

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



INTERPORE 2026 NANTES

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

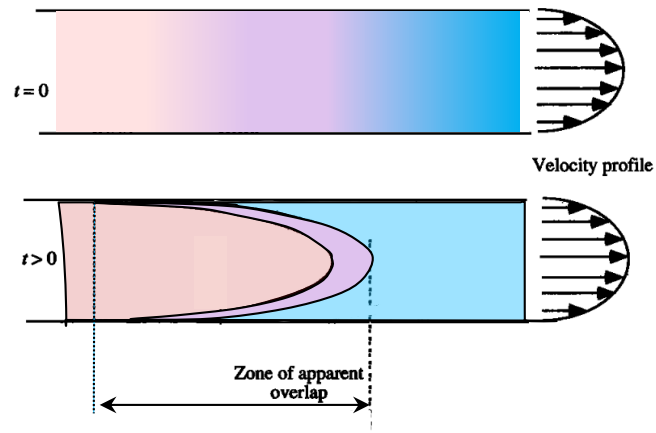
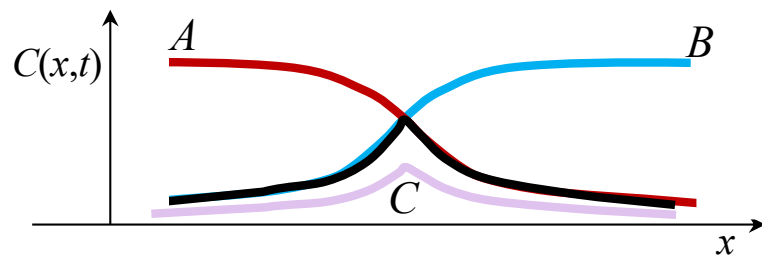


Figure 2. Illustration of the concept of segregation-induced scale dependence of transformation in laminar shear flow. Un-

1-D Upscaled product concentration 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

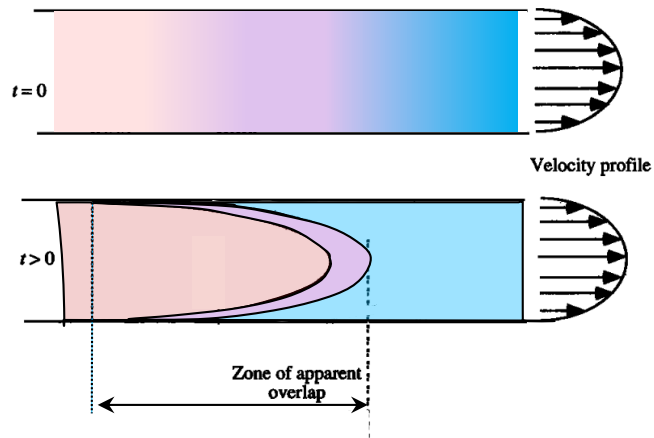
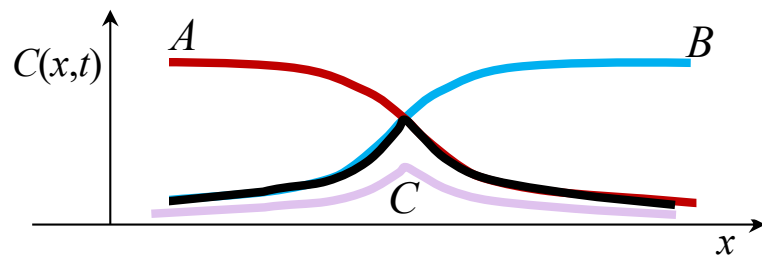


Figure 2. Illustration of the concept of segregation-induced scale dependence of transformation in laminar shear flow. Un-

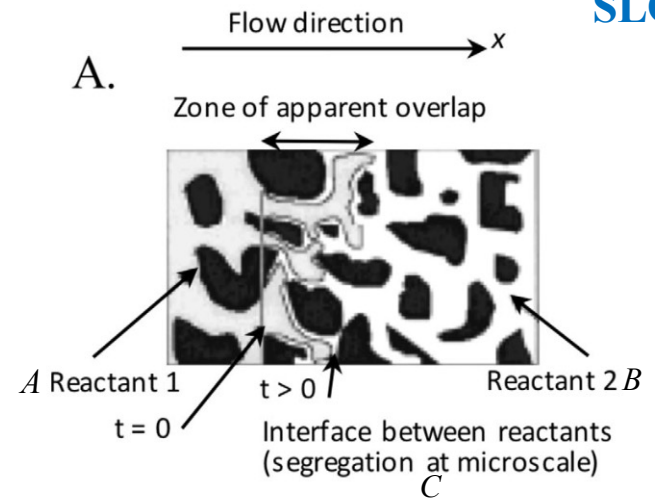
1-D Upscaled product concentration C is overestimated



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

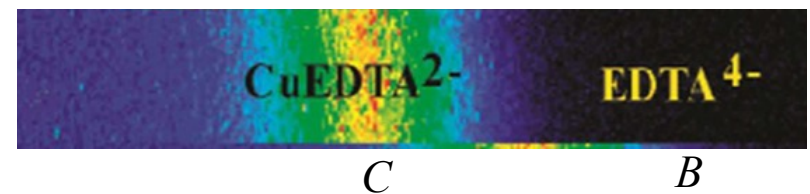
Raje & Kapoor 2000.

RK00
SLOW



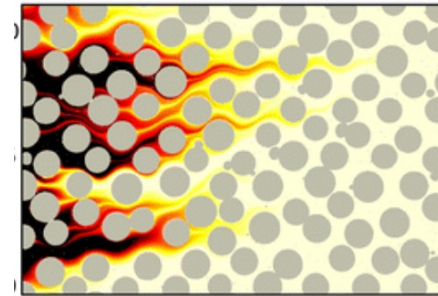
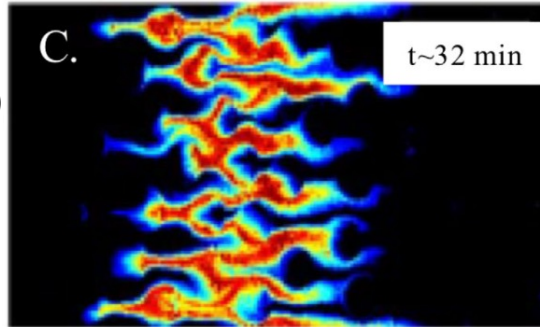
Gramling, Harvey & Meigs 2002.

G02
FAST



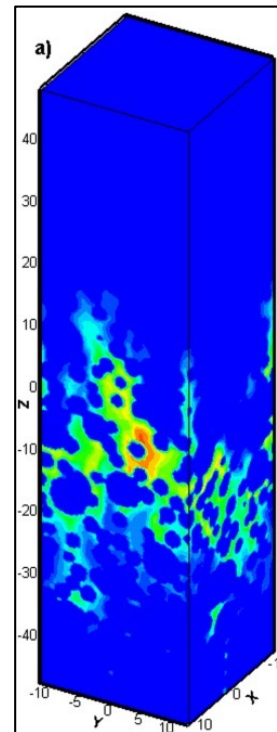
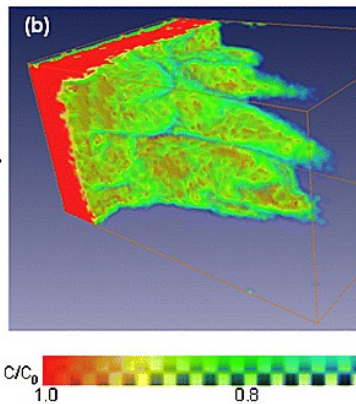
We can see the “segregation zones”

Oates & Harvey
2006 FAST (G02)
Bead pack

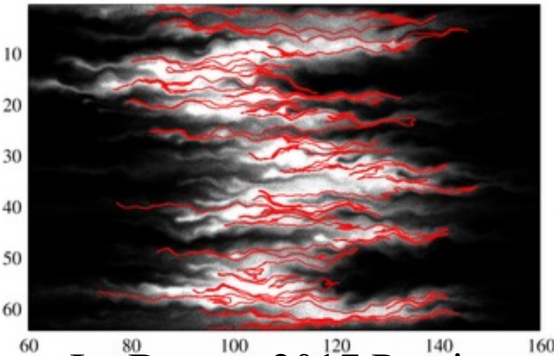


de Anna EST 2014

Yoon 2008
Passive tracer
 $MgCl_2$
sandbox

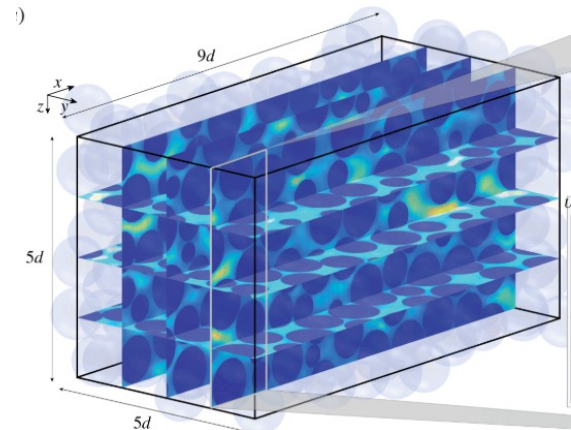
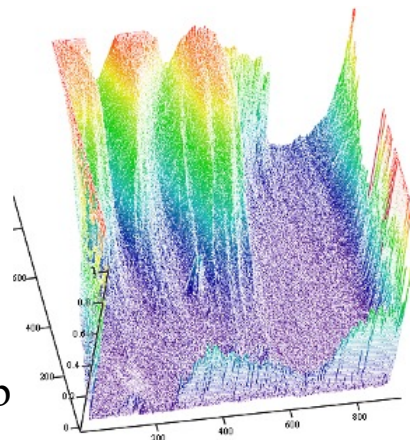


Scheibe 2013
In silico



Le Borgne 2017 Passive tracer

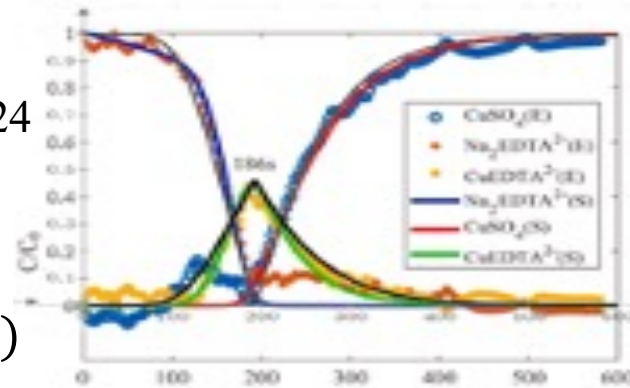
Klise 2008
KI(odine)
Massillon
Sandstone slab



Souzy 2020 Passive tracer

The “Bimolecular reaction upscaling” game*

Xu 2024

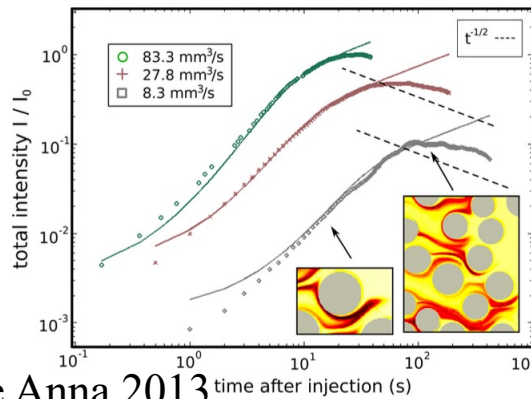
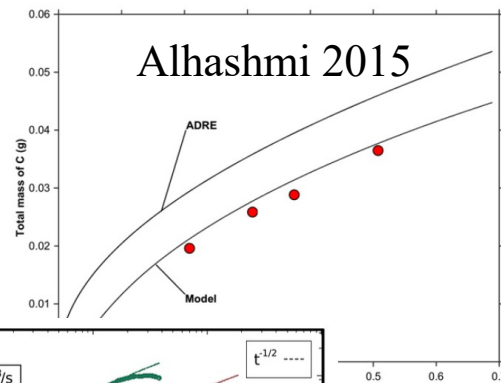


Target Metrics

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

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

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

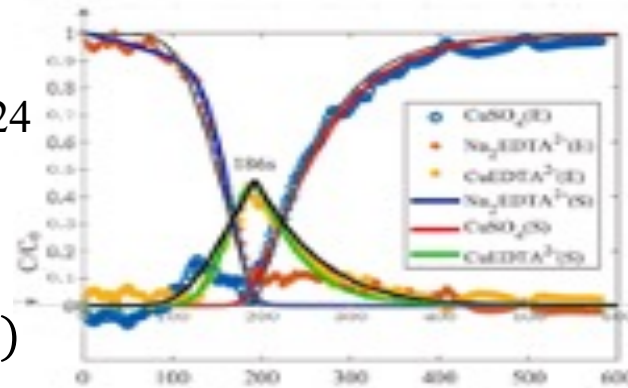


de Anna 2013

* A Parade of Modeling Innovations Wow !

The “Bimolecular reaction upscaling” game*

Xu 2024

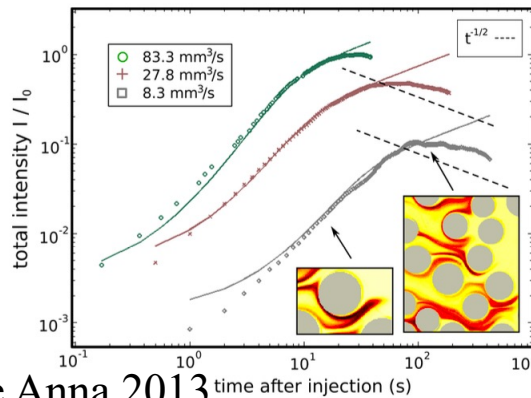
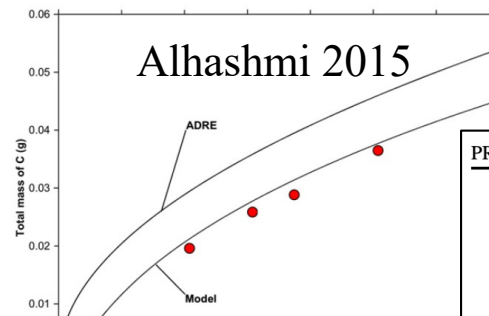


Target Metrics

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

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

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



de Anna 2013

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

Stretching, Coalescence, and Mixing in Porous Media

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Marco Dentz
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(Received ...)
PHYSICAL REVIEW FLUIDS 10, 024501 (2025)

Linking mixing interface deformation to concentration gradients in porous media

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Notre Dame, Indiana 46556, USA

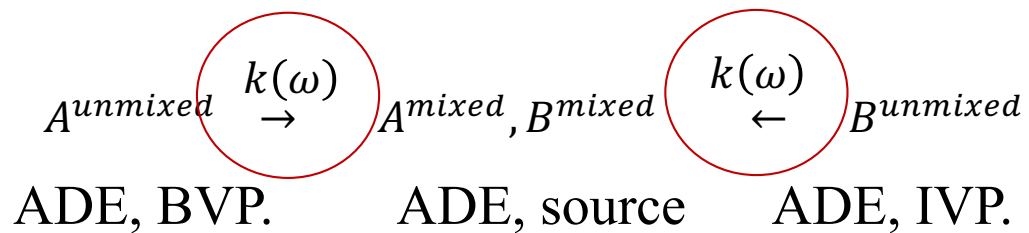
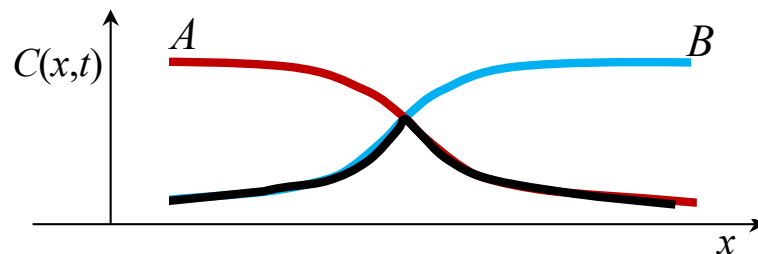
Guillem Sole-Mari
Geosciences Rennes, University of Rennes, Rennes 35042, France

Annual Review of Fluid Mechanics

Fluid Deformation and Mixing in Porous Media as Drivers for Chemical and Biological Processes

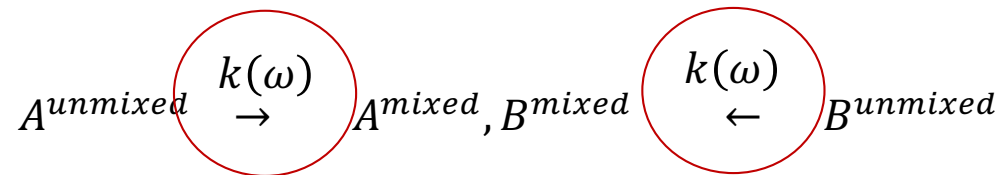
Tanguy Le Borgne^{1,2} and Joris Heyman¹

Our approach



E.G., for the unmixed BVP influent solute $A^{unmixed}$

$$\frac{\partial A^u}{\partial t} + v \frac{\partial A^u}{\partial x} + 1 \frac{\partial A^u}{\partial \omega} - D \frac{\partial^2 A^u}{\partial x^2} = -k(\omega)A^u$$



Mixing via 1st-order **mobile-mobile** mass transfer with rate coeff:

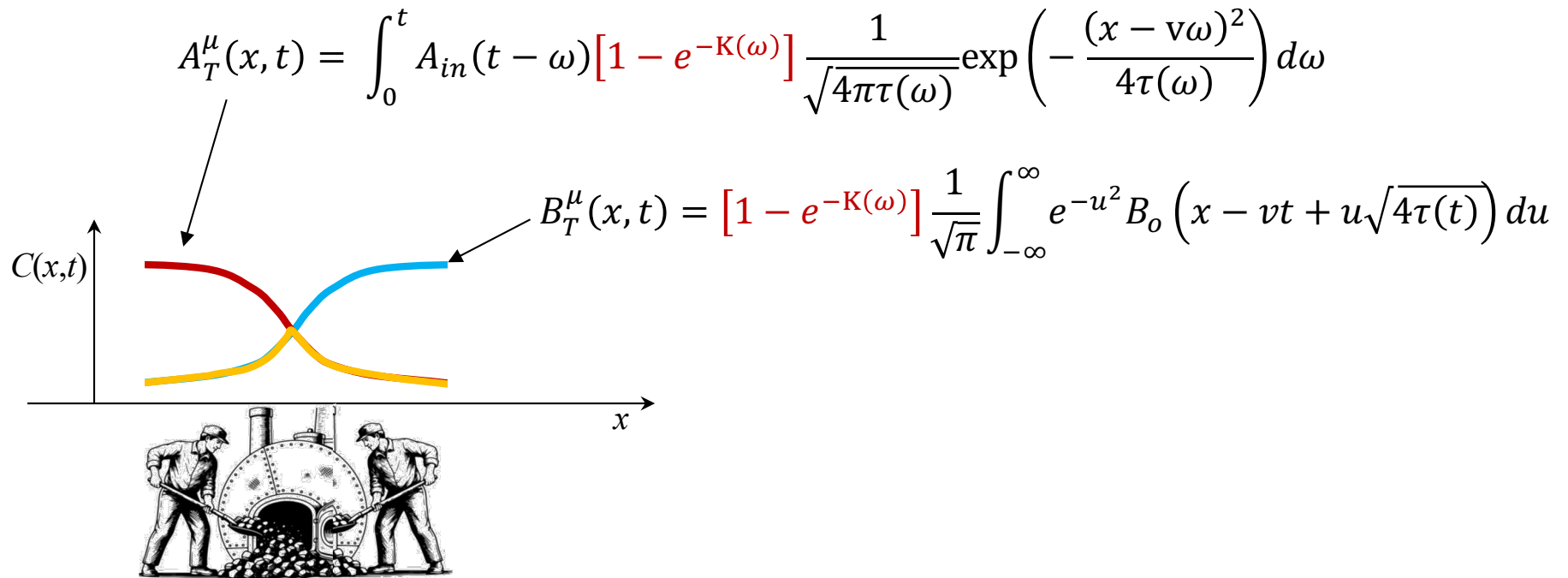
$$k(\omega) = \frac{\gamma}{\sqrt{\omega}}$$

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

...

when rate is dispersion-limited (Le Borgne and Heyman *ARFM* 2026)

1-D Solution



Exploits irreversibility of mixing

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

***Closed-form solutions** (for fast rxn; easy finite differences for slow reactions)
- Pre-Asymptotic Dispersion, transient velocity*

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

Buckingham Π

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

If γ depends on:

α, v

Then:

$$\gamma \propto \sqrt{\frac{v}{\alpha}}$$

D_m, α, v

$$\gamma \propto \sqrt{\frac{v}{\alpha}} f\left(\frac{D_m}{\alpha v}\right)$$

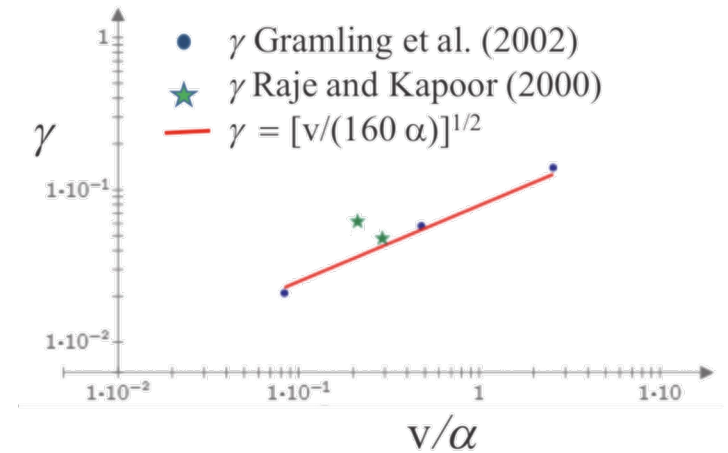
d_{50}, D_m, α, v

$$\gamma \propto \sqrt{\frac{v}{\alpha}} f\left(\frac{D_m}{d_{50}v}, \frac{\alpha}{d_{50}}\right)$$

$v, d_{50}, D_m, \alpha, v$

$$\gamma \propto \sqrt{\frac{v}{\alpha}} f\left(\frac{D_m}{d_{50}v}, \frac{\alpha}{d_{50}}, \frac{v}{v d_{50}}\right)$$

pore Pé, ..., Pore Re



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

"New" Experiments

	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

"New" Experiments

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

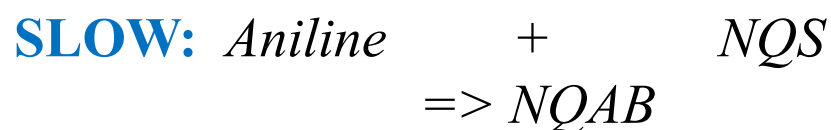
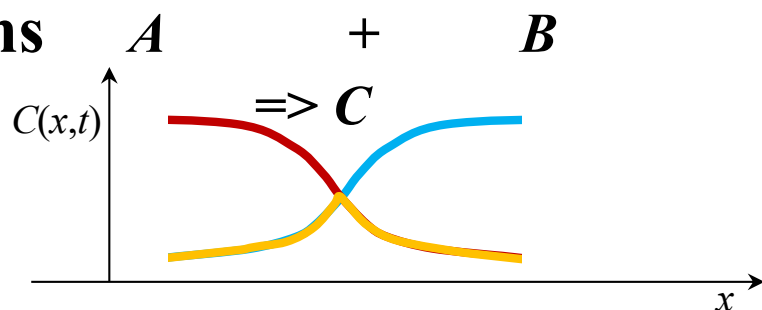
$$k(\omega) = \frac{\gamma}{\sqrt{\omega}} \text{ approach, fit the}$$

γ in each simulation,

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

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

Reactions

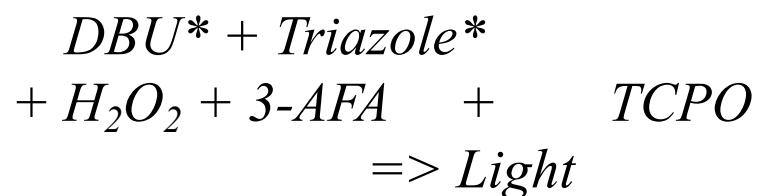


Colorimetric $C(x,t)$
RK00, Zhang 2014, BTCs.



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

ADJUSTABLE/FAST:



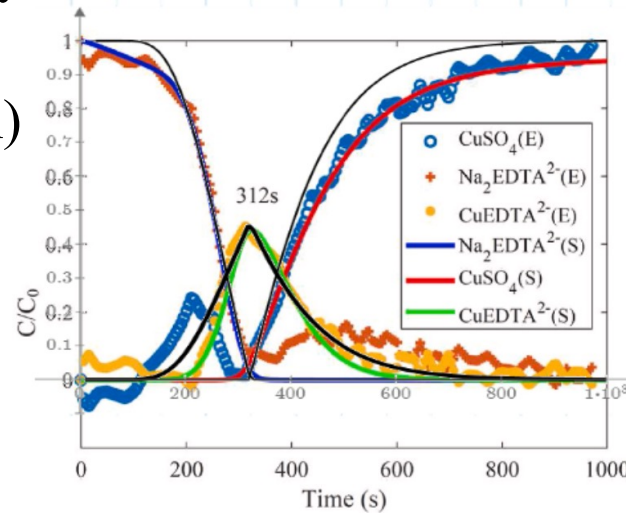
Chemoluminescent dC/dt
de Anna 2014, rate of C total

* catalysts

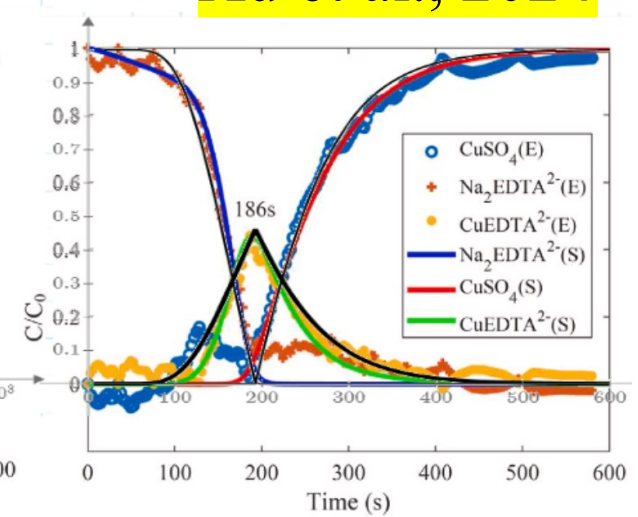
** simulated: Alhashmi 2015, Sole-Mari 2023

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"



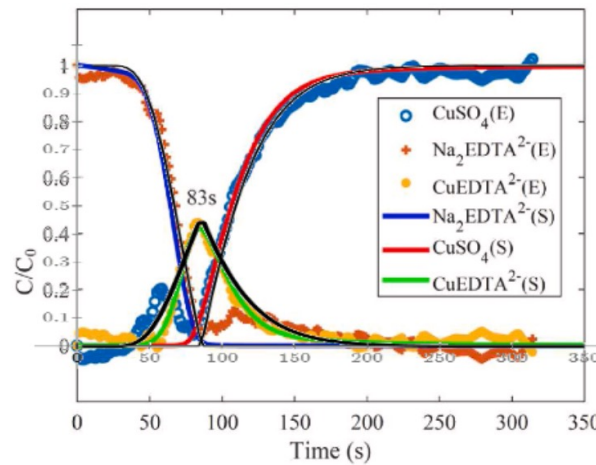
(a) $Q=1.5$ mL/s



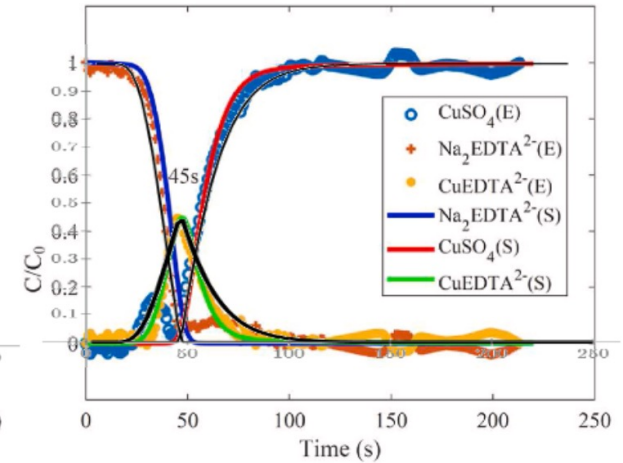
(b) $Q=2.5$ mL/s

All (yes, All) parameters
 refit per each experiment and
 each solute.

Also anomalies... look =>



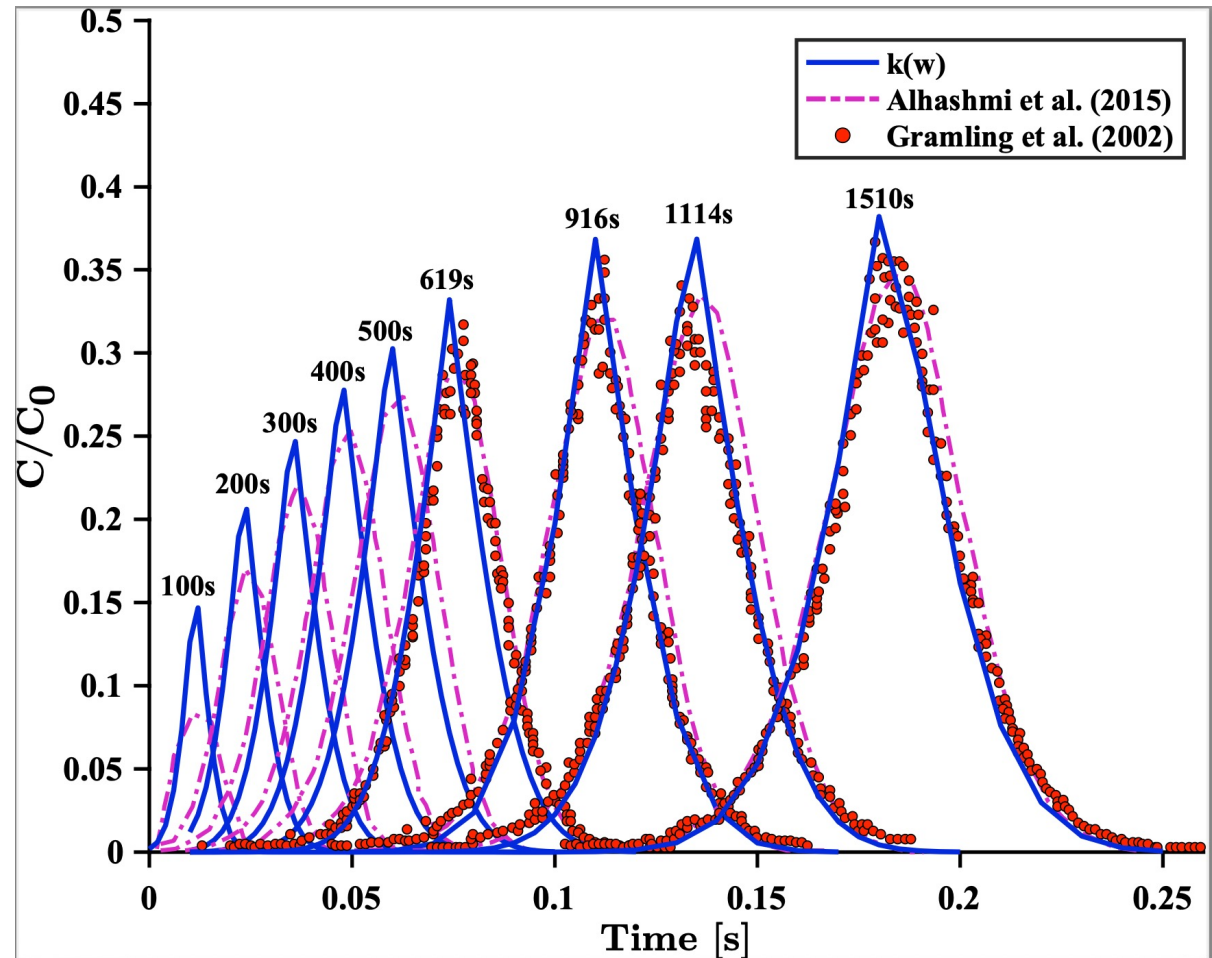
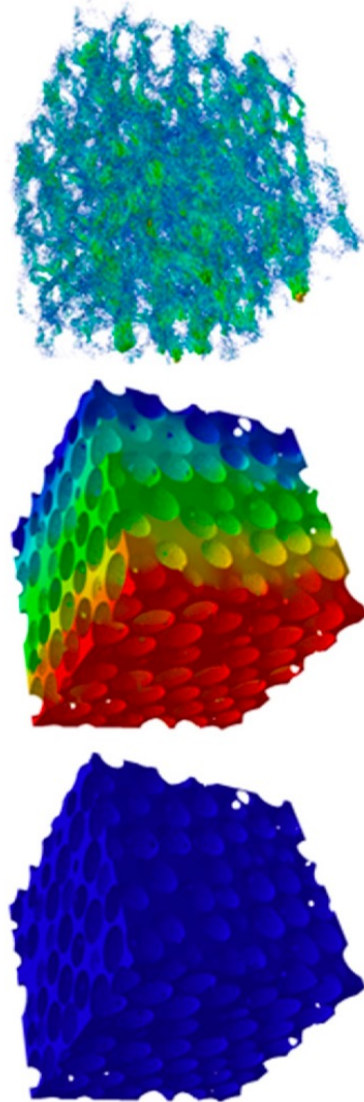
(c) $Q=5.0$ mL/s



(d) $Q=10.0$ mL/s

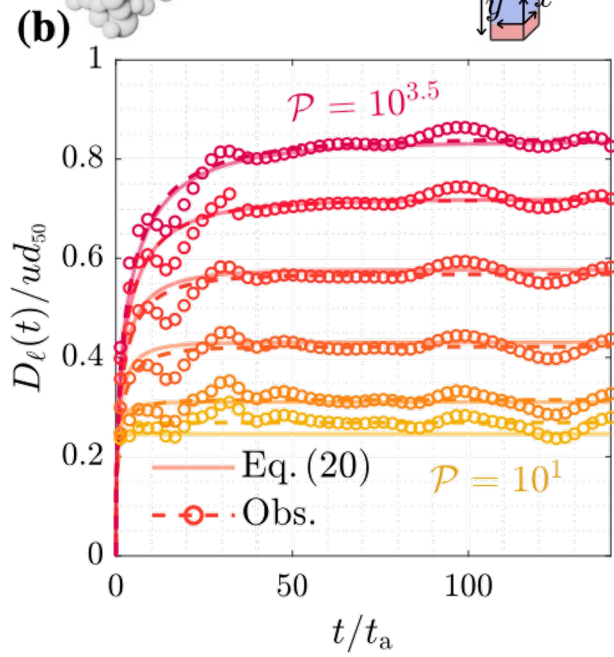
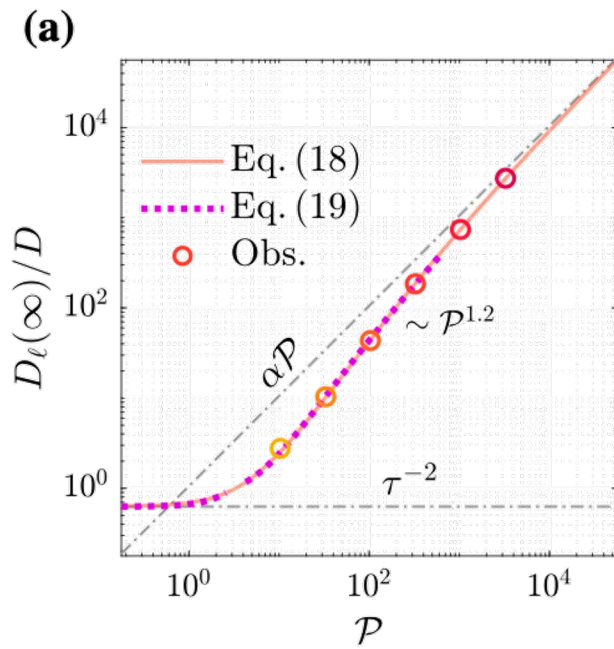
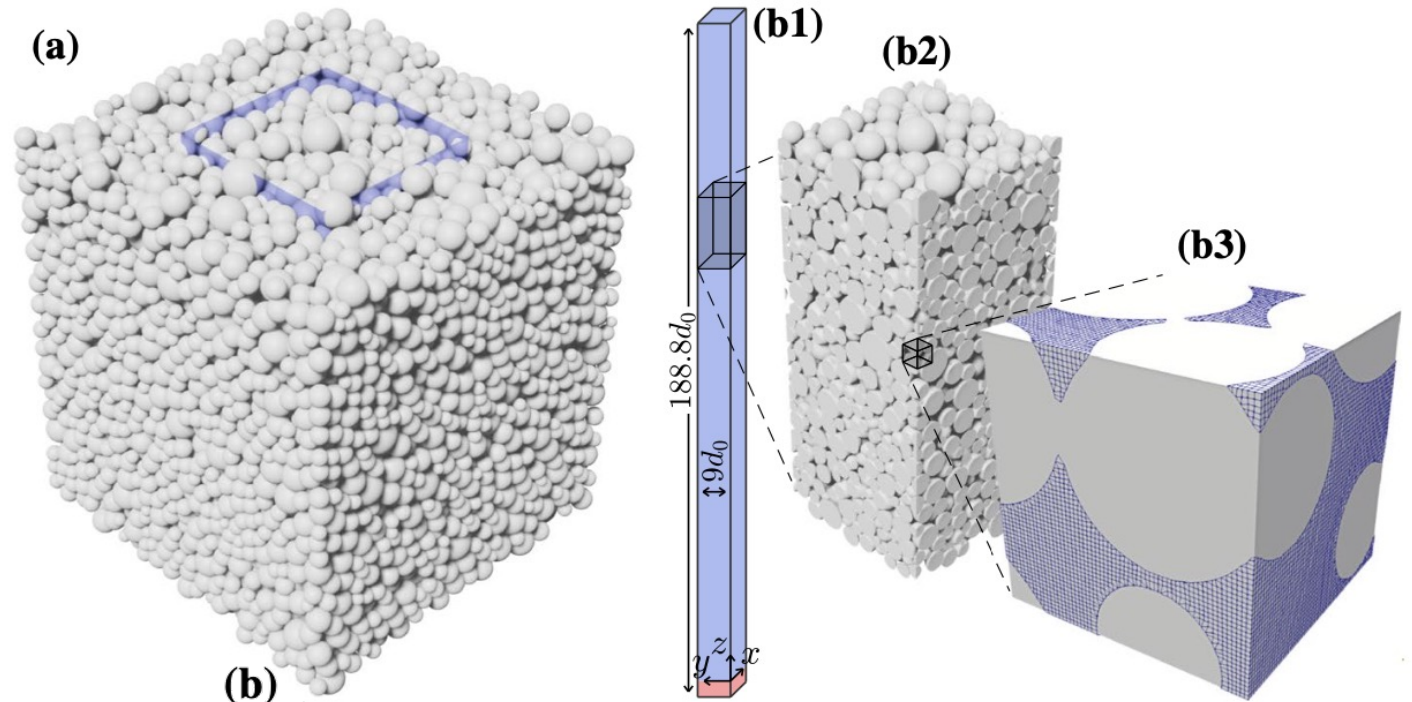
Our new solutions are in **black** and involve
 fitting one dispersion coeff. (for all) and four
 insane γ values.

Alhashmi et al. 2015 Simulation, Particle tracking

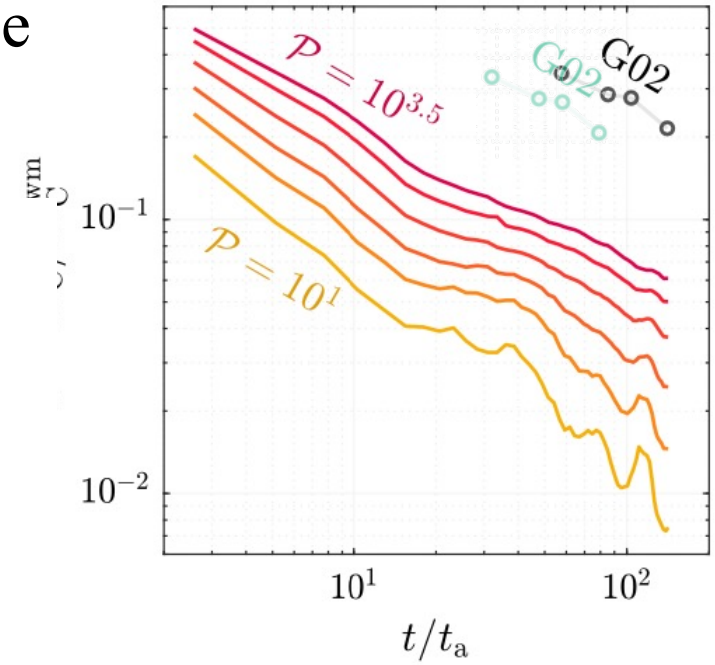
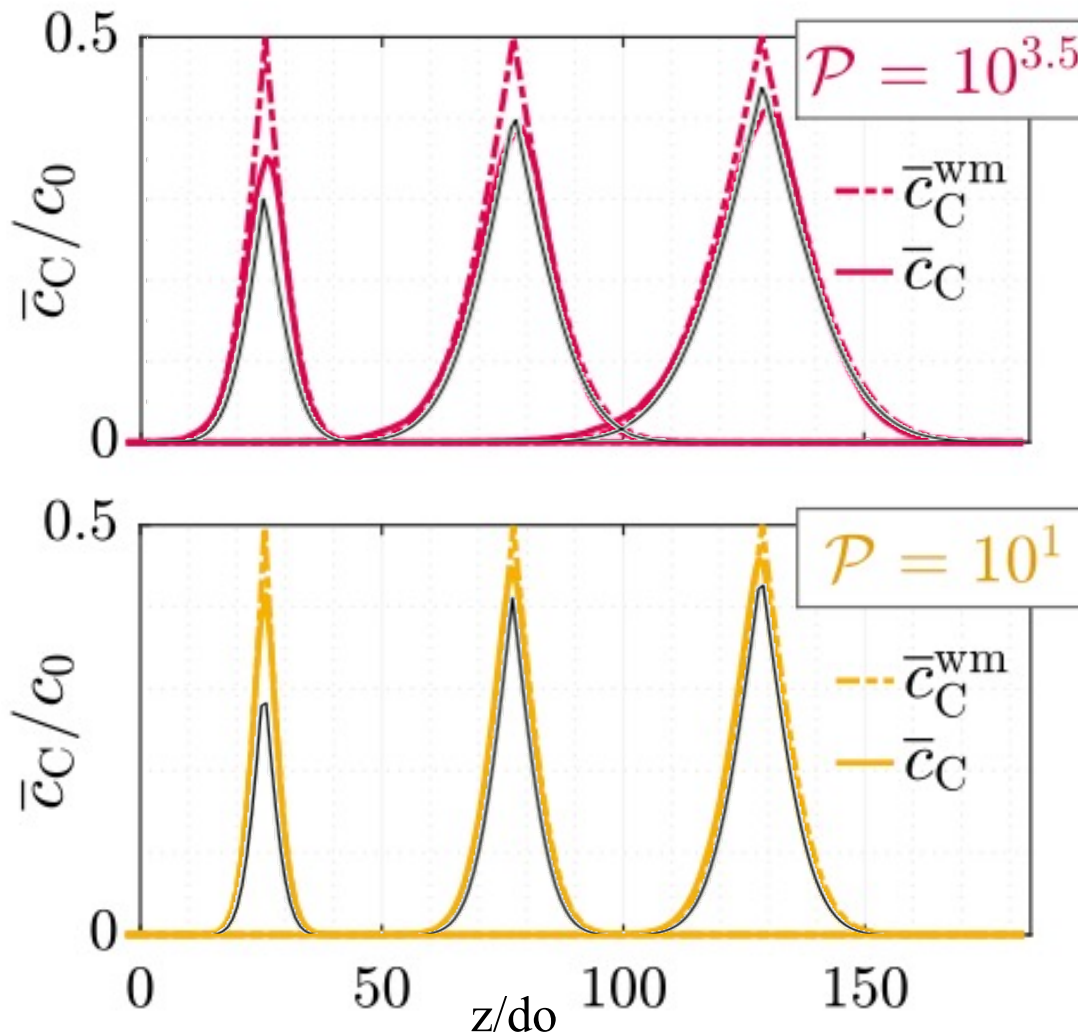


Replicated G02, including early time PAD is our solution in **blue**

Sole-Mari et al., 2023 Simulation, Eulerian



Sole-Mari et al, 2023 Monodisperse case



	G02	S-M23
\mathcal{P}	$10^{3.35}$	$10^{3.5}$
d_o [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.

Zhang, 2023

Zhang, 2014

Slow system

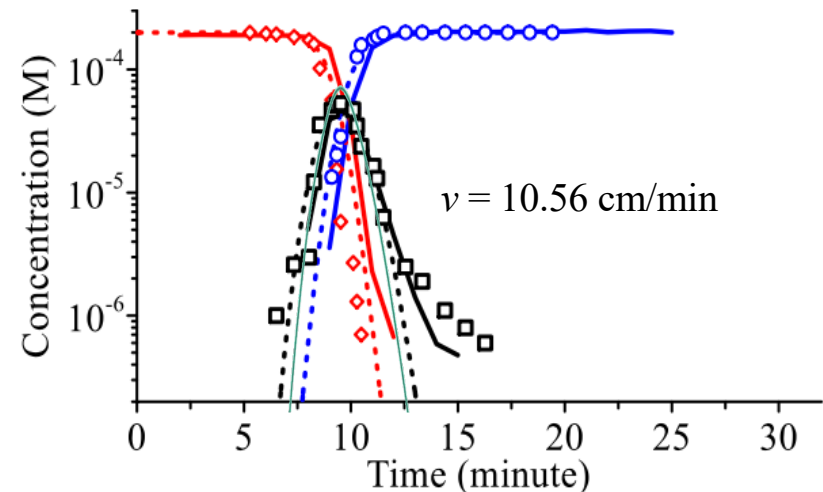
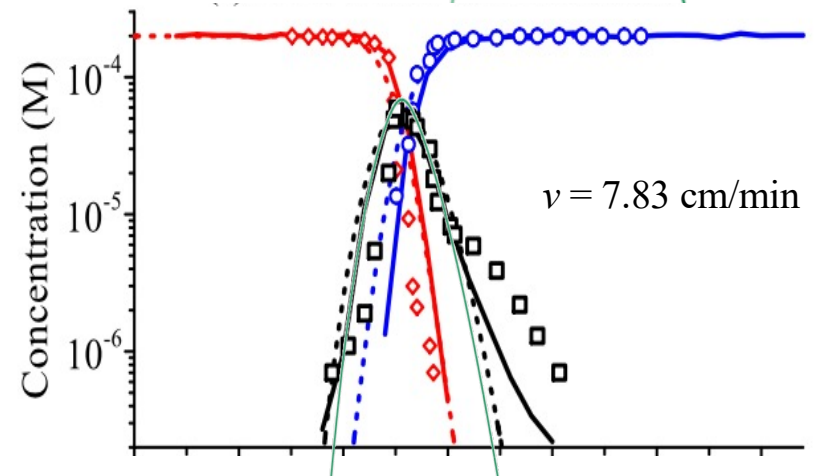
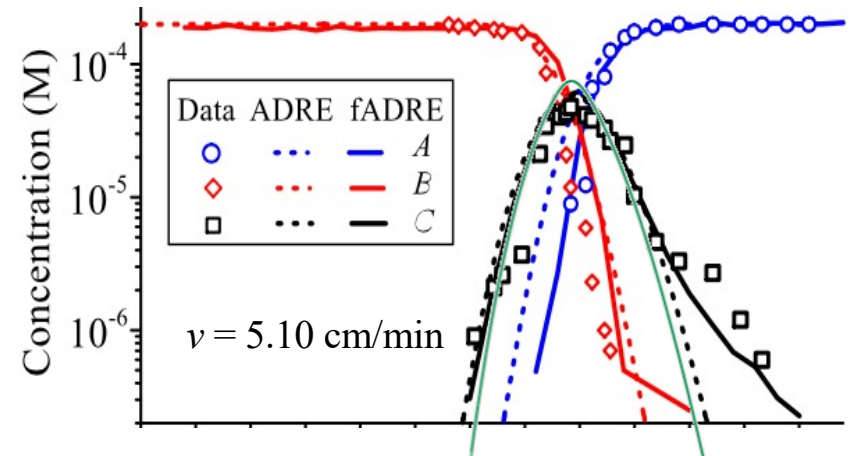
Aniline + NQS -> NQAB.

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

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

Environmental Science & Technology

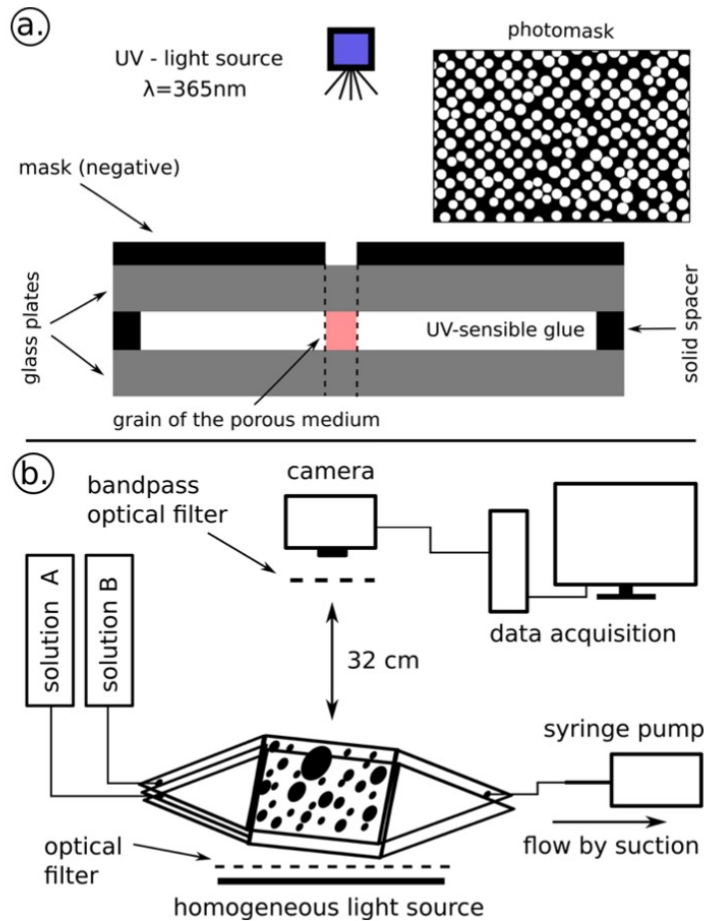
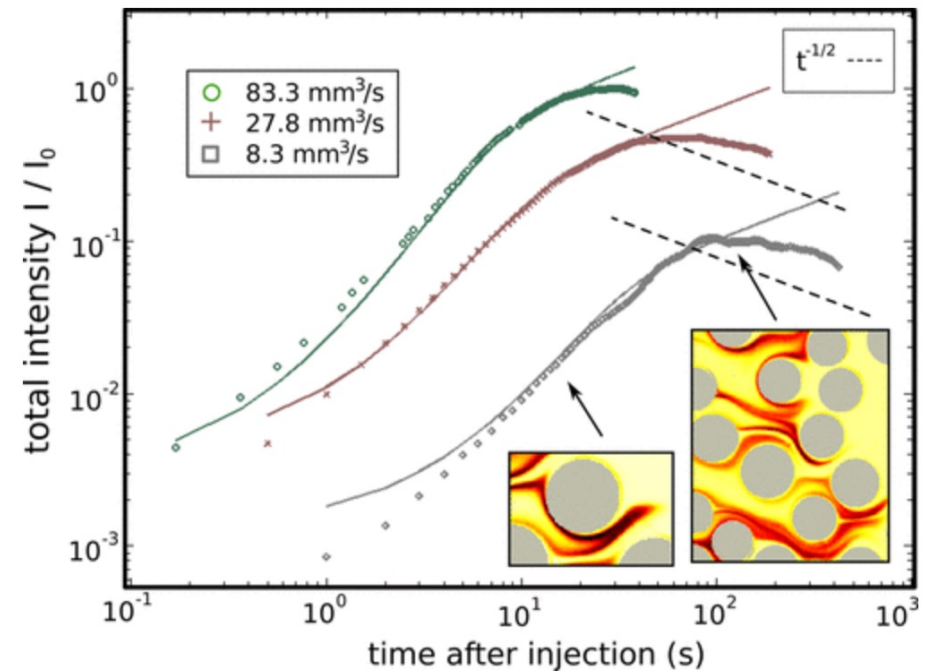


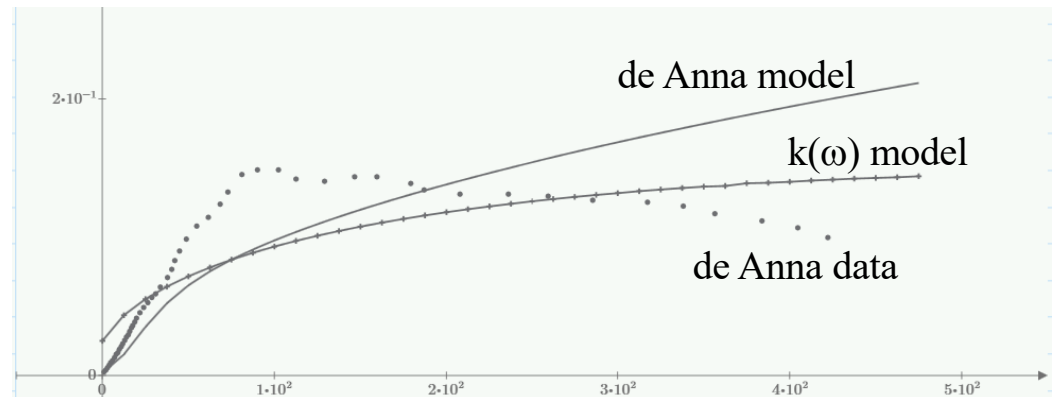
Figure 1. a. Principle of the soft lithography technique. The two glass



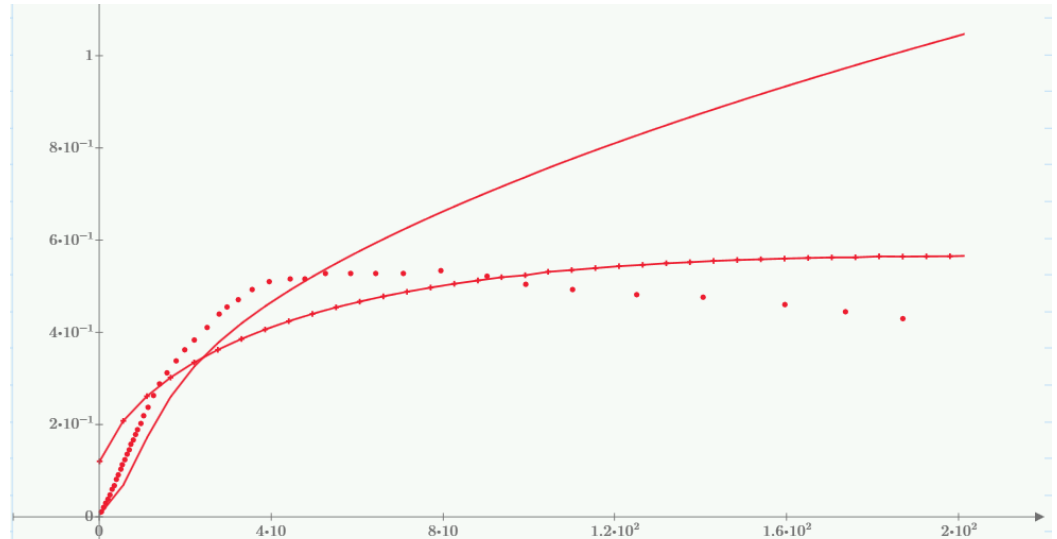
With Thanks to Yves Méheust for help with some conditions (domain, c_0 ...)

de Anna et al, 2014

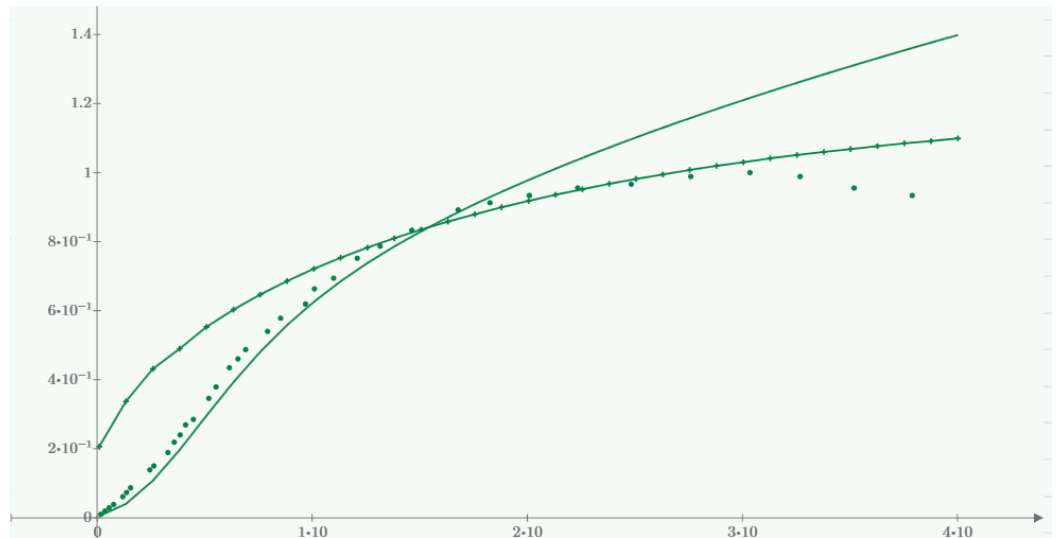
Slow



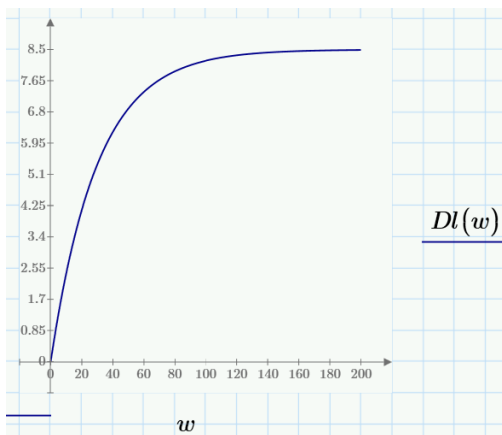
Medium



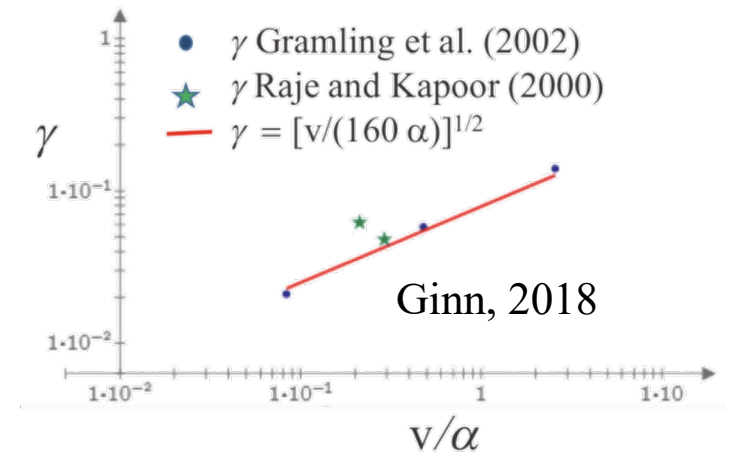
Fast

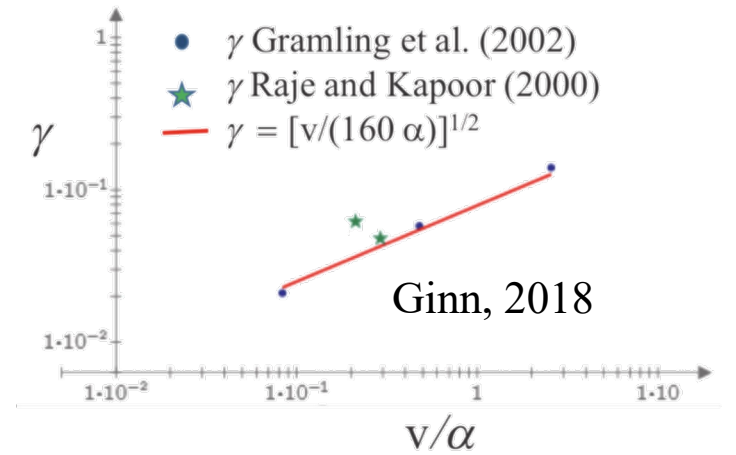
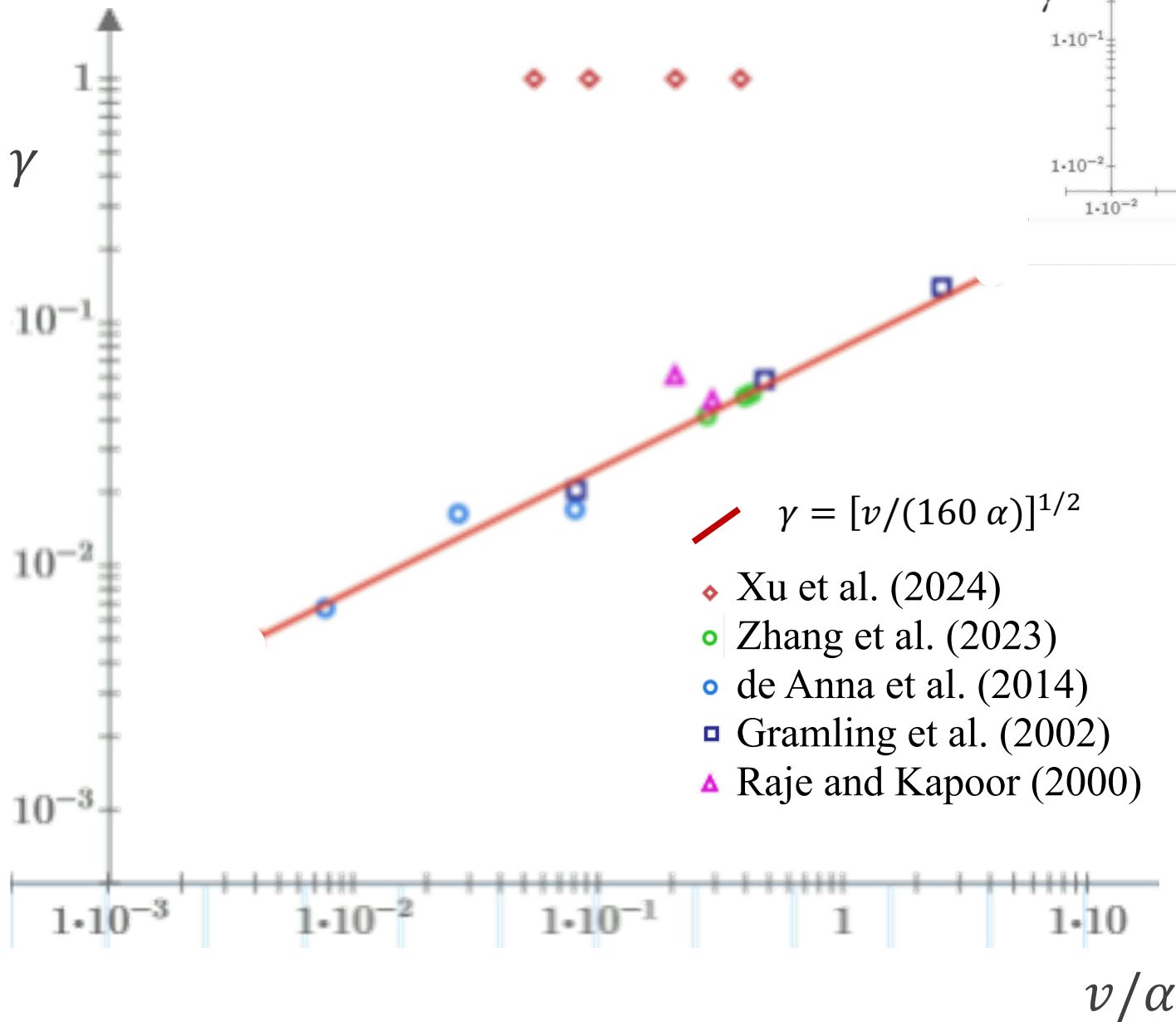


Fitted only γ
yes PAD



How did the γ model do ?





With minor exceptions,
 No parameter fitting
 otherwise.

Closing Notes from a practical 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 \Rightarrow two regimes ...
- Farhat et al. 2025 \Rightarrow three
- which ones matter in particular contexts (Molz & Widdowson) ?

Thank You.

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

$$\begin{aligned}
 & \text{ORIGIN} := 1 \quad vw := 1 \quad \text{units are mm and s} \quad do := 2 \quad mm \quad L := 200 \cdot do \quad v := 0.103 \quad mm \quad ta := \frac{do}{v} \quad T1 := 25.7 \cdot ta \quad T2 := 77.2 \cdot ta \quad T3 := 128.7 \cdot ta \quad Pe := 10^{3.5} \quad Dm := \frac{v \cdot do}{Pe} \quad \alpha := 1.05 \\
 & Pc := 228 \quad \beta(P) := \frac{1}{1 + \sqrt{\frac{Pc}{P}}} \quad tau := 1.263 \quad \gamma_{what} := 0.0275 \quad \text{from figure 4c?} \quad tc := \gamma_{what} \cdot \beta(Pe)^2 \cdot Pc \cdot ta \quad 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) \quad \tau(v, w) := \int_0^w D(u) \, du \\
 & k(w, g) := \frac{g}{\sqrt{w}} \quad K(w, g) := \int_0^w k(u, g) \, du \quad co(u) := \Phi(u) \quad cin(u, v) := v \cdot \frac{\Phi(u)}{vw} \quad \gamma p(u) := \sqrt{\frac{u}{160 \cdot \alpha}} \quad gamma := \gamma p(v) \quad gamma = 0.025 \quad N := 200 \quad i := 1..N \quad 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(x - v \cdot t + u \cdot \sqrt{4 \cdot \tau(v, t)}) \, du \quad \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)) \quad c1_i := c(z_i, T1, v) \quad c2_i := c(z_i, T2, v) \quad 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(x - v \cdot t + u \cdot \sqrt{4 \cdot \tau(v, t)}) \, du - \max(c(x, t, v), 0) \quad \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) \quad ai2_i := \alpha in(z_i, T2, v) \quad ai3_i := \alpha in(z_i, T3, v) \quad ab1_i := \alpha b(z_i, T1, v) \quad ab2_i := \alpha b(z_i, T2, v) \quad ab3_i := \alpha b(z_i, T3, v)
 \end{aligned}$$

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

Yes PAD

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.

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Largely Untouched

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

Liu et al.,
2020

Xu et al.,
2024

Behavior characteristics of bimolecular reactive transport in heterogeneous porous media

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

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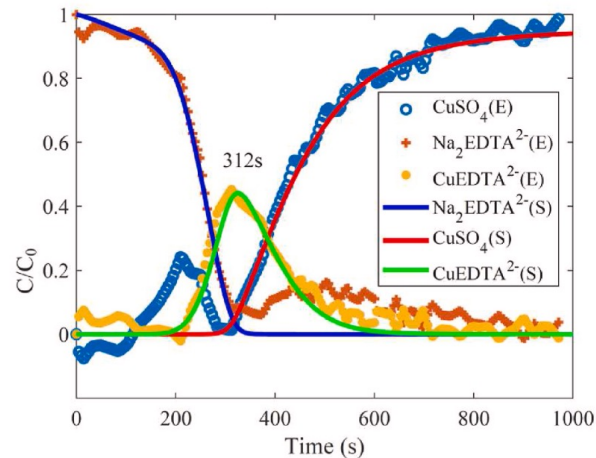
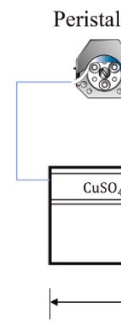
^c UMR 9013 - LaMcube - Laboratoire de Mecanique, Multiphysique, Multi

^d School of Resources and Environmental Engineering, Hefei University of

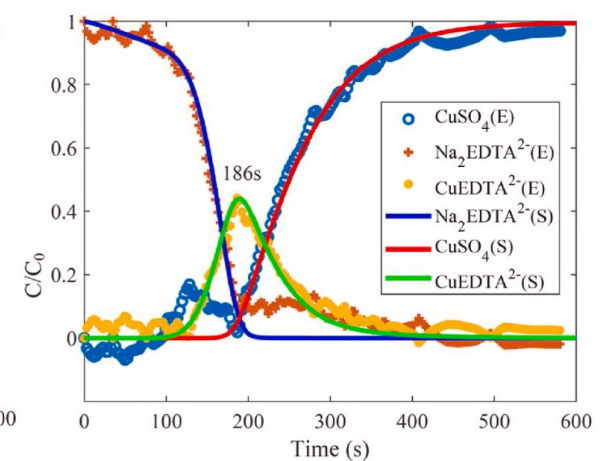
HIGHLIGHTS

- The work investigates transport-reaction kinetics of CuSO_4 and $\text{Na}_2\text{EDTA}^{2-}$ 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.

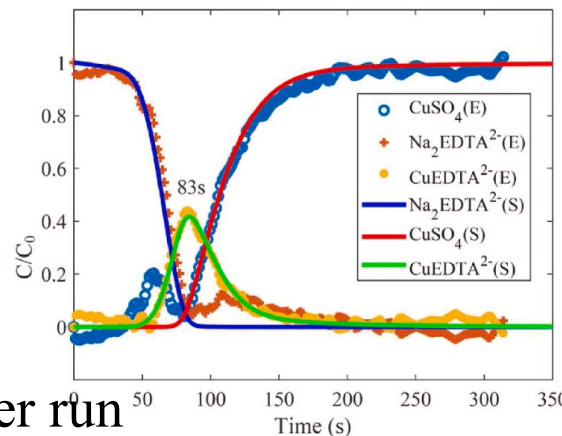
GRAPH



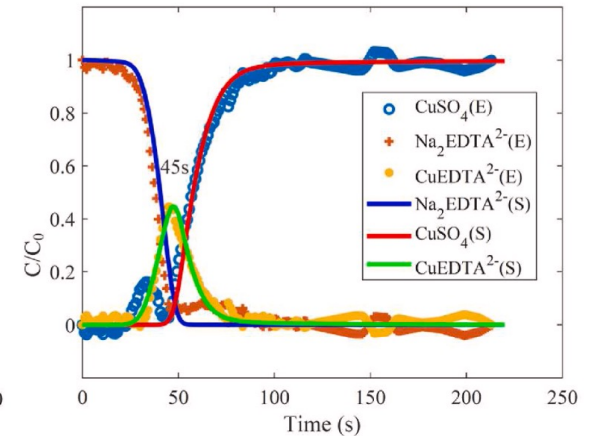
(a) $Q=1.5$ mL/s



(b) $Q=2.5$ mL/s



(c) $Q=5.0$ mL/s

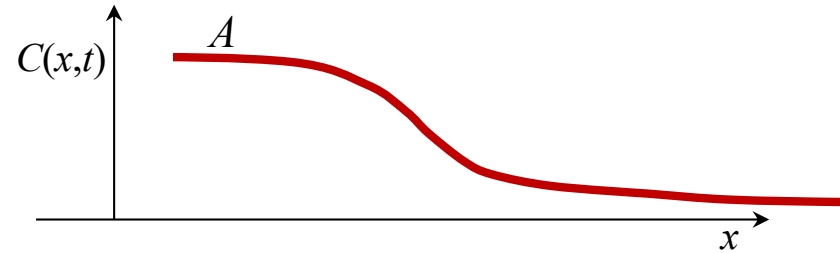


(d) $Q=10.0$ mL/s

All (yes, All) parameters refit per run
Also some anomalies... looky here

E.G., for the unmixed BVP influent solute $A^{unmixed}$

$$\frac{\partial A^u}{\partial t} + v \frac{\partial A^u}{\partial x} + 1 \frac{\partial A^u}{\partial \omega} - D \frac{\partial^2 A^u}{\partial x^2} = -k(\omega)A^u$$



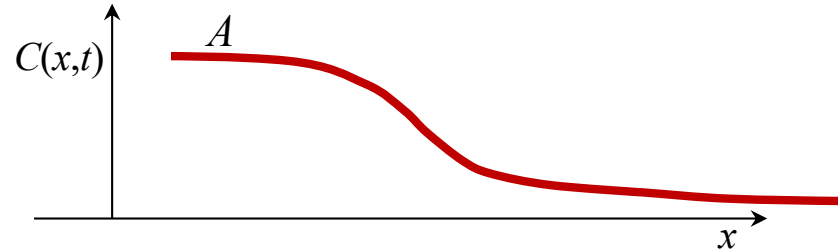
$$k(\omega) = \frac{\gamma}{\sqrt{\omega}}$$

E.G., for the unmixed BVP influent solute $A^{unmixed}$

$$\frac{\partial A^u}{\partial t} + v \frac{\partial A^u}{\partial x} + 1 \frac{\partial A^u}{\partial \omega} - D \frac{\partial^2 A^u}{\partial x^2} = -k(\omega)A^u$$

Buckingham Π

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



If γ depends on:

Then:

α, v

$$\gamma \propto \sqrt{\frac{v}{\alpha}}$$

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

D_m, α, v

$$\gamma \propto \sqrt{\frac{v}{\alpha}} f\left(\frac{D_m}{\alpha v}\right)$$

d_{50}, D_m, α, v

$$\gamma \propto \sqrt{\frac{v}{\alpha}} f\left(\frac{D_m}{d_{50}v}, \frac{\alpha}{d_{50}}\right)$$

$v, d_{50}, D_m, \alpha, v$

$$\gamma \propto \sqrt{\frac{v}{\alpha}} f\left(\frac{D_m}{d_{50}v}, \frac{\alpha}{d_{50}}, \frac{v}{v d_{50}}\right)$$

pore Pé, ..., Pore Re

Dilettantism in Hydrology: Transition or Destiny?


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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.

[18] Our results should be contrasted with those of Edery et al. [2009, 2010] who showed that a particle tracking scheme in conjunction with an ADE-based depiction of transport could not reproduce the concentration profiles of the product, neither at the peak, nor at the tails. The agreement observed in Figure 1 is of similar quality to that obtained by Edery et al. [2010; their Figure 1a] when their PT scheme is implemented within a non-Fickian model based on a CTRW approach. They simulated the bimolecular reaction by introducing two types of particles (marked “A” and “B”) into the simulation domain and then letting them migrate within the system until the relative distance between two given A and B particles was smaller than a prescribed value, R . When this happens, the two particles are replaced by a “C” particle, mimicking the occurrence of a reaction.

Therefore, the model of Edery et al. [2009, 2010] has essentially two key adjustable parameters, one governing the probabilistic distribution of the particles transitions times, and a second one being the “effective” reaction radius, R . The latter is found to be orders of magnitude larger than the molecular interaction radius, which specifies the capability of two molecules to react and is usually in the order of nanometers. Establishing a relationship between these two parameters and those appearing in our model is not trivial and needs to be further investigated.