(w) := Dm \cdot \left(\frac{1}{tau^2} + \alpha \cdot Pe \cdot \beta(Pe) \cdot \left(1 - \exp\left(-\sqrt{\frac{w}{tc}}\right)\right)\right)$ $\tau(v,w) := \int_0^w D(u)\,du$

$k(w,g) := \frac{g}{\sqrt{w}}$ $K(w,g) := \int_0^w k(u,g)\,du$ $co(u) := \Phi(u)$ $cin(u,v) := v \cdot \frac{\Phi(u)}{vw}$ $\gamma p(u) := \sqrt{\frac{u}{160 \cdot \alpha}}$ $gamma := \gamma p(v)$ $gamma = 0.025$ $N := 200$ $i := 1..N$ $z_i := do \cdot i$

$\beta im(x,t,v) := (1 - \exp(-K(t,\gamma p(v)))) \cdot \frac{1}{\sqrt{\pi}} \cdot \int_{-\infty}^{\infty} \exp(-(u^2)) \cdot co\left(x - v \cdot t + u \cdot \sqrt{4 \cdot \tau(v,t)}\right) du$ $\beta bm(x,t,v) := \int_0^t (1 - \exp(-K(w,\gamma p(v)))) \cdot cin(t-w,v) \cdot \frac{1}{\sqrt{4 \cdot \pi \cdot \tau(v,w)}} \cdot \exp\left(\frac{-(x - v \cdot w)^2}{4 \cdot \tau(v,w)}\right) dw$

$c(x,t,v) := min(\beta im(x,t,v), \beta bm(x,t,v))$ $c1_i := c(z_i, T1, v)$ $c2_i := c(z_i, T2, v)$ $c3_i := c(z_i, T3, v)$

$\alpha in(x,t,v) := 1 \cdot \frac{1}{\sqrt{\pi}} \cdot \int_{-\infty}^{\infty} \exp(-(u^2)) \cdot co\left(x - v \cdot t + u \cdot \sqrt{4 \cdot \tau(v,t)}\right) du - \max(c(x,t,v), 0)$ $\alpha b(x,t,v) := \int_0^t 1 \cdot cin(t-w,v) \cdot \frac{1}{\sqrt{4 \cdot \pi \cdot \tau(v,w)}} \cdot \exp\left(\frac{-(x - v \cdot w)^2}{4 \cdot \tau(v,w)}\right) dw - \max(c(x,t,v), 0)$

$ai1_i := \alpha in(z_i, T1, v)$ $ai2_i := \alpha in(z_i, T2, v)$ $ai3_i := \alpha in(z_i, T3, v)$ $ab1_i := \alpha b(z_i, T1, v)$ $ab2_i := \alpha b(z_i, T2, v)$ $ab3_i := \alpha b(z_i, T3, v)$

This is the $Pe = 10^{3.5}$ case Yes PAD

Zhang, 2023

Zhang, **2014**

Slow system

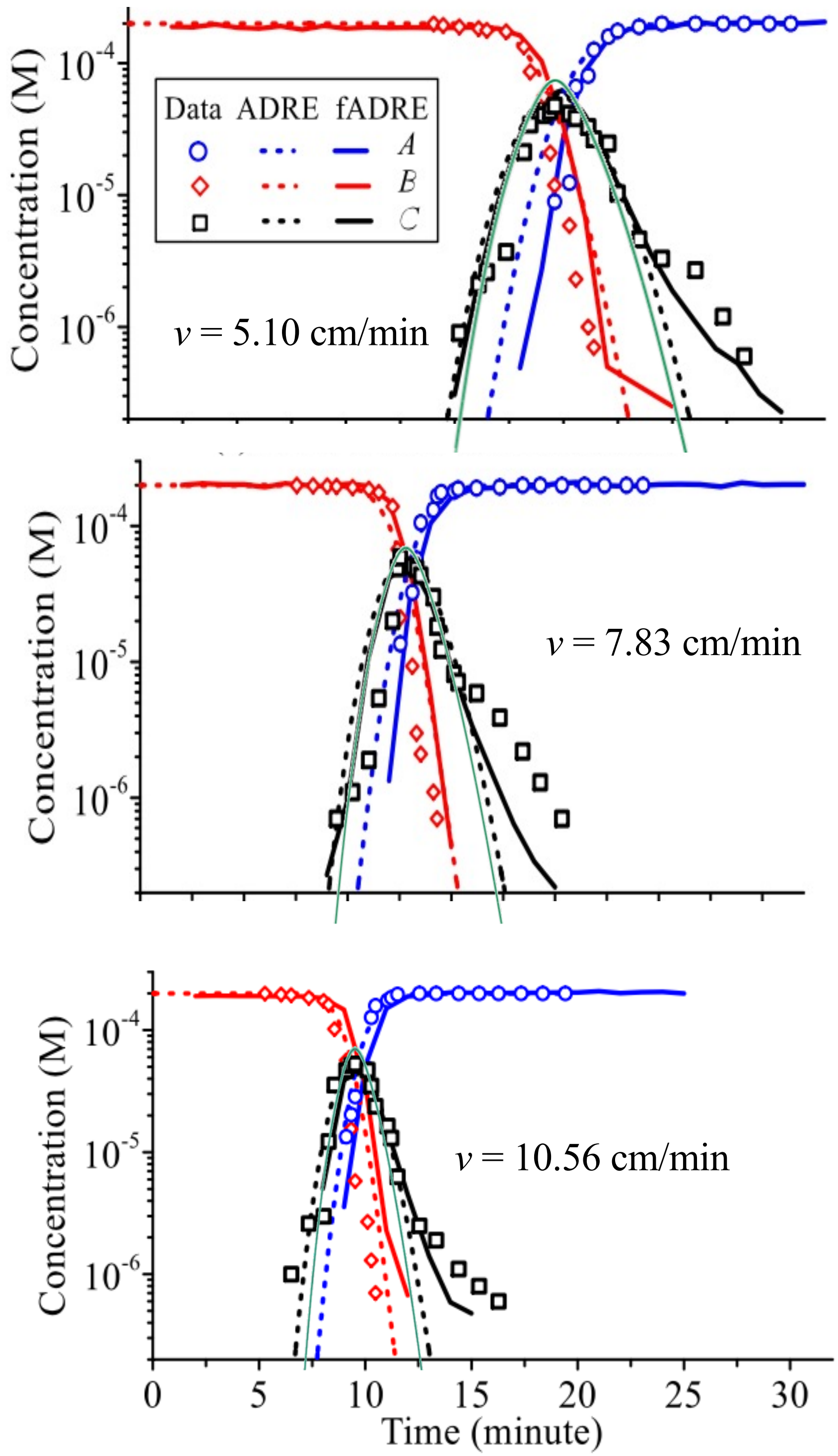
Aniline + NQS -> NQAB.

1m long sand (0.4-0.5mm – this case, also 2-3mm) columns 4cm diameter

Slow, numerical (EFD) solution.

Our solution in **green**

Aside from a tweak of the dispersion coeffs following the authors, fitted γ only.



de Anna et al, 2014

With Thanks to Yves Méheust for help with some conditions (domain, c_o ...)

Environmental Science & Technology

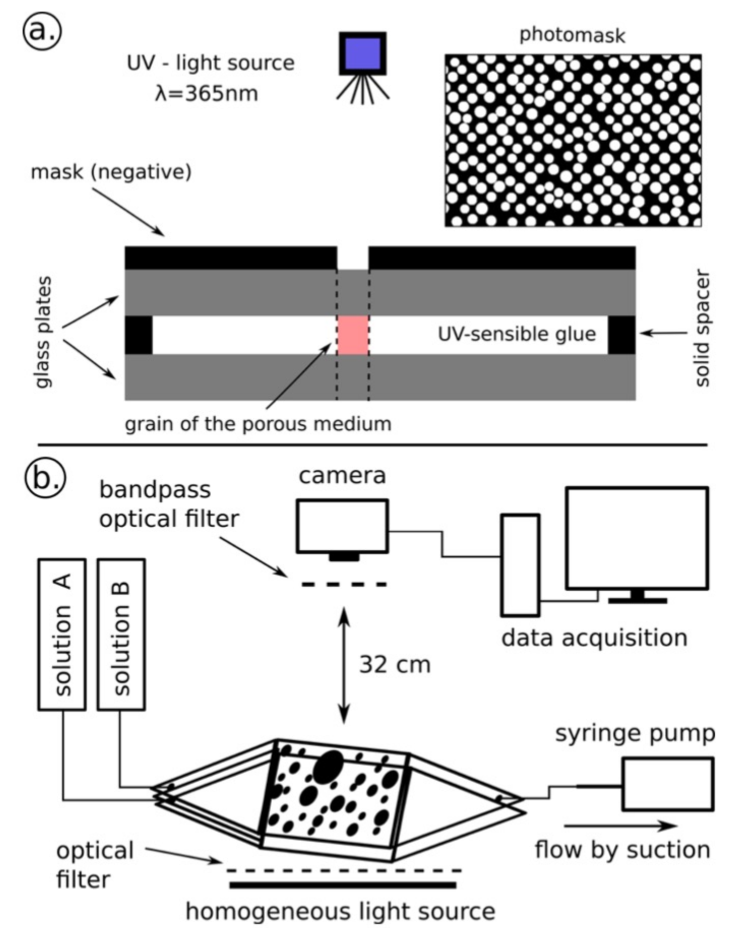
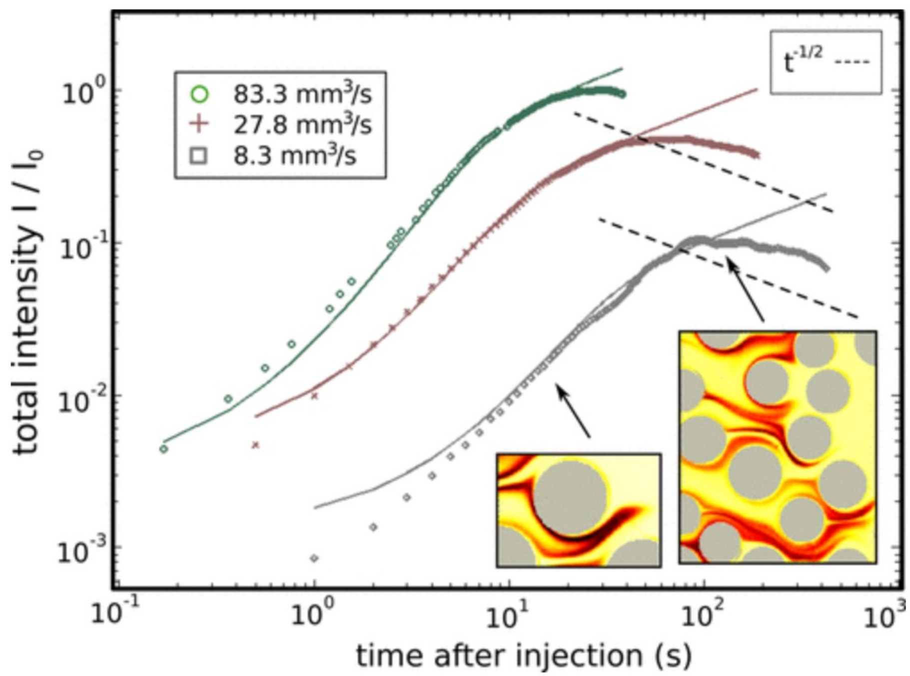
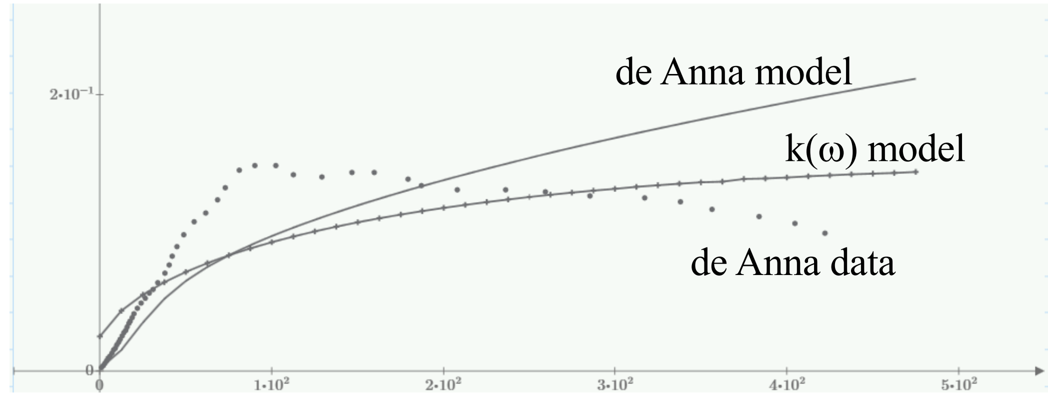


Figure 1. a. Principle of the soft lithography technique. The two glass

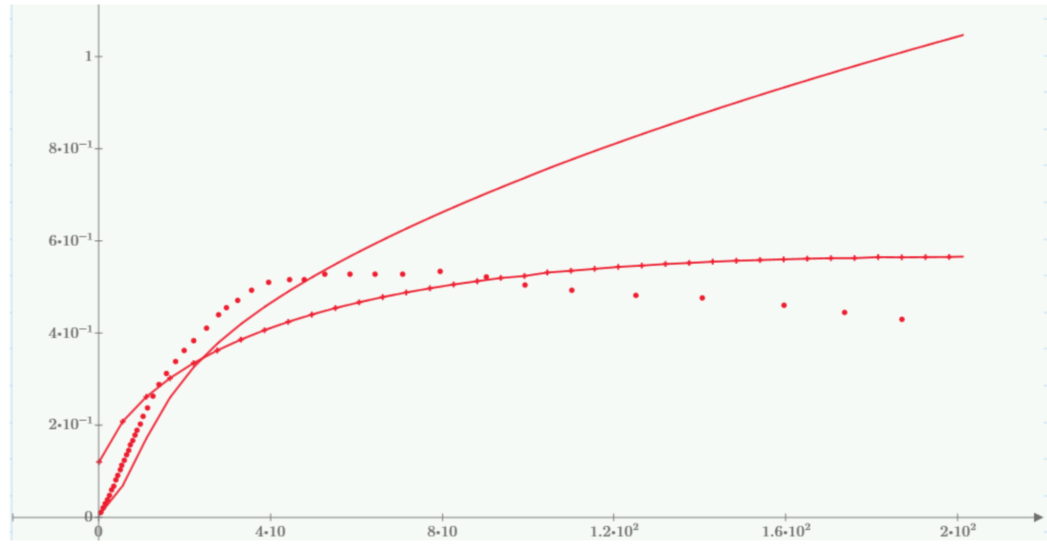


de Anna et al, 2014

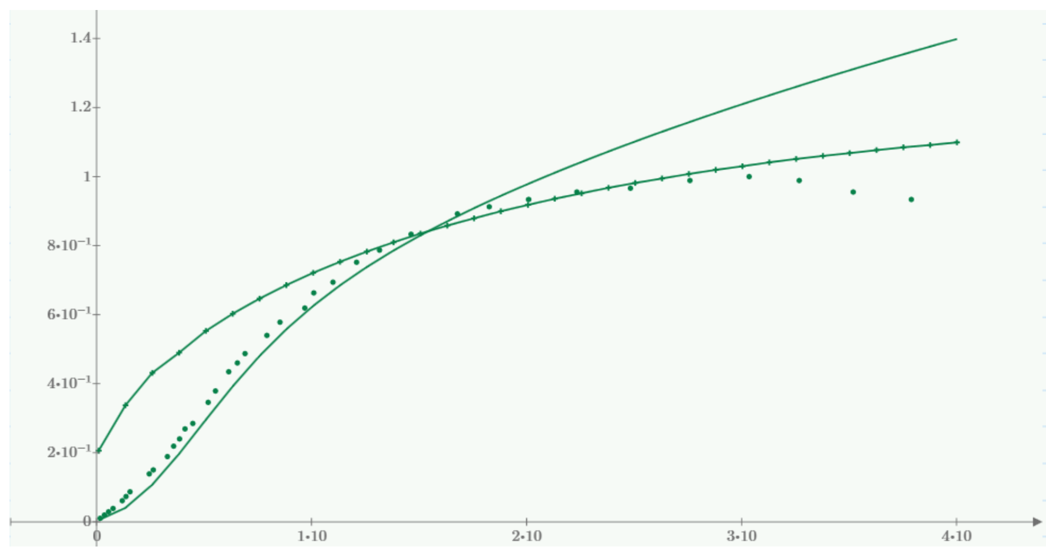
Slow



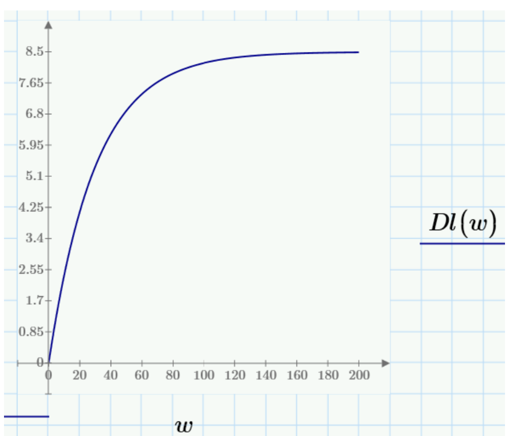
Medium



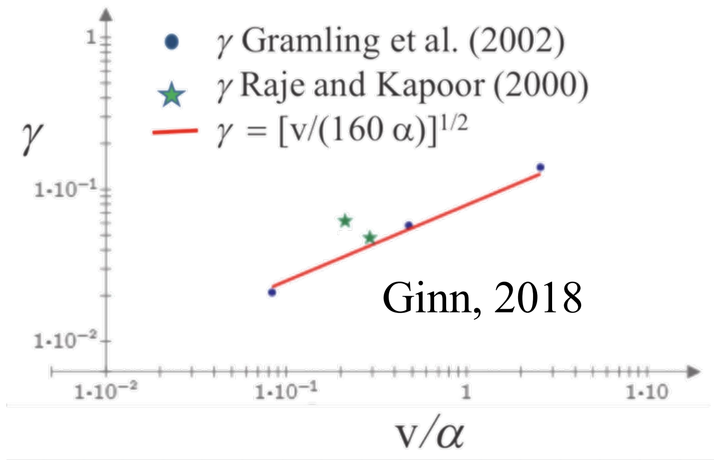
Fast



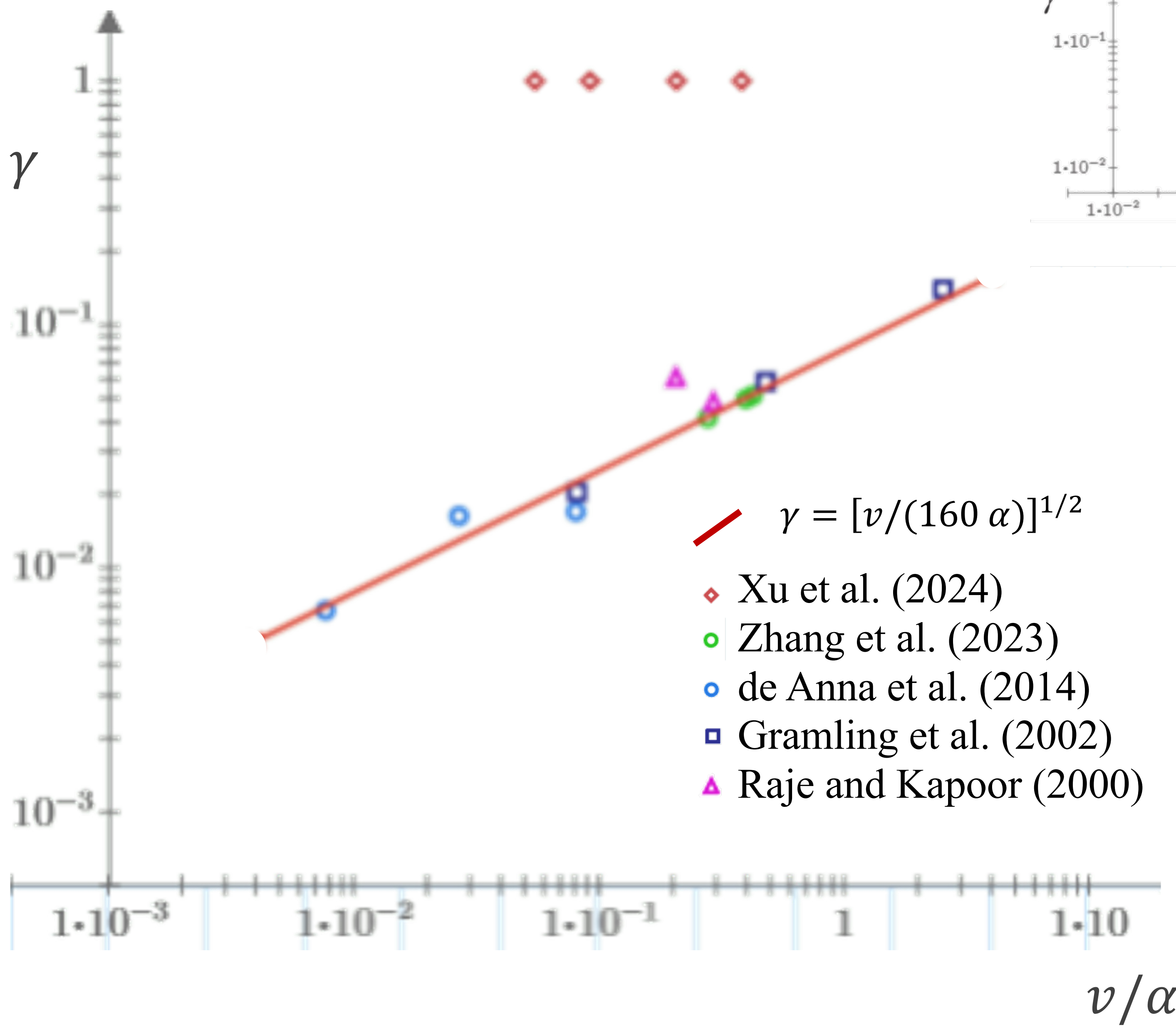
Fitted only γ
yes PAD

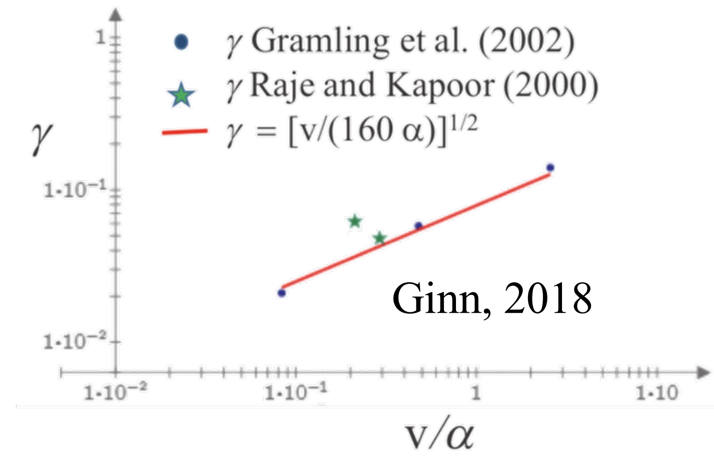


Results


γ Gramling et al. (2002)
γ Raje and Kapoor (2000)
γ = [v/(160 α)]^1/2
γ
1
1·10⁻¹
1·10⁻²
1·10⁻²
1·10⁻¹
1
1·10
Ginn, 2018
v/α

Results





With minor exceptions, No parameter fitting otherwise.

Closing Notes from an engineering perspective*

Theory repair

- General: tested across all relevant data
- Parsimonious / Occam's Razor
- Compatible with the unbroken part of the model

The result of a mixing theory controls the reaction rate

- $k(\omega)$ so far says rate $\propto \omega^{-1/2}$ (should it be $\omega^{-f(\omega)}$?)
- de Anna et al. 2014 => two regimes …
- Farhat et al. 2025 => three
- which ones matter in particular contexts?**

Thank You.

* Careful ! Klemeš, V., 1986, Dilettantism in Hydrology: Transition or Destiny ?, *WRR*
** Molz & Widdowson's bioremediation question…

v/α

Supported by NSF EAR 2142165 &CBET 1855211, and by the Boeing Fund in Environmental Engineering at WSU.

Liu et al., 2020

Xu et al., 2024

Behavior characteristics of bimolecular reactive transport in heterogeneous porous media

Yajing Liu [a], Jiazhong Qian [a], Yong Liu [b,*], Fulin Li [c,**], Yunhai Fang [a]

Chemosphere

The bimolecular reactive transport in heterogeneous porous media: Sub-diffusion in interpretation of laboratory experiment

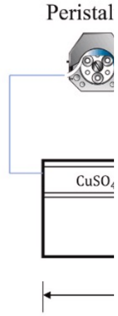
Yi Xu [a,b], Jean-Philippe Carlier [c], HongGua

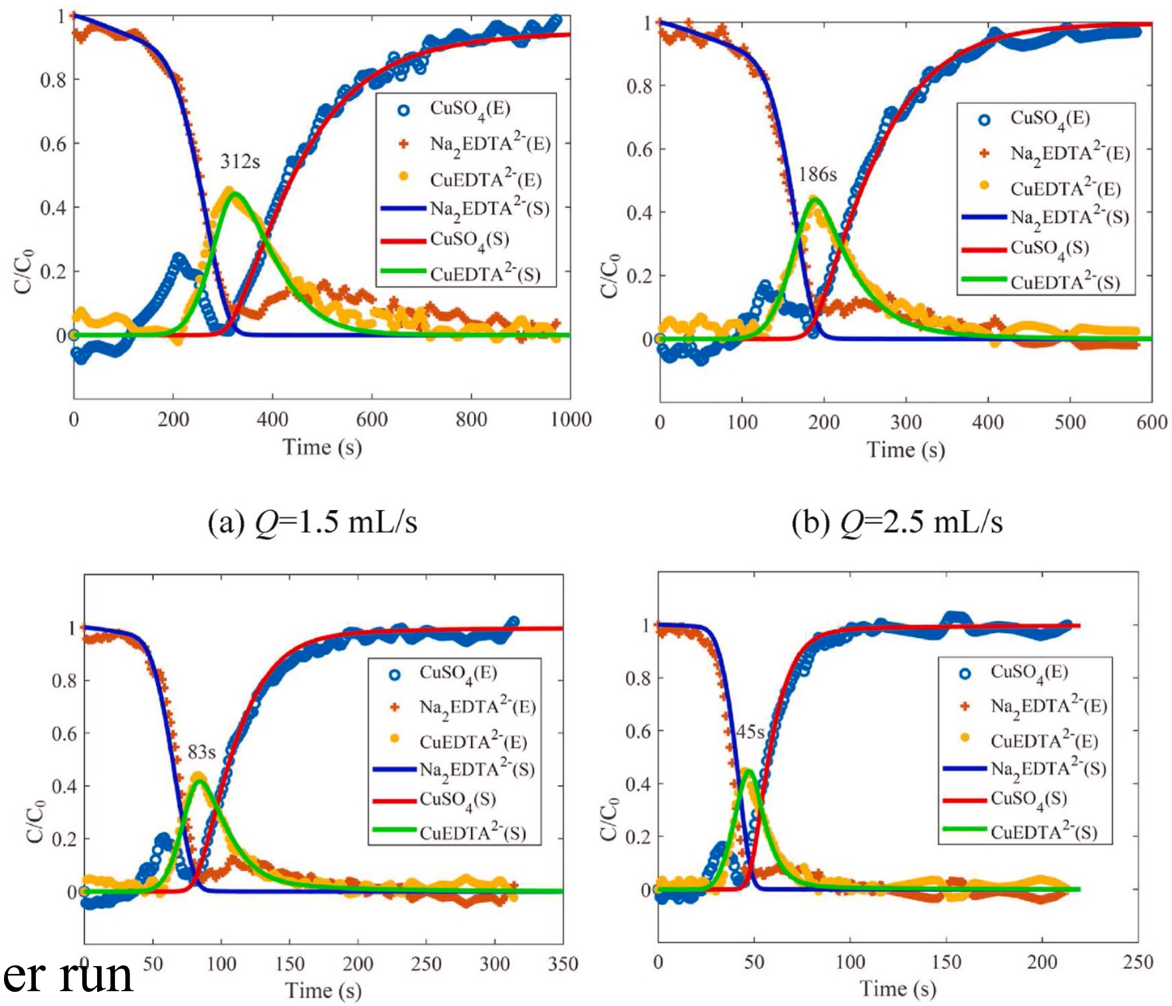
[a] The National Key Laboratory of Water Disaster Prevention, Hohai Unive
[b] College of Mechanics and Engineering Science, Hohai University, Nanjin
[c] UMR 9013 - LaMcube - Laboratoire de Mecanique, Multiphysique, Multi
[d] School of Resources and Environmental Engineering, Hefei University of

HIGHLIGHTS

- The work investigates transport-reaction kinetics of $CuSO_4$ and Na_2EDTA^{2-} in porous media.
- The truncated fractional order bimolecular reaction model describes the sub-diffusion and incomplete mixing phenomenon.
- Physical model parameters are discussed to study the factors affecting solute transport.

GRAPH





(a) Q=1.5 mL/s

(b) Q=2.5 mL/s

(c) Q=5.0 mL/s

(d) Q=10.0 mL/s

All (yes, *All*) parameters refit per run

Also some anomalies… looky here

WATER RESOURCES RESEARCH, VOL. 22, NO. 9, PAGES 177S–188S, AUGUST 1986

Dilettantism in Hydrology: Transition or Destiny?

V. KLEMEŠ

National Hydrology Research Institute, Environment Canada, Ottawa, Ontario

The unsatisfactory state of hydrology is, in the final analysis, the result of the dichotomy between the theoretical recognition of hydrology as a science in its own right and the practical impossibility of studying it as a primary discipline but only as an appendage of hydraulic engineering, geography, geology, etc. As a consequence, the perspectives of hydrologists tend to be heavily biased in the direction of their nonhydrologic primary disciplines and their hydrologic backgrounds have wide gaps which breed a large variety of misconceptions. This state of affairs often paralyzes hydrologists' ability to differentiate between hydrology and water management, hydrology and statistics, facts and assumptions, science and convenience, etc., with consequent dangers both to scientific development of hydrology and to its practical utility. The danger increases with the proliferation of computerized "hydrologic" models whose cheaply arranged ability to fit data is presented as proof of their soundness and as a justification for using them for user-attractive but hydrologically indefensible extrapolations. These points are illustrated, among other things, by discussion of flood frequency analysis. The paper concludes with some thoughts concerning minimum standards for the testing of hydrologic simulation models that would ensure at least a modest level of credibility, and with a few suggestions for ingredients of a long-term cure that can prevent hydrology from joining alchemy and astrology in the annals of dilettantism.

MODELS THAT WORK WELL—THE GREATEST DANGER TO PROGRESS IN HYDROLOGY

HYDROLOGIC MATHEMATISTRY AS A BASIS OF INDEFENSIBLE EXTRAPOLATIONS

Hydrology, having no solid foundations of its own and moving clumsily along on an assortment of crutches borrowed from different disciplines, has always been an easy victim of this practice. Every new mathematical tool has left behind a legacy of misconceptions invariably heralded as scientific breakthroughs. The Fourier analysis, as was pointed out by *Yevjevich* [1968], had seduced the older generation of hydrologists into decomposing hydrologic records into innumerable harmonics in the vain hope that their reconstitution will facilitate prediction of future hydrologic fluctuations (fortunately, few computers were available at the time so that the Fourier fever did not become an epidemic); various statistical methods developed for evaluation of differences in repeatable experiments have been misused to create an illusion of a scientific analysis of unrepeatable hydrologic events; linear algebra has served to transform the idea of a unit hydrograph from a crude but useful approximation of a soundly based concept into a pretentious masquerade of spurious rigor now exercised in the modelling of flood events; time series analysis has been used to remake inadequate 20-year streamflow records into "adequate" 1000-year records, or even more adequate 10,000-year records; and the theory of pattern recognition is now being courted in the vain hope that it will lend scientific legitimacy to the unscientific concept of mindless fitting that dominates contemporary hydrologic modelling. In all these cases, mathematics has been used to redefine a hydrologic problem rather than solve it. *Box* [1976] calls such use of mathematics "mathematistry" and laments:

> In such areas as sociology, psychology, education, and even, I sadly say, engineering, investigators who are not themselves statisticians sometimes take mathematistry seriously. Overawed by what they do not understand, they mistakenly distrust their own common sense and adopt inappropriate procedures devised by mathematicians with no scientific experience.