Kinetic model for gas-surface uptake experiments in a fast flow reactor

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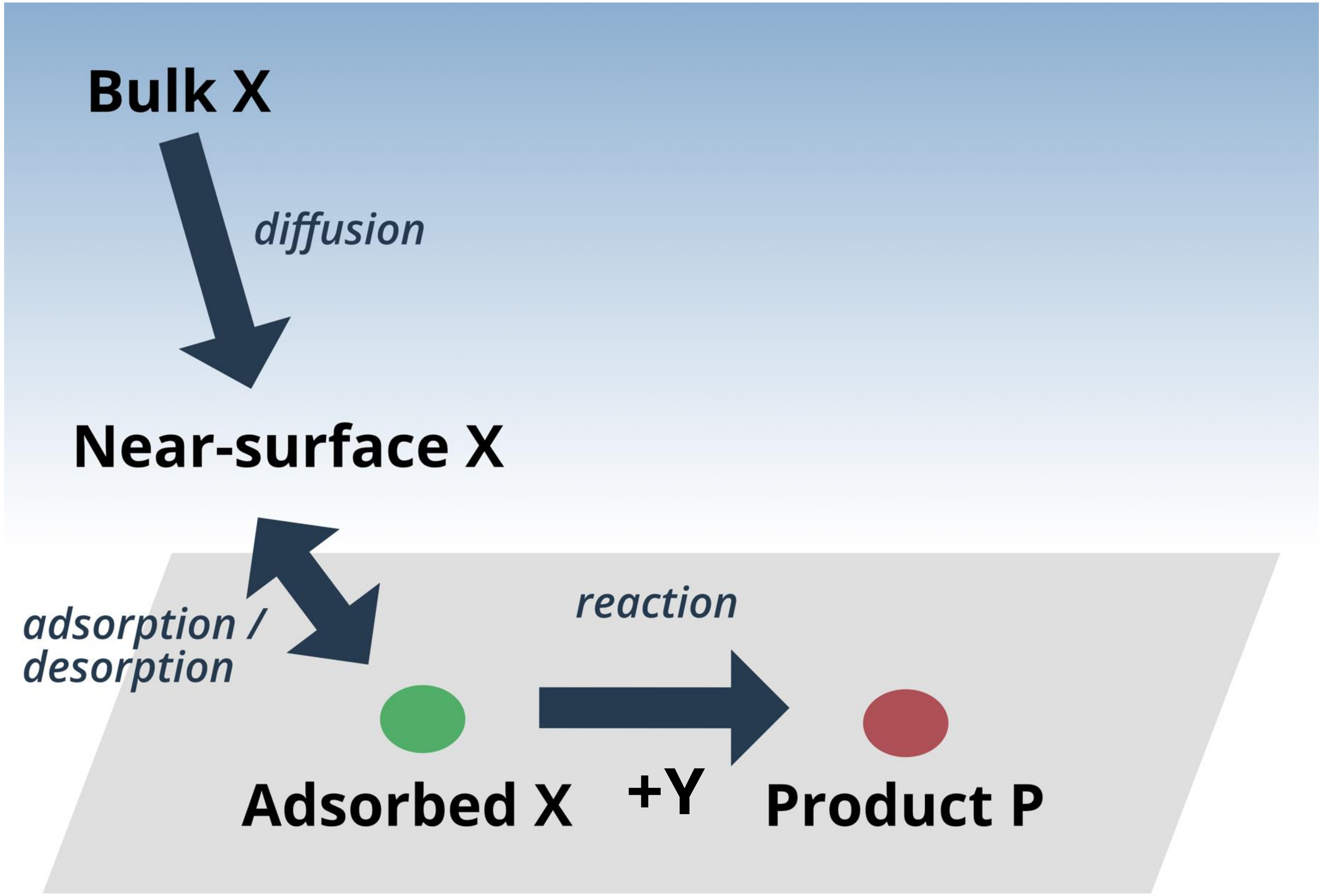
Background



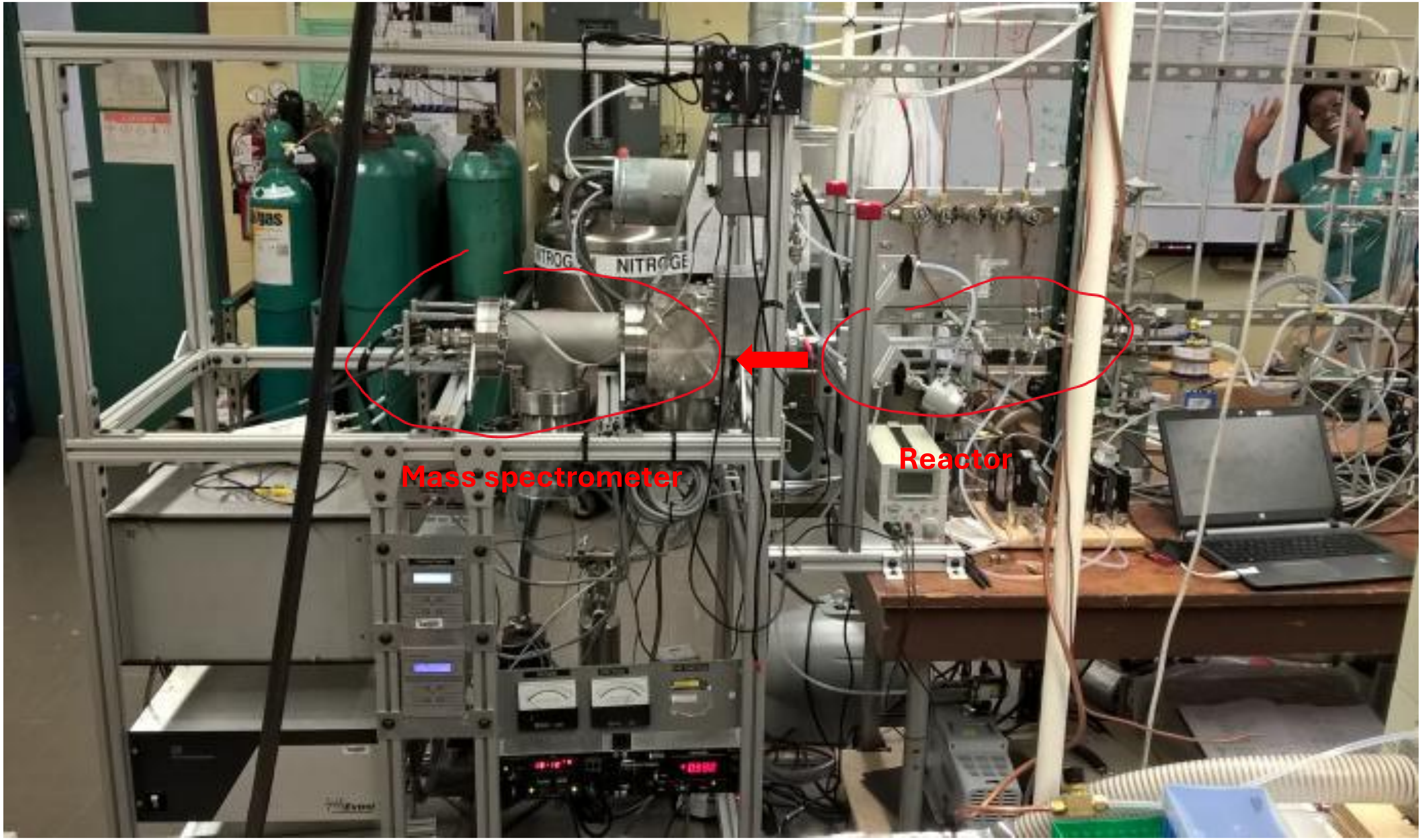
$$X_g + S \longleftrightarrow X_s$$
$$X_s + Y \longrightarrow P + S$$

System and components

Component	Description	Unit
X	Reagent in the gas phase	cm^{-3}
S	Adsorption site on the surface	cm^{-2}
X_s	Reagent in adsorbate phase (bound to an S site)	cm^{-2}
Y	Reaction site on the surface	cm^{-2}
P	Product on the surface (irreversibly forms consuming Y and X_s, releasing S)	cm^{-2}

$$\mathrm{X}_g + \mathrm{S} \longleftrightarrow \mathrm{X}_s$$

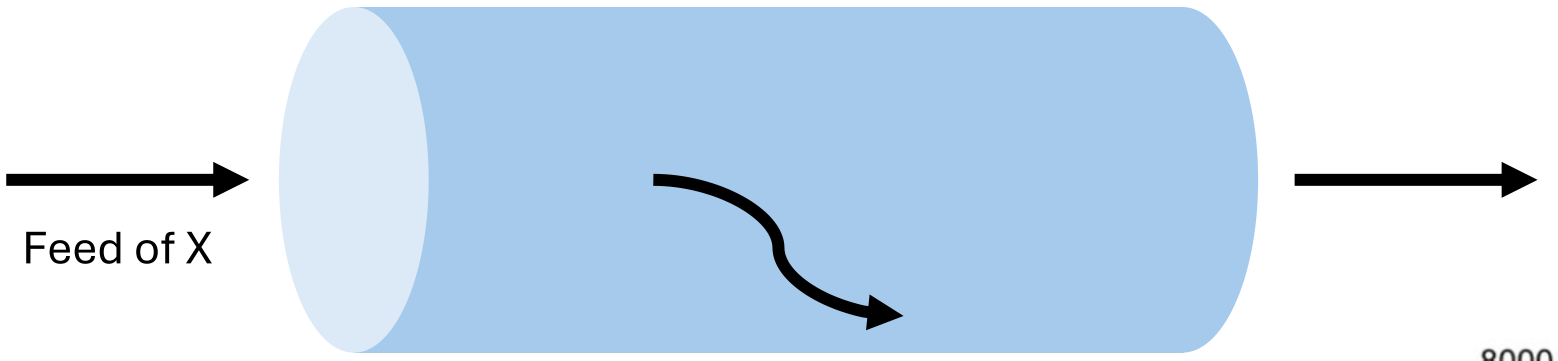
$$\mathrm{X}_s + \mathrm{Y} \longrightarrow \mathrm{P} + \mathrm{S}$$

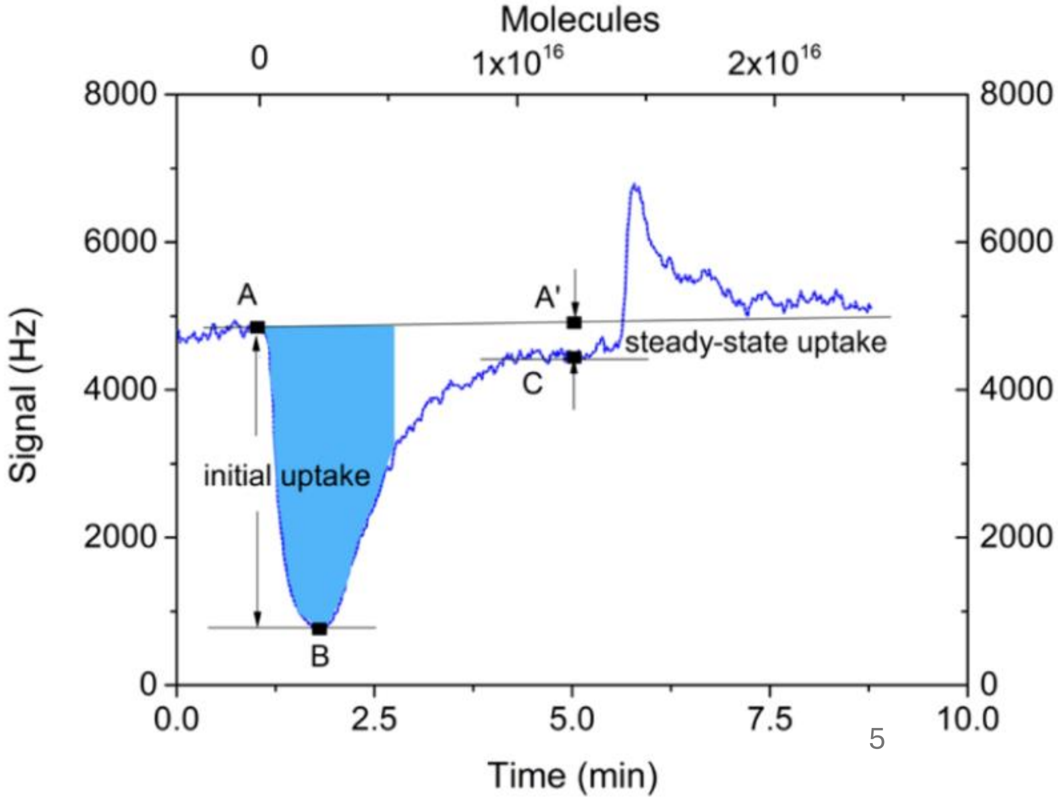

Mass spectrometer
Reactor

Experiment

$$X_g + S \longleftrightarrow X_s$$

$$X_s + Y \longrightarrow P + S$$





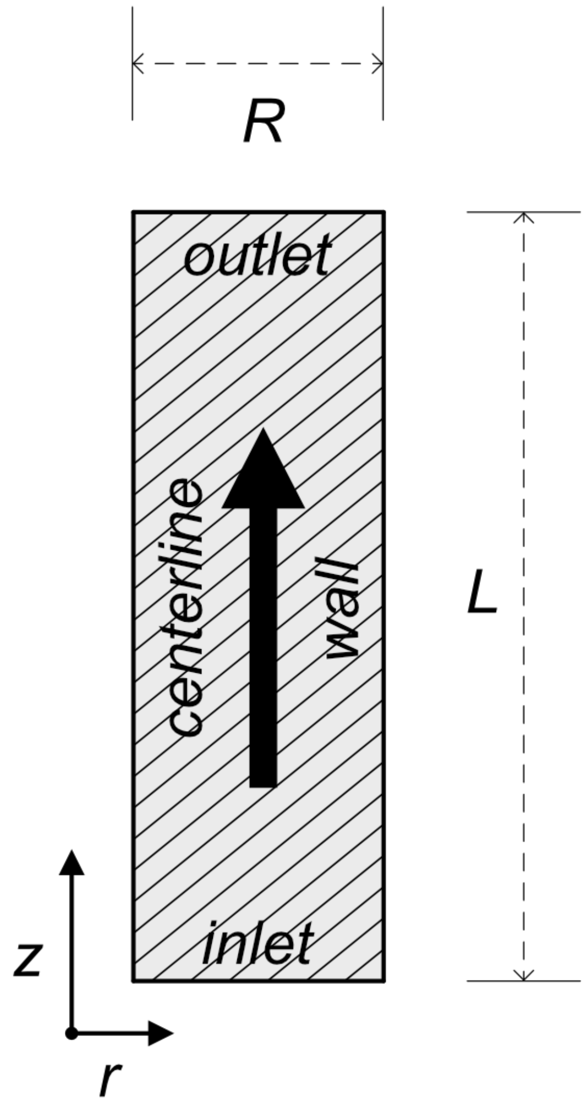
Mao, N., Antley, J., Cooper, M., Shah, N., Kadam, A., & Khalizov, A. (**2021**). Heterogeneous Chemistry of Mercuric Chloride on Inorganic Salt Surfaces. *The Journal of Physical Chemistry A*, *125*(18), 3943-3952.

- Give credit to Poschl and Ammann here
- They didn’t have diffusion or gas phase transport (no distinction between X and near-surface X)
- We will account for the gas-phase processes and test how important diffusion to the surface is

Model

Model for gas-phase component X:

$$\underbrace{\frac{\partial X}{\partial t}}_{\text{Time dependence}} + \underbrace{2u_{\mathrm{z}}\left[1-\frac{r^2}{R^2}\right]\frac{\partial X}{\partial z}}_{\text{Advection}} = \underbrace{D_{\mathrm{i}}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial X}{\partial r}\right)}_{\text{Radial diffusion}} + \underbrace{D_{\mathrm{i}}\frac{\partial^2 X}{\partial z^2}}_{\text{Axial diffusion}}$$



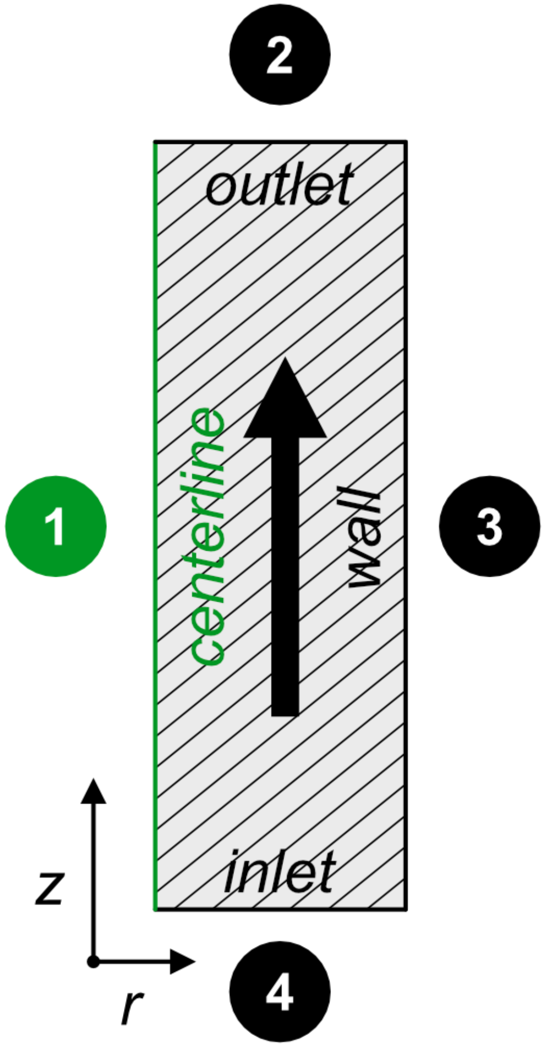
Model

Model for gas-phase component X:

$$\frac{\partial X}{\partial t} + 2u_\mathrm{z}\left[1 - \frac{r^2}{R^2}\right]\frac{\partial X}{\partial z} = D_\mathrm{i}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial X}{\partial r}\right) + D_\mathrm{i}\frac{\partial^2 X}{\partial z^2}$$

Centerline boundary condition:

$$\frac{\partial X}{\partial r} = 0$$ (axial symmetry)



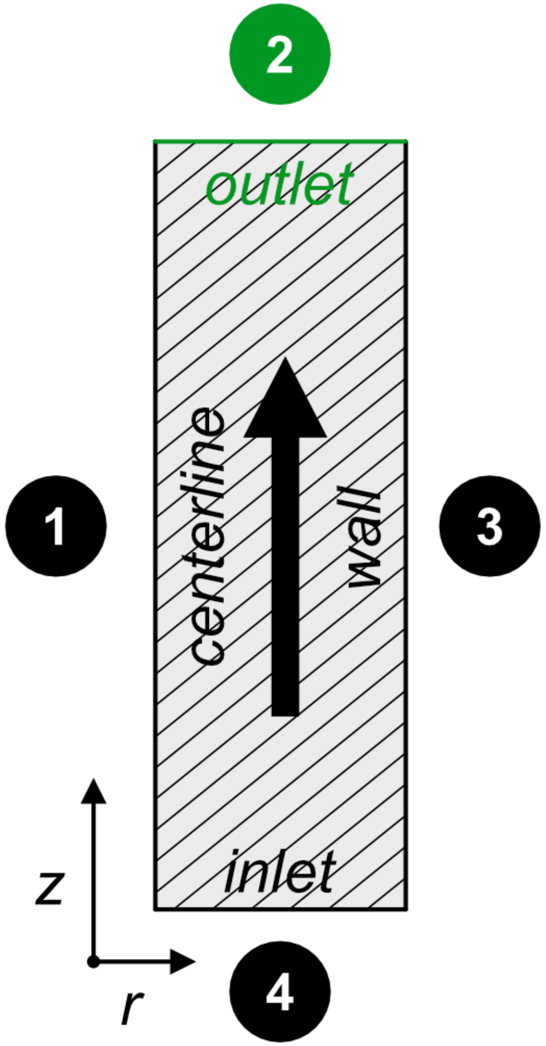
Model

Model for gas-phase component X:

$$\frac{\partial X}{\partial t} + 2u_\mathrm{z}\left[1 - \frac{r^2}{R^2}\right]\frac{\partial X}{\partial z} = D_\mathrm{i}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial X}{\partial r}\right) + D_\mathrm{i}\frac{\partial^2 X}{\partial z^2}$$

Outlet boundary condition:

$$\frac{\partial X}{\partial z} = 0 \qquad \text{(no flux)}$$



Model

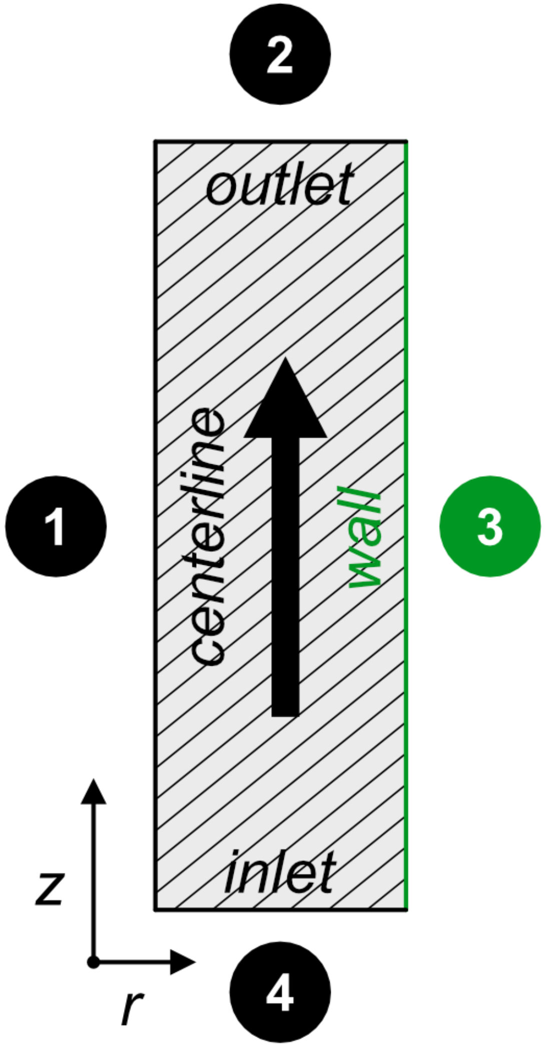
Model for gas-phase component X:

$$\frac{\partial X}{\partial t} + 2u_\mathrm{z}\left[1 - \frac{r^2}{R^2}\right]\frac{\partial X}{\partial z} = D_\mathrm{i}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial X}{\partial r}\right) + D_\mathrm{i}\frac{\partial^2 X}{\partial z^2}$$

Wall boundary condition:

$$D_\mathrm{i}\frac{\partial X}{\partial r} = k_\mathrm{ads} X S - \frac{R}{2} k_\mathrm{des} X_\mathrm{s}$$

(adsorption / desorption flux)



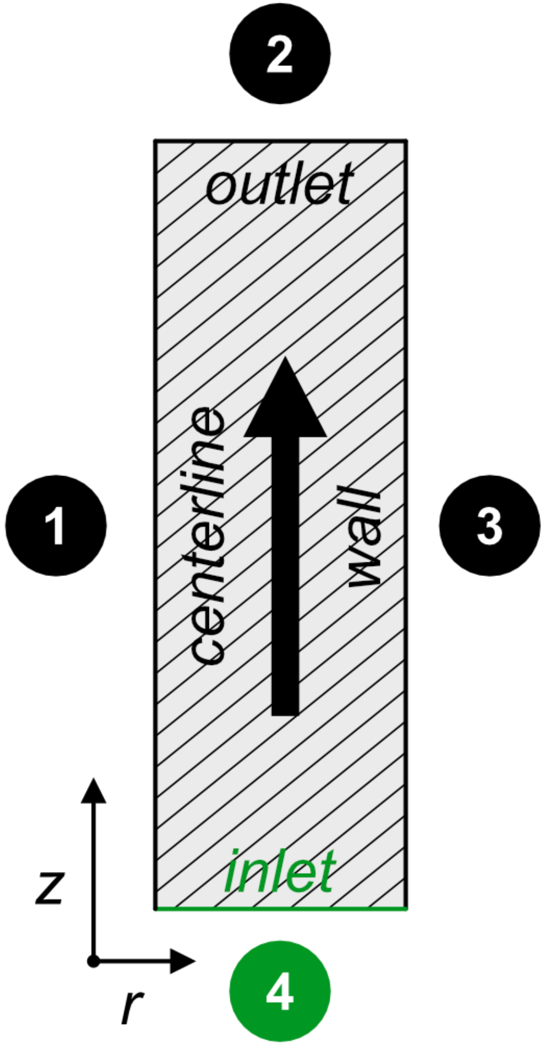
Model

Model for gas-phase component X:

$$\frac{\partial X}{\partial t} + 2u_\mathrm{z}\left[1 - \frac{r^2}{R^2}\right]\frac{\partial X}{\partial z} = D_\mathrm{i}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial X}{\partial r}\right) + D_\mathrm{i}\frac{\partial^2 X}{\partial z^2}$$

Inlet boundary condition:

$X = X_0$ (constant feed of X)



Model

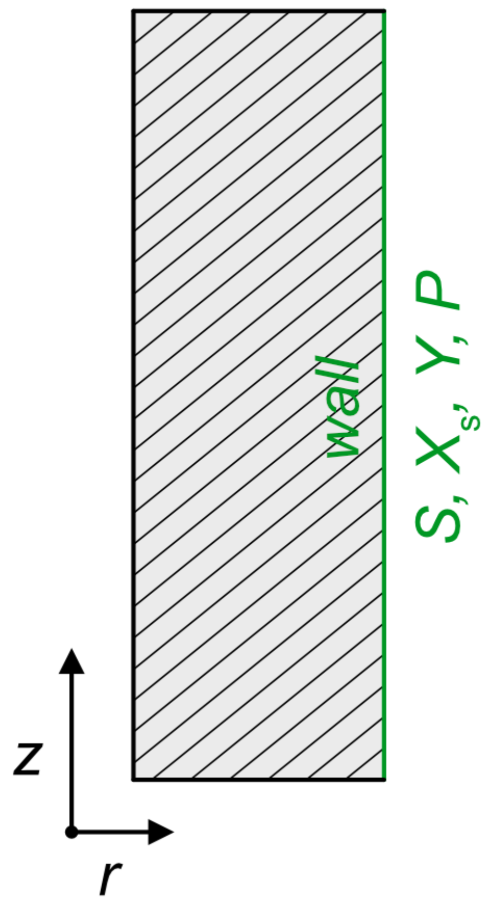
Model for surface-bound components S, X_s, Y, P:

$$\frac{\partial S}{\partial t} = -k_{\mathrm{ads}} X S + \frac{R}{2} k_{\mathrm{des}} X_{\mathrm{s}} + k_{\mathrm{rxn}} X_{\mathrm{s}} Y$$

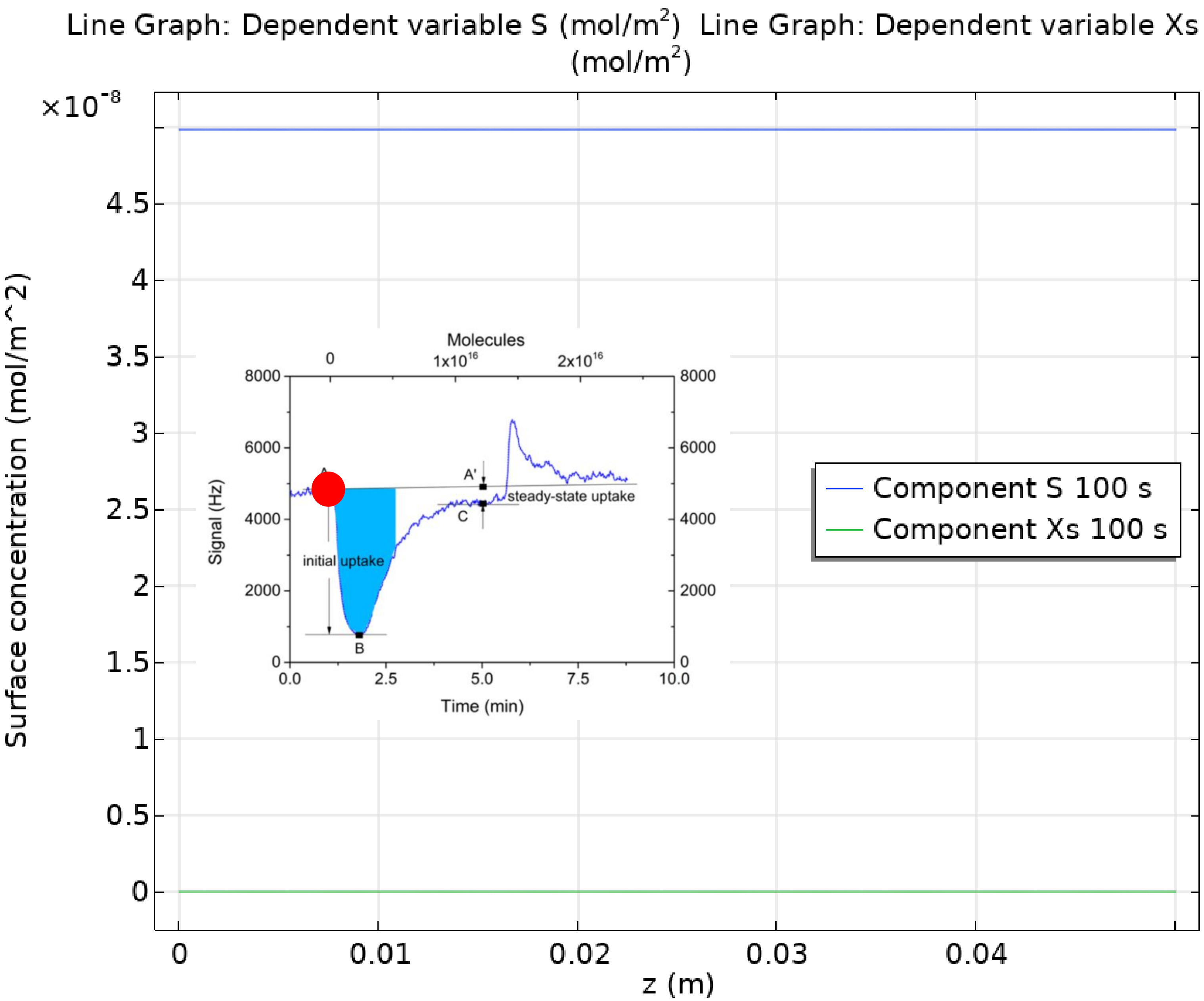
$$\frac{\partial X_{\mathrm{s}}}{\partial t} = k_{\mathrm{ads}} X S - \frac{R}{2} k_{\mathrm{des}} X_{\mathrm{s}} - k_{\mathrm{rxn}} X_{\mathrm{s}} Y$$

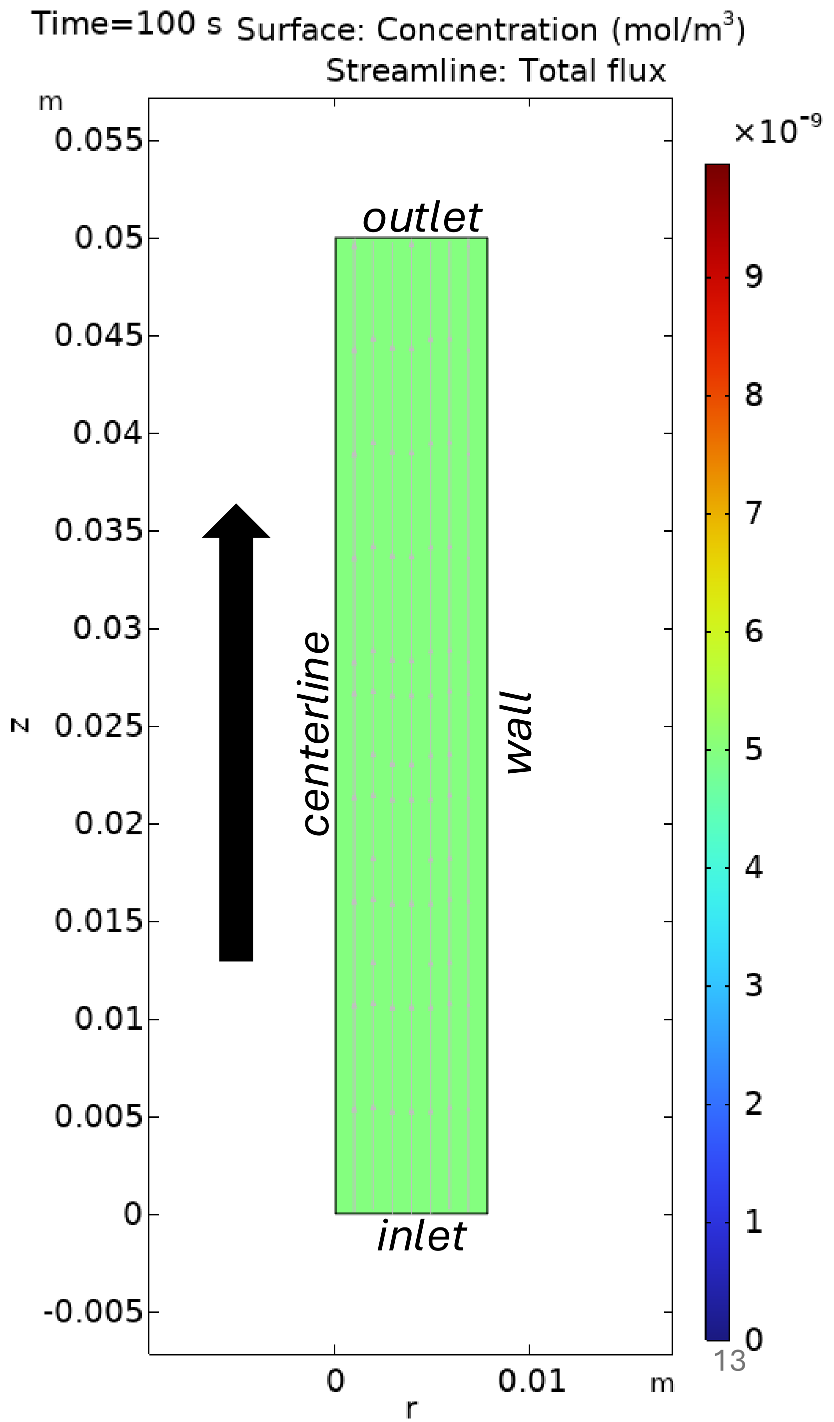
$$\frac{\partial Y}{\partial t} = -k_{\mathrm{rxn}} X_{\mathrm{s}} Y$$

$$\frac{\partial P}{\partial t} = k_{\mathrm{rxn}} X_{\mathrm{s}} Y$$



Concentration *vs* time





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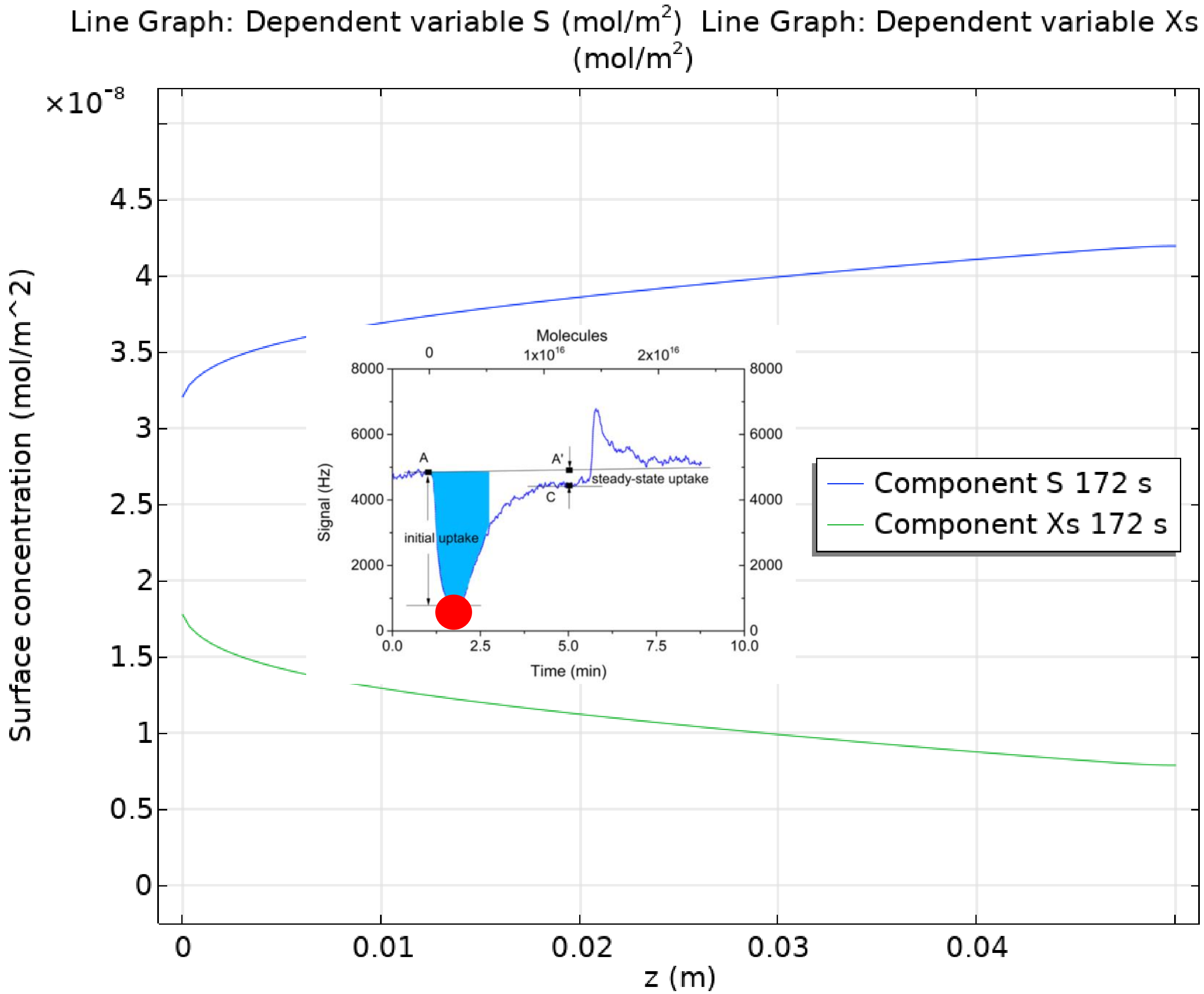

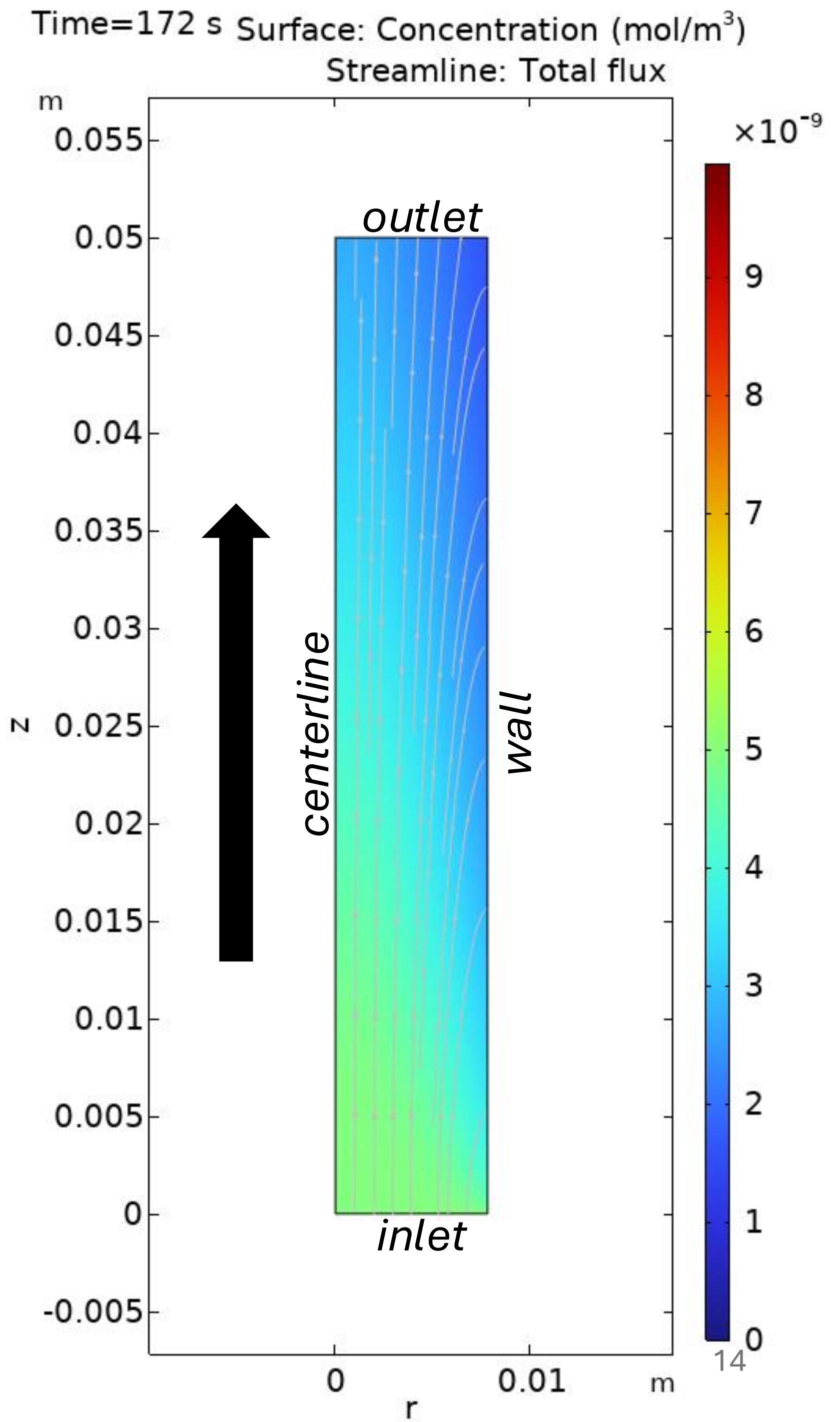

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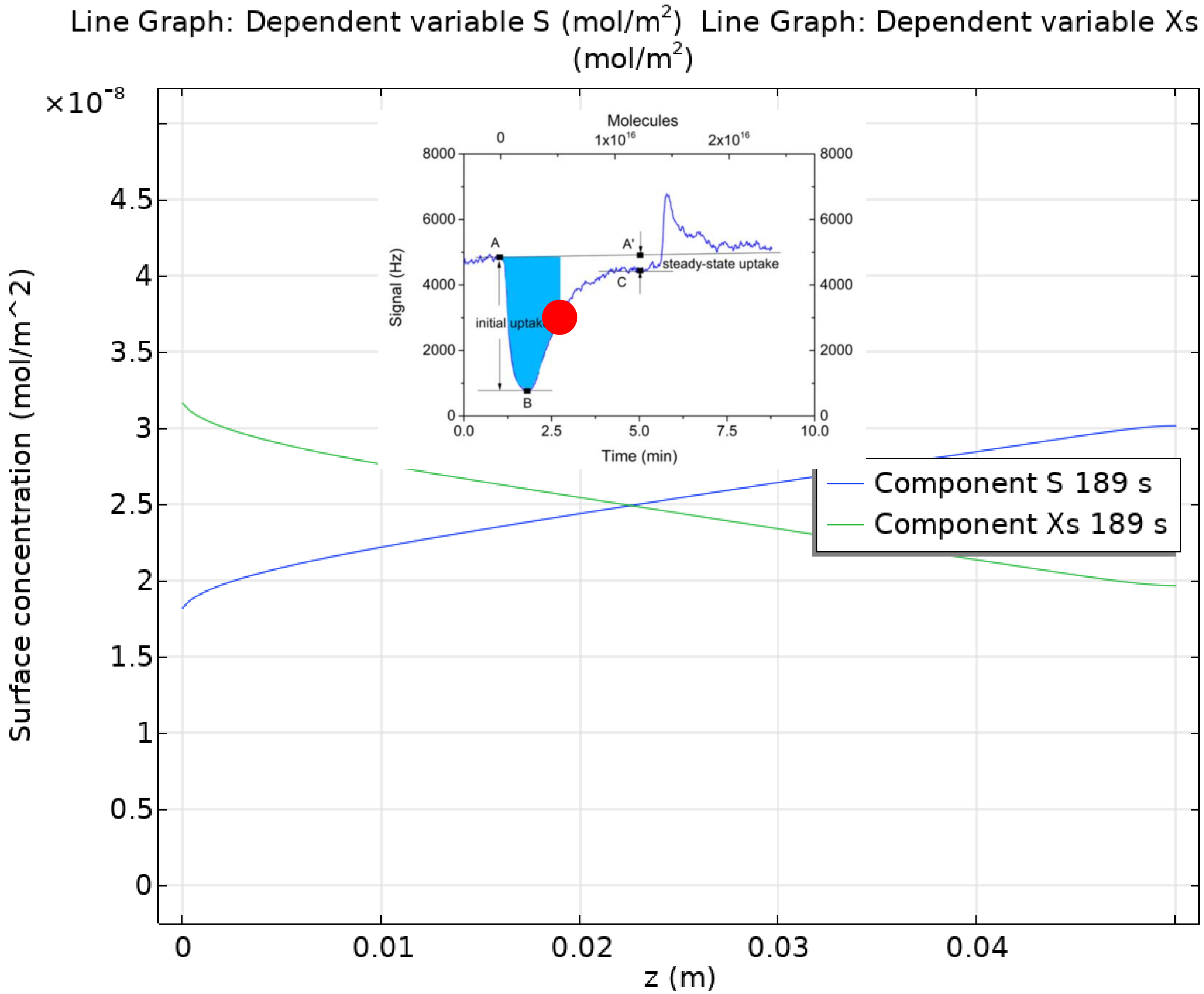

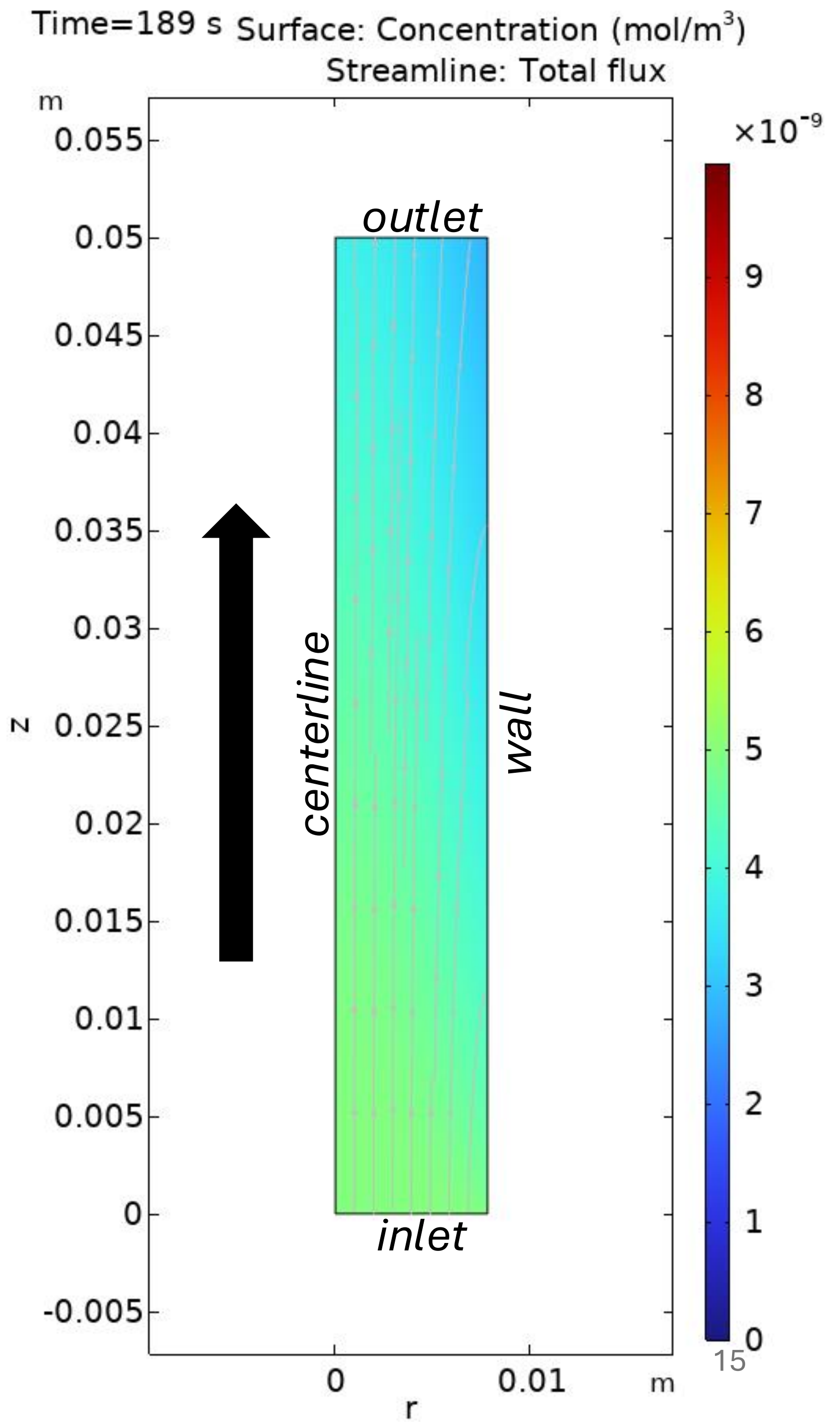

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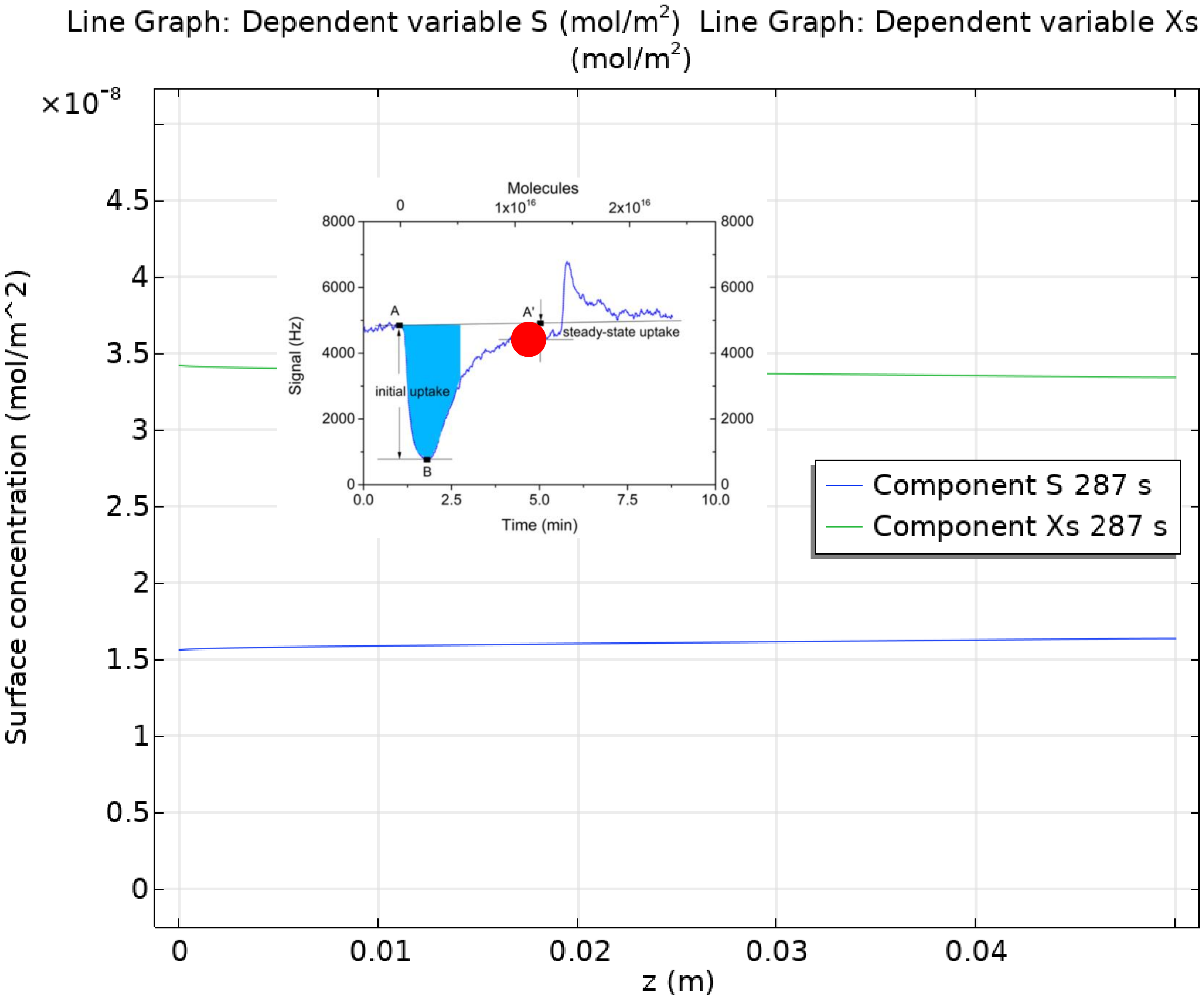

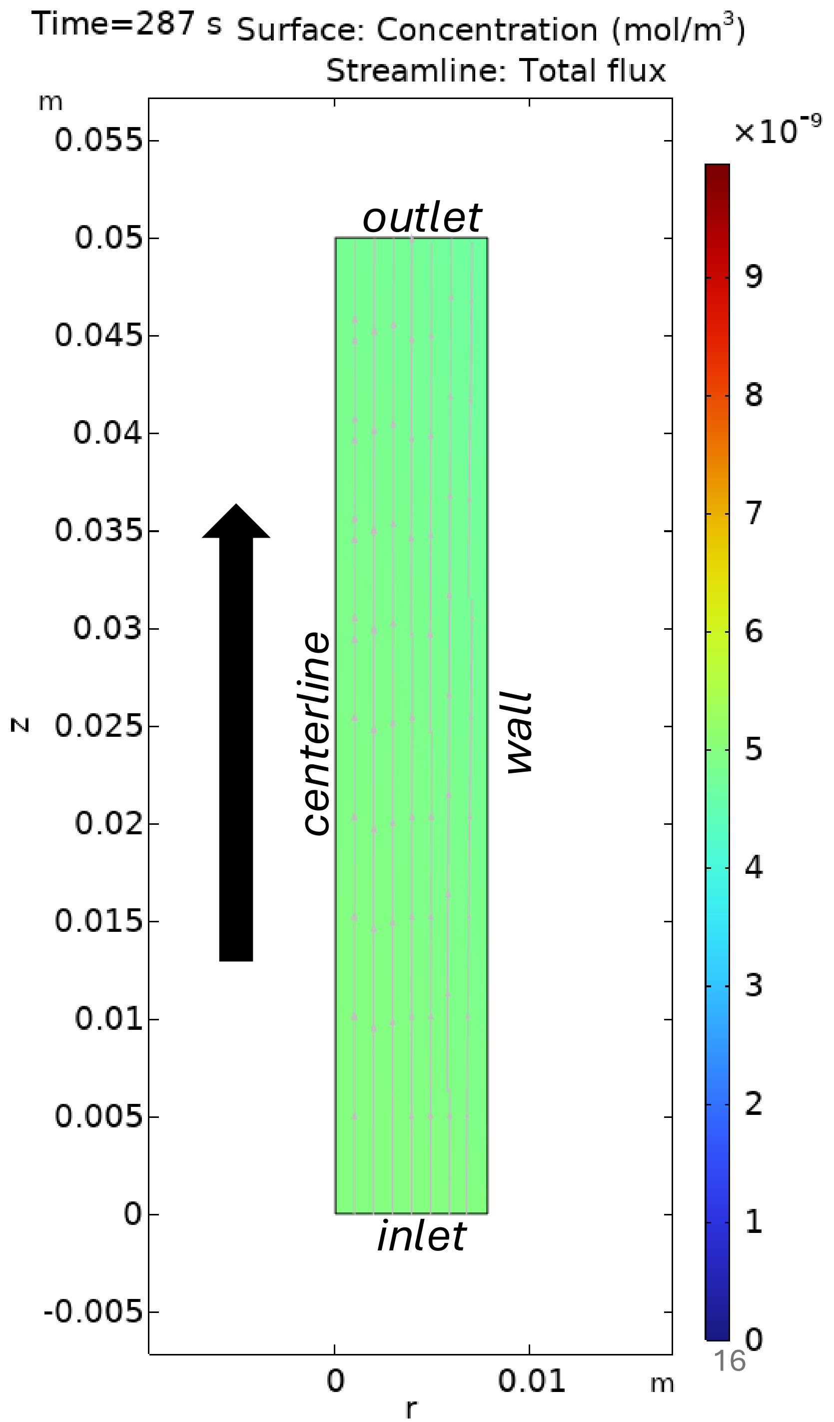

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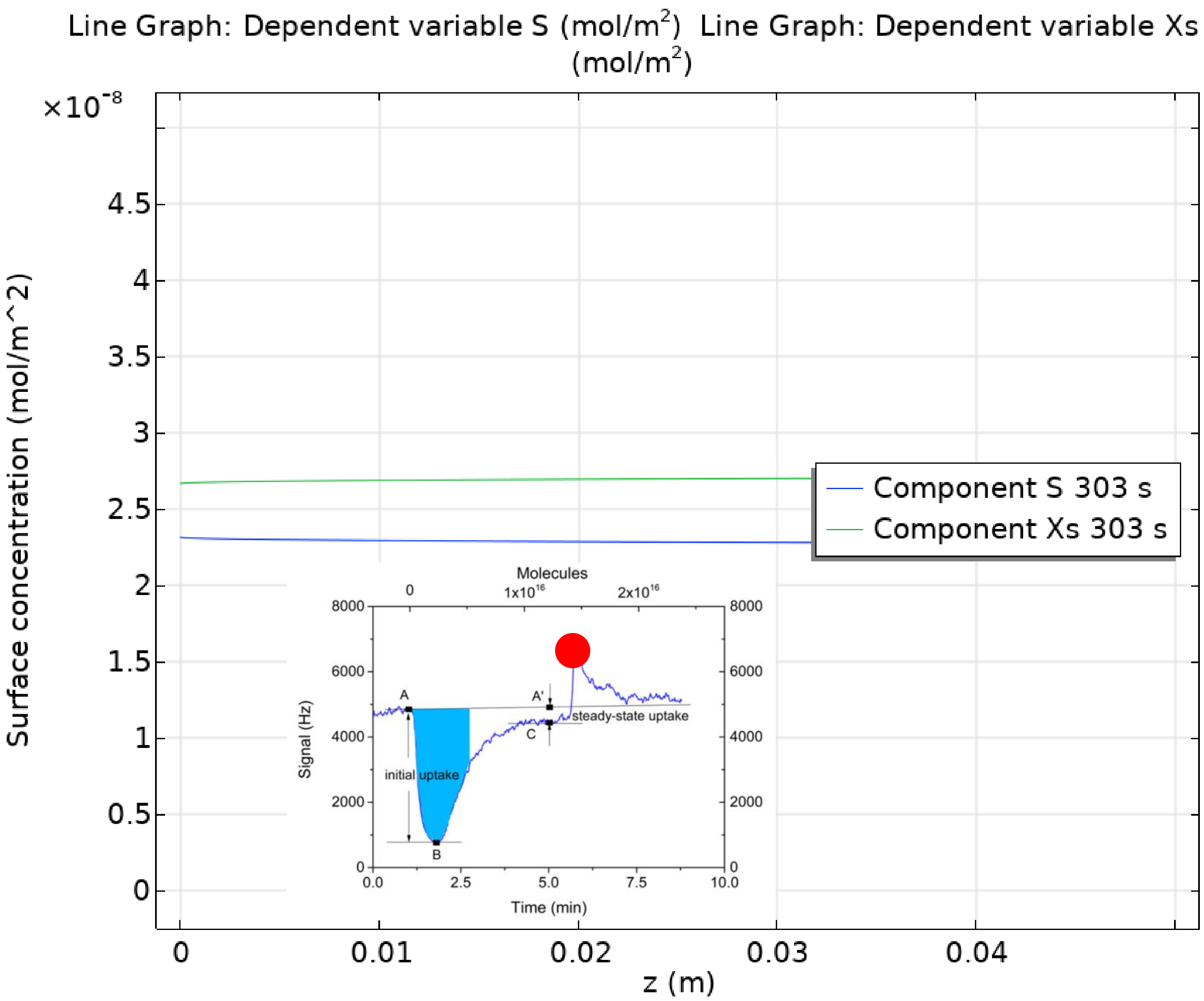

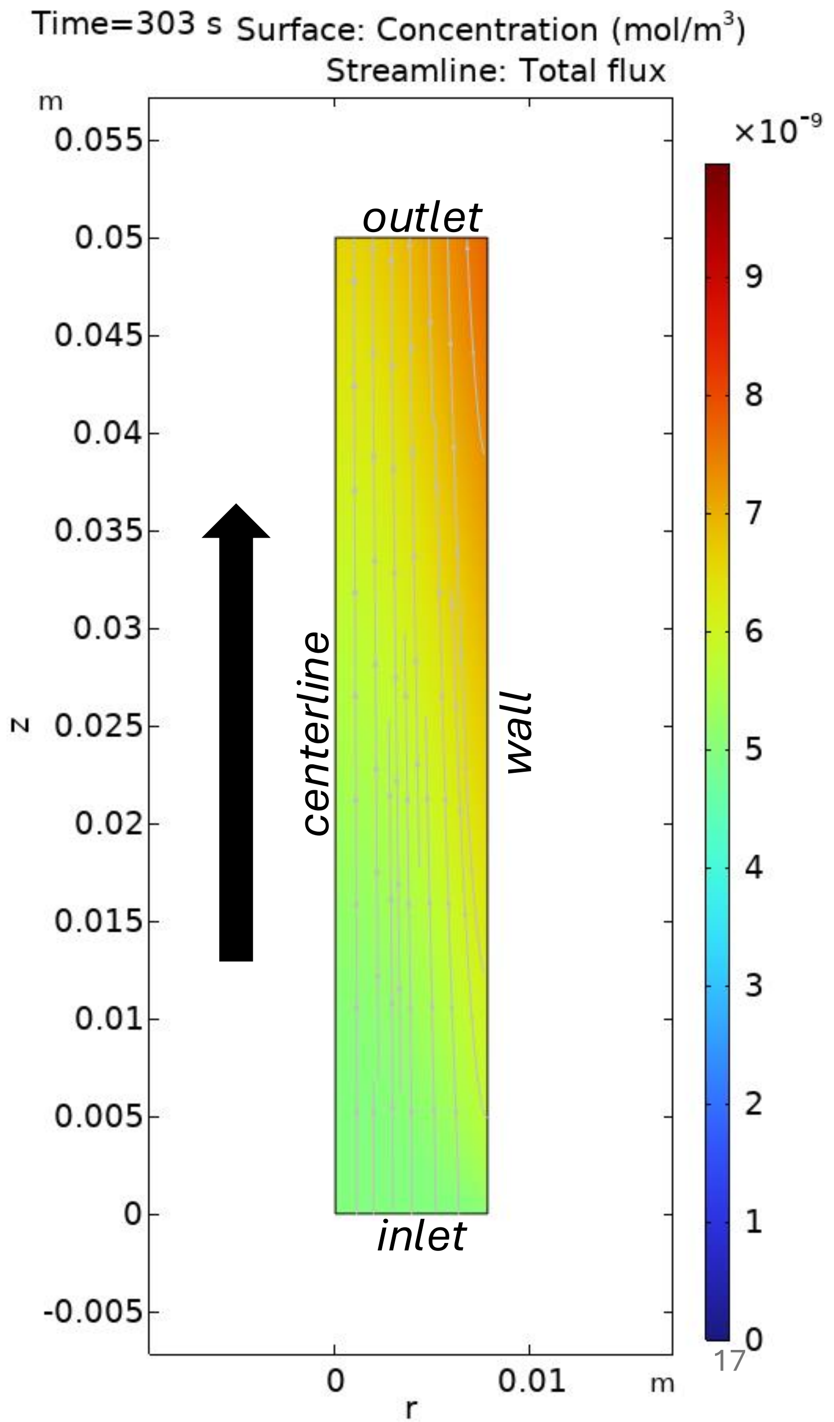

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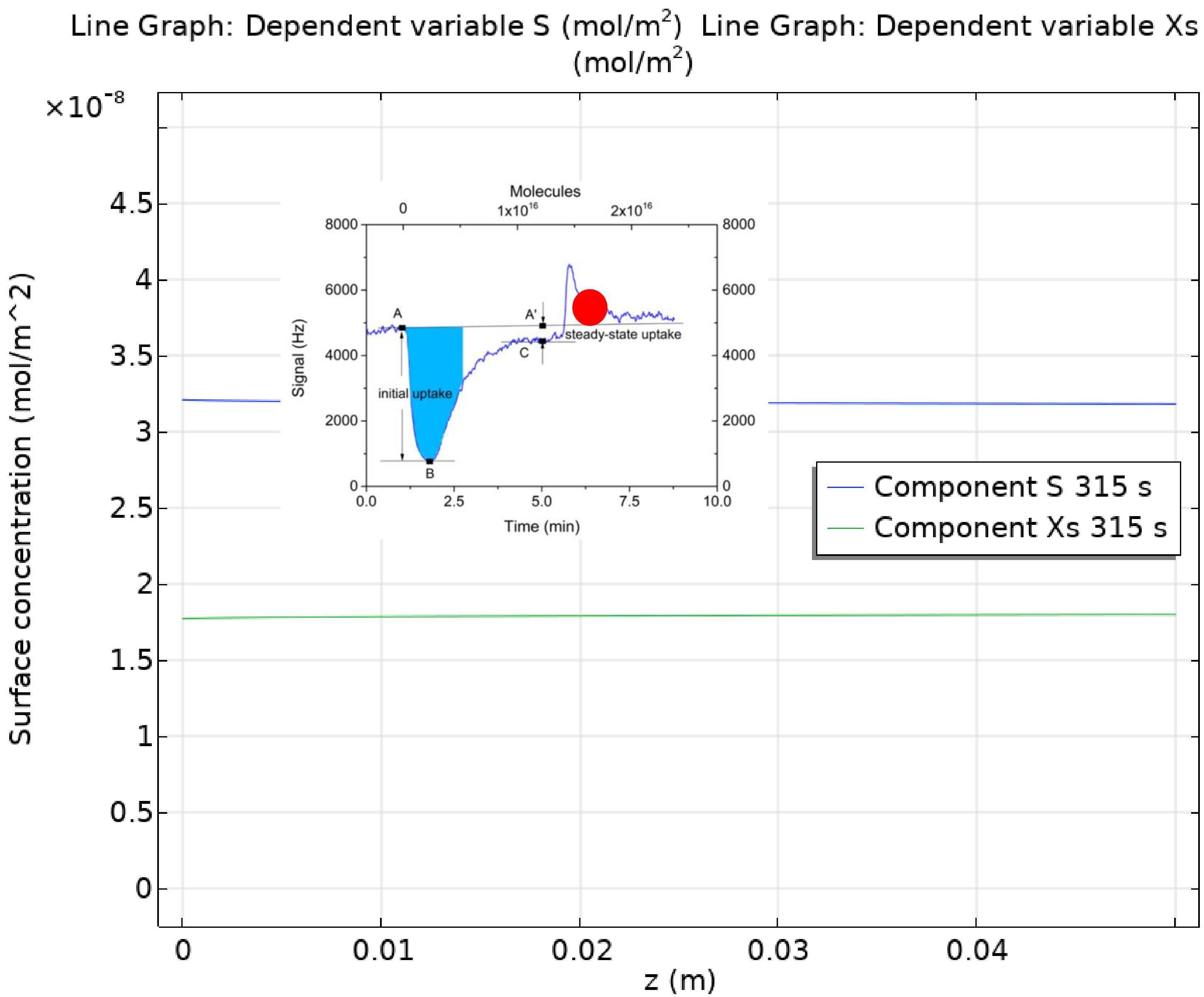

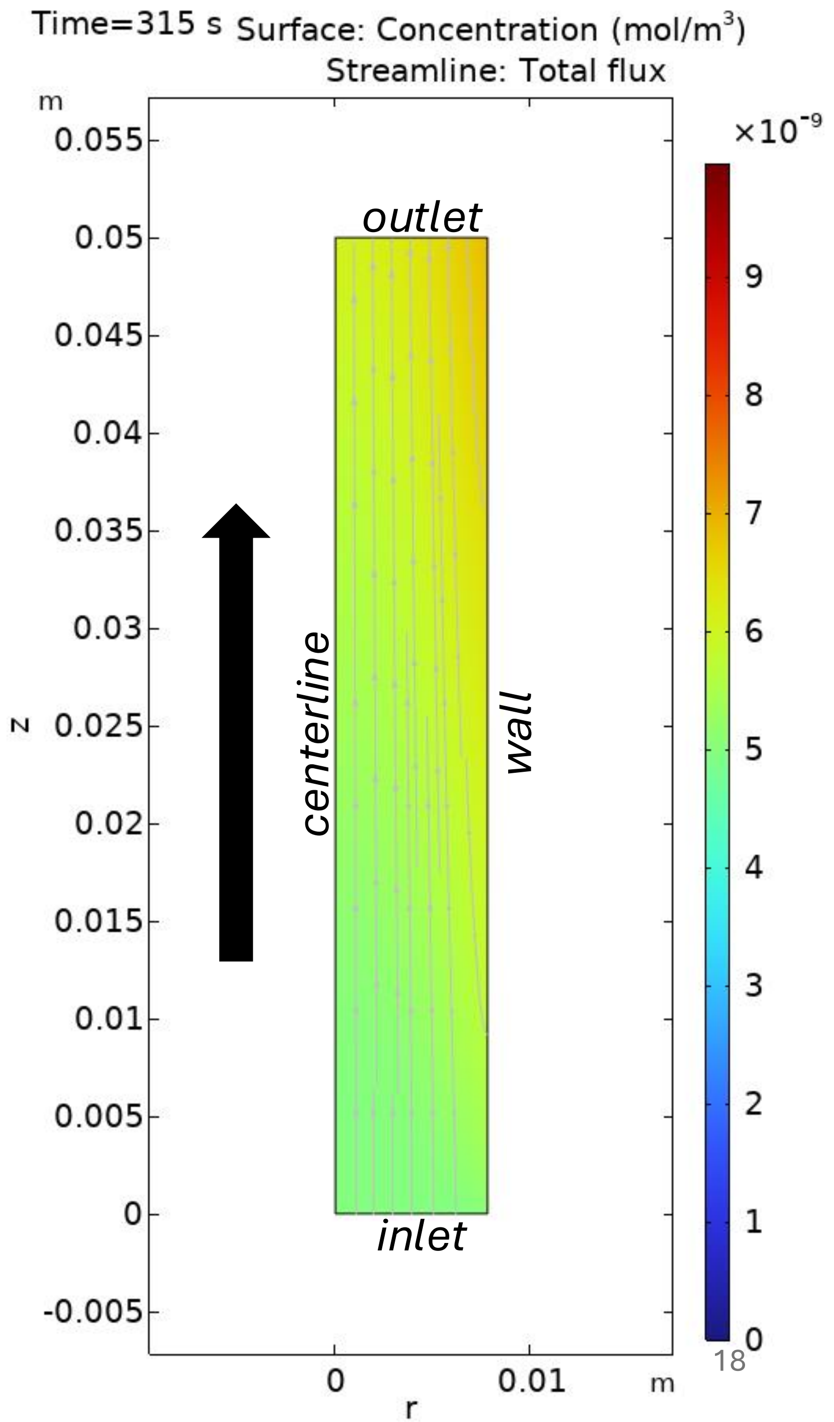

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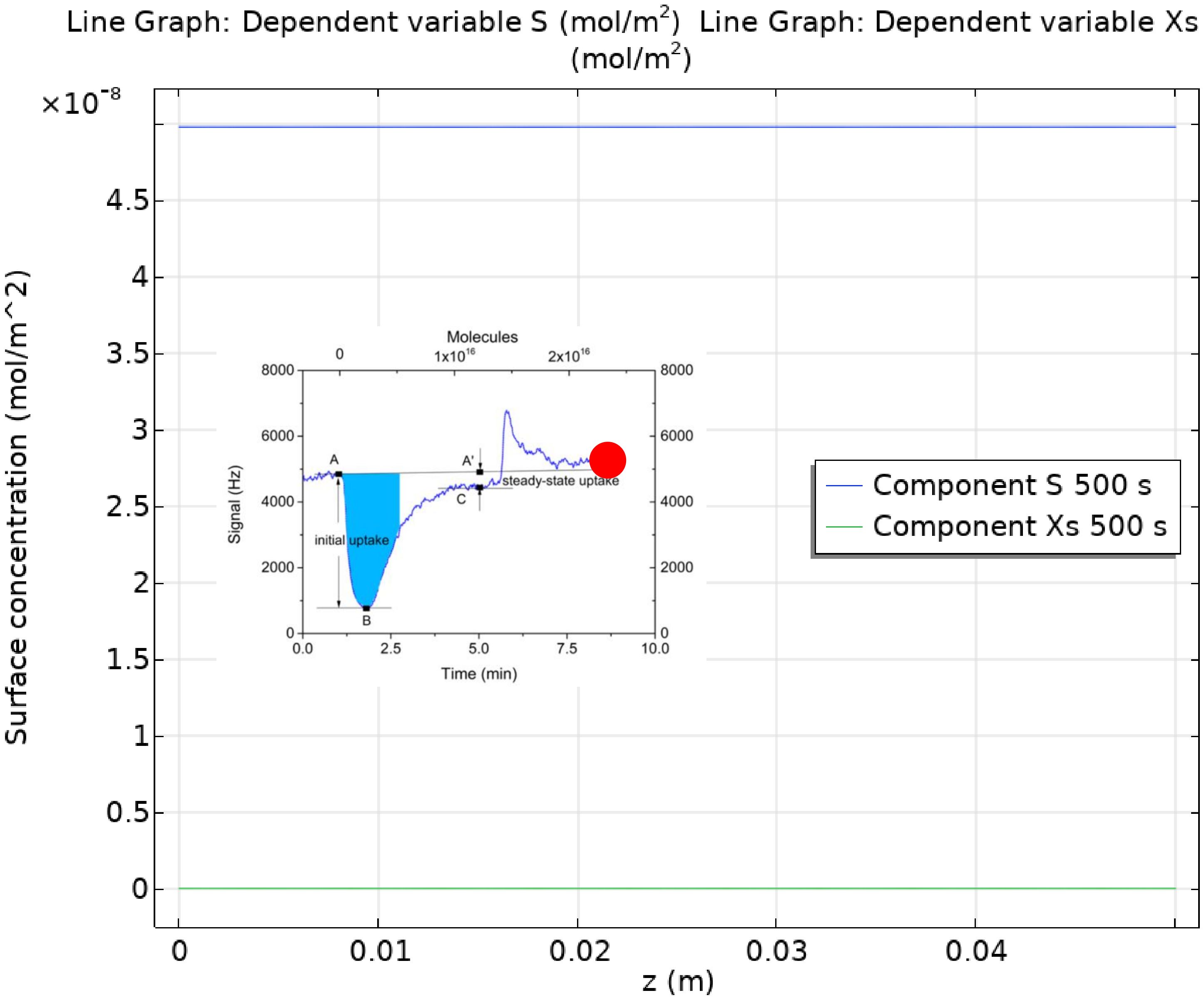

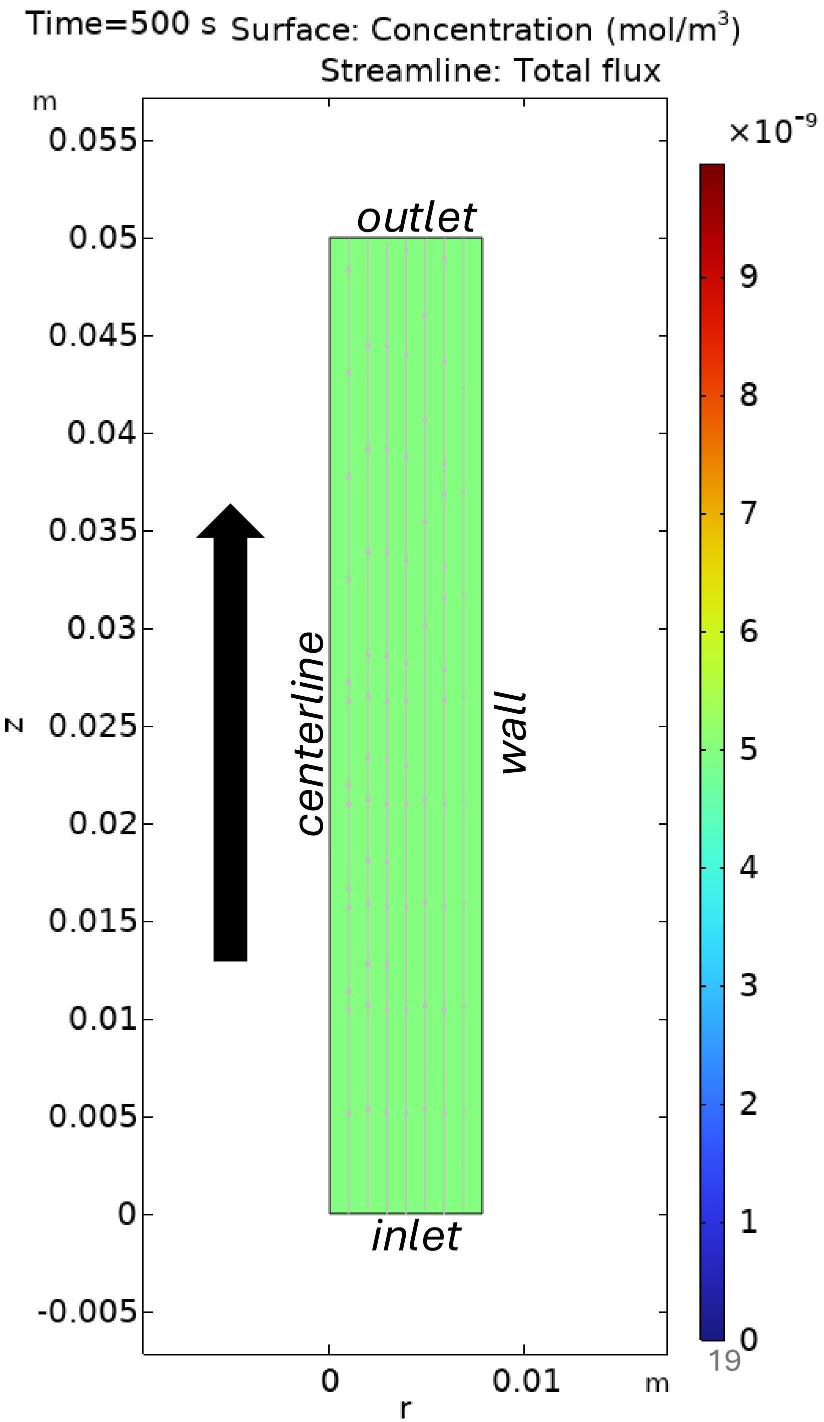

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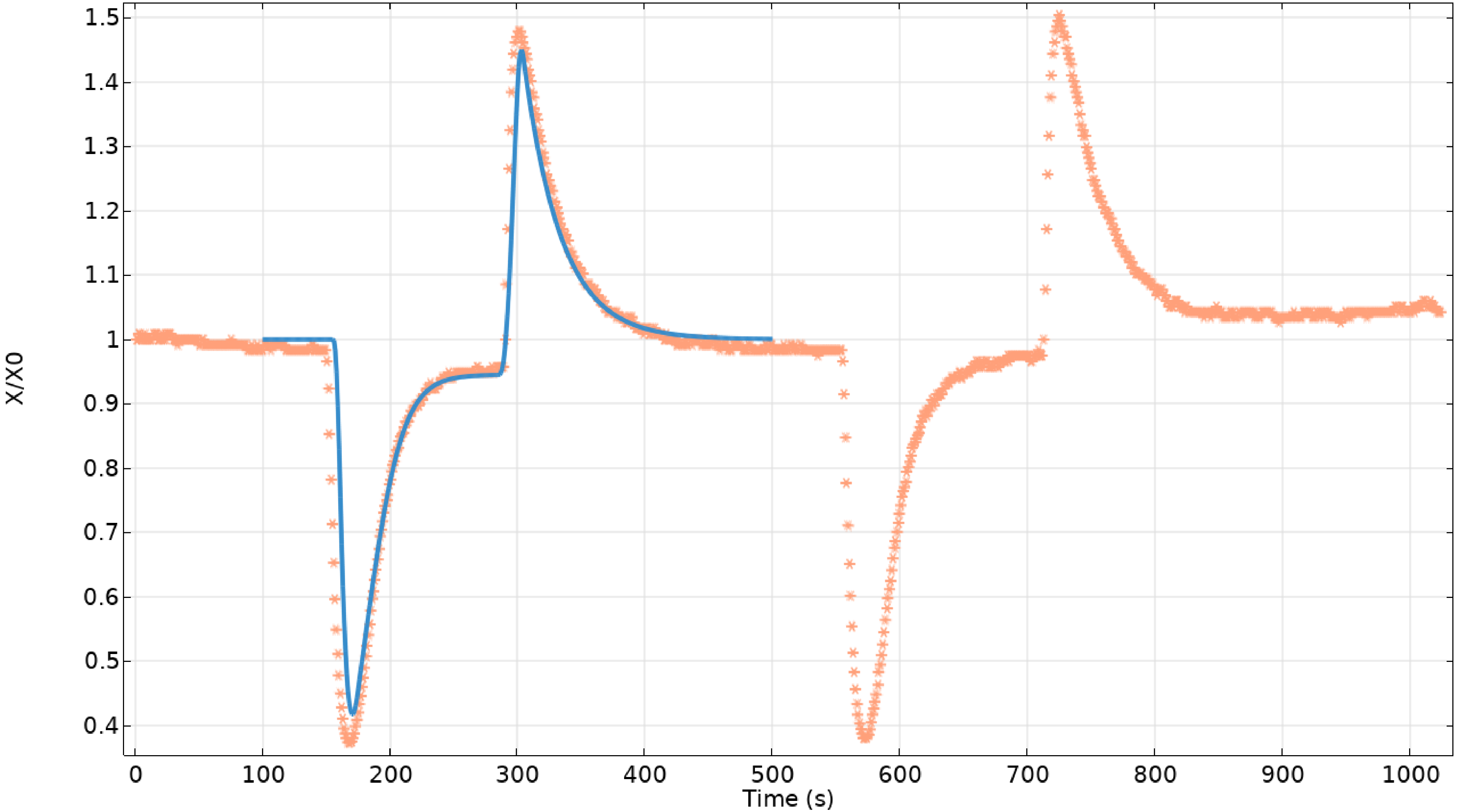


Experimental data – $HgCl_2$ *on levoglucosan*

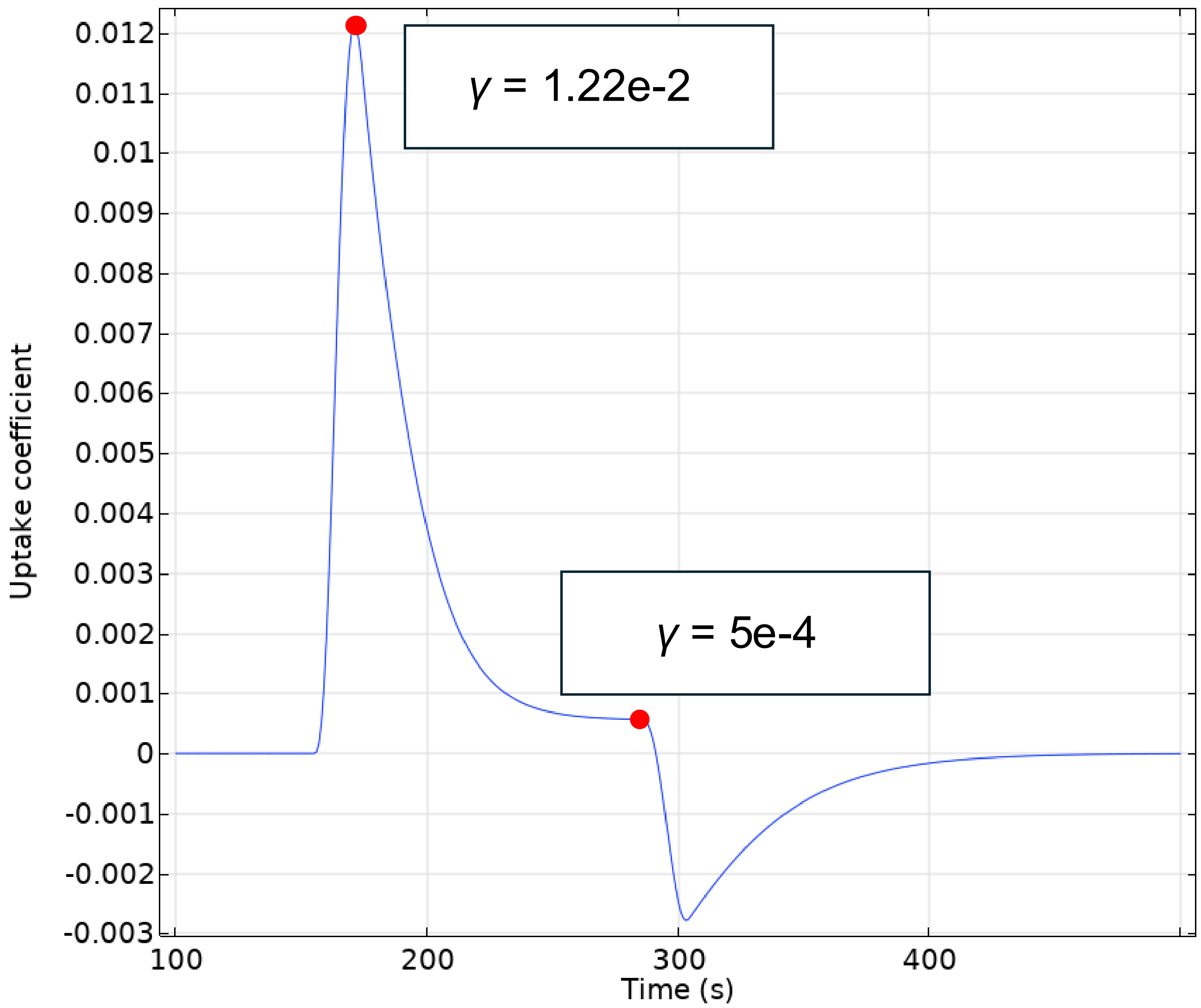
Uptake coefficients

$$k_{\text{thermal}} = \sqrt{\frac{RT}{2\pi M}}$$

$$\gamma = \frac{k_{\text{ads}} X S - \frac{R}{2} k_{\text{des}} X_{\text{s}}}{k_{\text{thermal}} X}$$

Determined uptake coefficients:

	Experiment	Model
γ initial	1.1e-2	1.2e-4
γ steady state	2.9e-4	5e-4



Model parameters and parameters retrieved from experiment

Mw	271.52 [g/mol]	0.27152 kg/mol	Molar mass of component X
T	300 [K]	300 K	Temperature
L	5 [cm]	0.05 m	Reactor length
Rd	(1.56/2) [cm]	0.0078 m	Reactor radius
F_stp	2.5 [cm^3/s]	2.5E-6 m^3/s	Volumetric flow rate (at STP)
P_st	760 [Torr]	1.0132E5 Pa	Standard pressure
P	2 [Torr]	266.64 Pa	Experimental pressure
F	F_stp*P_st/P	9.5E-4 m^3/s	Volumetric flow rate (corrected)
A	pi*Rd*Rd	1.9113E-4 m^2	Cross sectional area of the reactor
Uflow	F/A	4.9703 m/s	Average flow velocity
X0	3.0e9 [1/cm^3]	3E15 $1/m^3$	Initial concentration of X
S0	3.0e12 [1/cm^2]	3E16 $1/m^2$	Initial concentration of S
Y0	1.0e14 [1/cm^2]	1E18 $1/m^2$	Initial concentration of Y
t_ads_start	165 [s]	165 s	Time when adsorption is enabled
t_ads_end	295 [s]	295 s	Time when adsorption is disabled
k_ads	2.5e-11 [cm^3/s]	2.5E-17 m^3/s	Adsorption rate constant
k_des	8.0e-2 [1/(cm*s)]	8 1/(m·s)	Desorption rate constant
k_rxn	3.0e-17 [cm^2/s]	3E-21 m^2/s	Reaction rate constant
Di	40[cm^2/s]	0.004 m^2/s	Diffusion coefficient

Major experimental inputs

Fitting parameters

Surface capacity	5.7e12	cm^{-2}
STP flow rate	2.33	$cm^3\ min^{-1}$

- Show examples of different curves, describe what information is needed to get all the parameters

1D model

$$\frac{\partial X}{\partial t} + u_{\mathrm{z}}\frac{\partial X}{\partial z} = -\frac{2}{R}k_{\mathrm{ads}}XS + k_{\mathrm{des}}X_{\mathrm{s}}$$

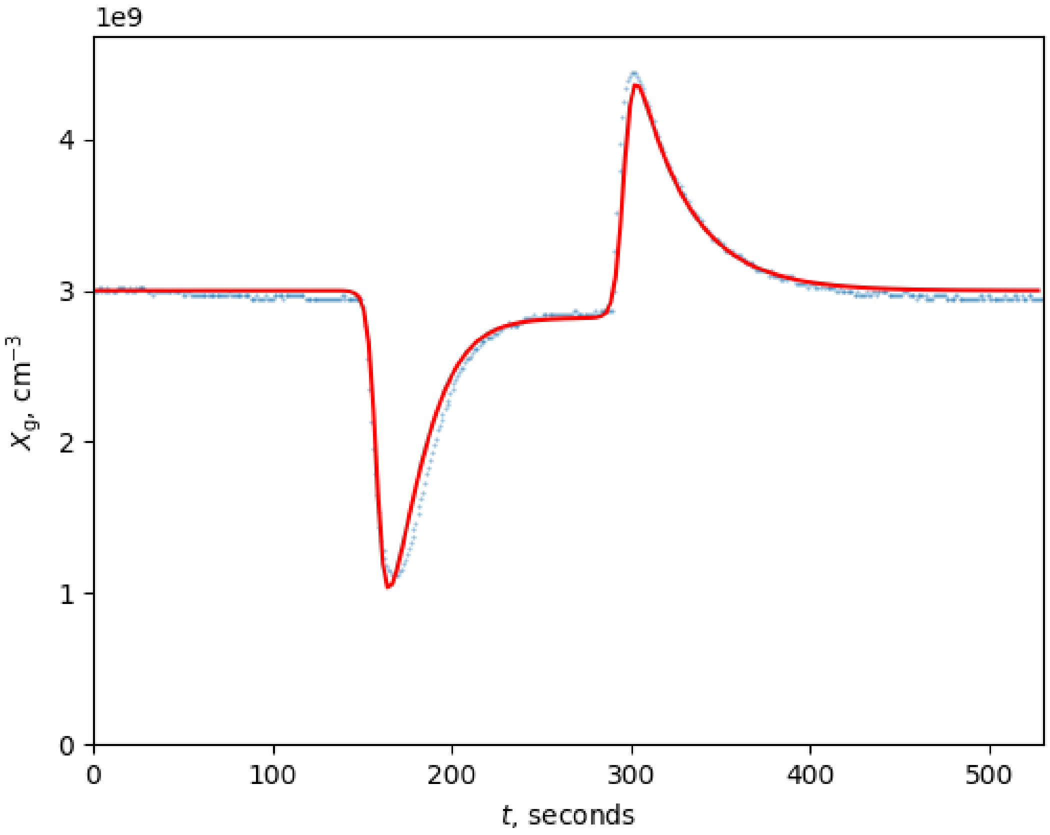
$$\frac{\partial S}{\partial t} = -k_{\mathrm{ads}}XS + \frac{R}{2}k_{\mathrm{des}}X_{\mathrm{s}} + k_{\mathrm{rxn}}X_{\mathrm{s}}Y$$

$$\frac{\partial X_{\mathrm{s}}}{\partial t} = k_{\mathrm{ads}}XS - \frac{R}{2}k_{\mathrm{des}}X_{\mathrm{s}} - k_{\mathrm{rxn}}X_{\mathrm{s}}Y$$

$$\frac{\partial Y}{\partial t} = -k_{\mathrm{rxn}}X_{\mathrm{s}}Y$$

$$\frac{\partial P}{\partial t} = k_{\mathrm{rxn}}X_{\mathrm{s}}Y$$

Same parameters as in 3D model (besides D_{i})



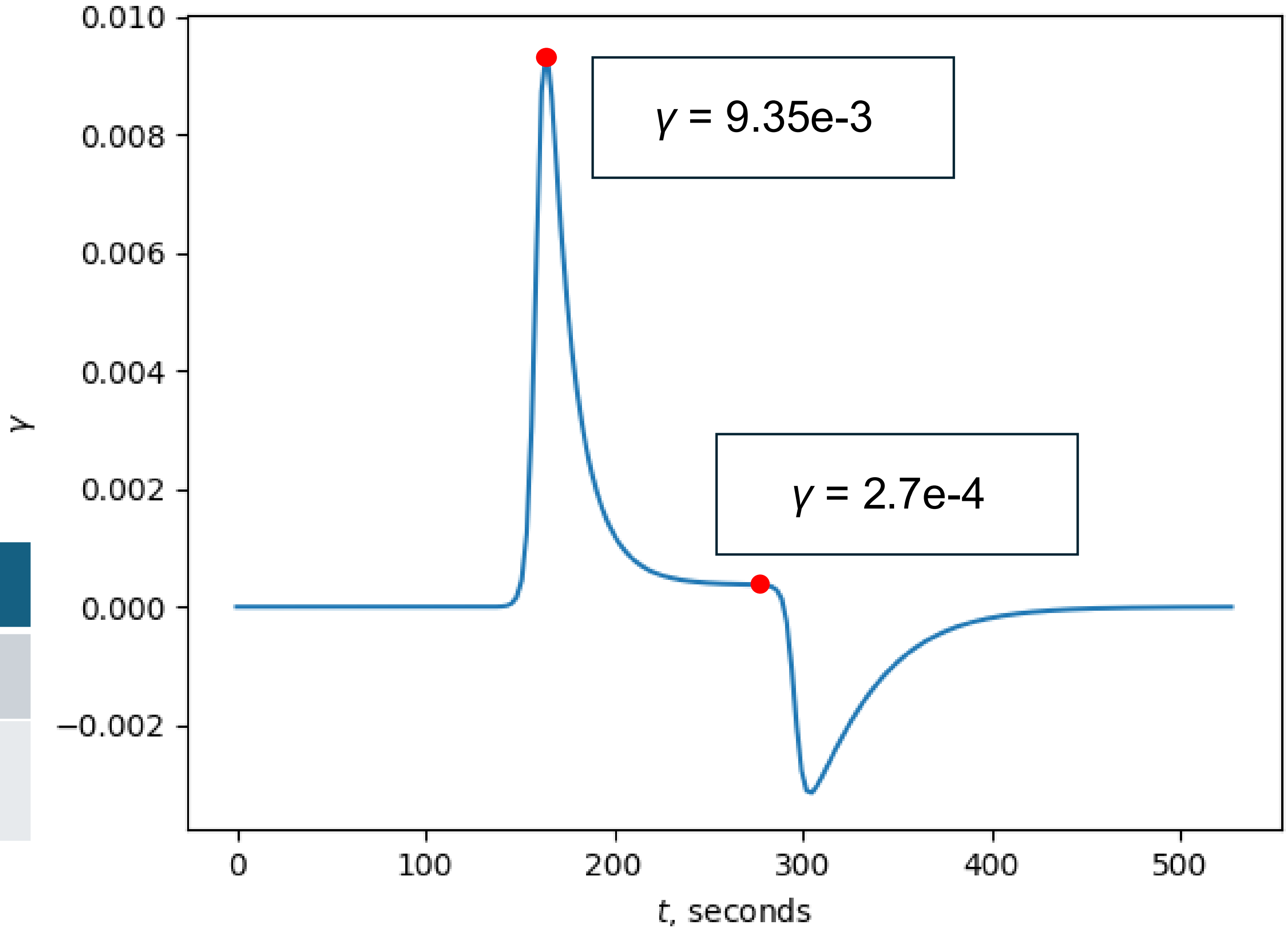
1D model - uptake coefficients

$$k_{\text{thermal}} = \sqrt{\frac{RT}{2\pi M}}$$

$$\gamma = \frac{k_{\text{ads}} X S - \frac{R}{2} k_{\text{des}} X_{\text{s}}}{k_{\text{thermal}} X}$$

Determined uptake coefficients:

	Experiment	Model
γ initial	1.1e-2	0.94e-2
γ steady state	2.9e-4	2.7e-4



Conclusions and future work

Conclusions:

- Both 1D and 3D models reproduce experimental uptake coefficients
- Parameters Y_0 and k_{rxn} are hard to extract / separate

Future work:

- Process a set of data with this model
- Add radial diffusion (as a first order rate law) and axial diffusion (explicitly) to the 1D model and observe the effect on results
- Automate fitting of experimental data to the model

Acknowledgement

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