Mechanistic Insights into Secondary Organic Aerosol Formation from Particle Growth Characteristics

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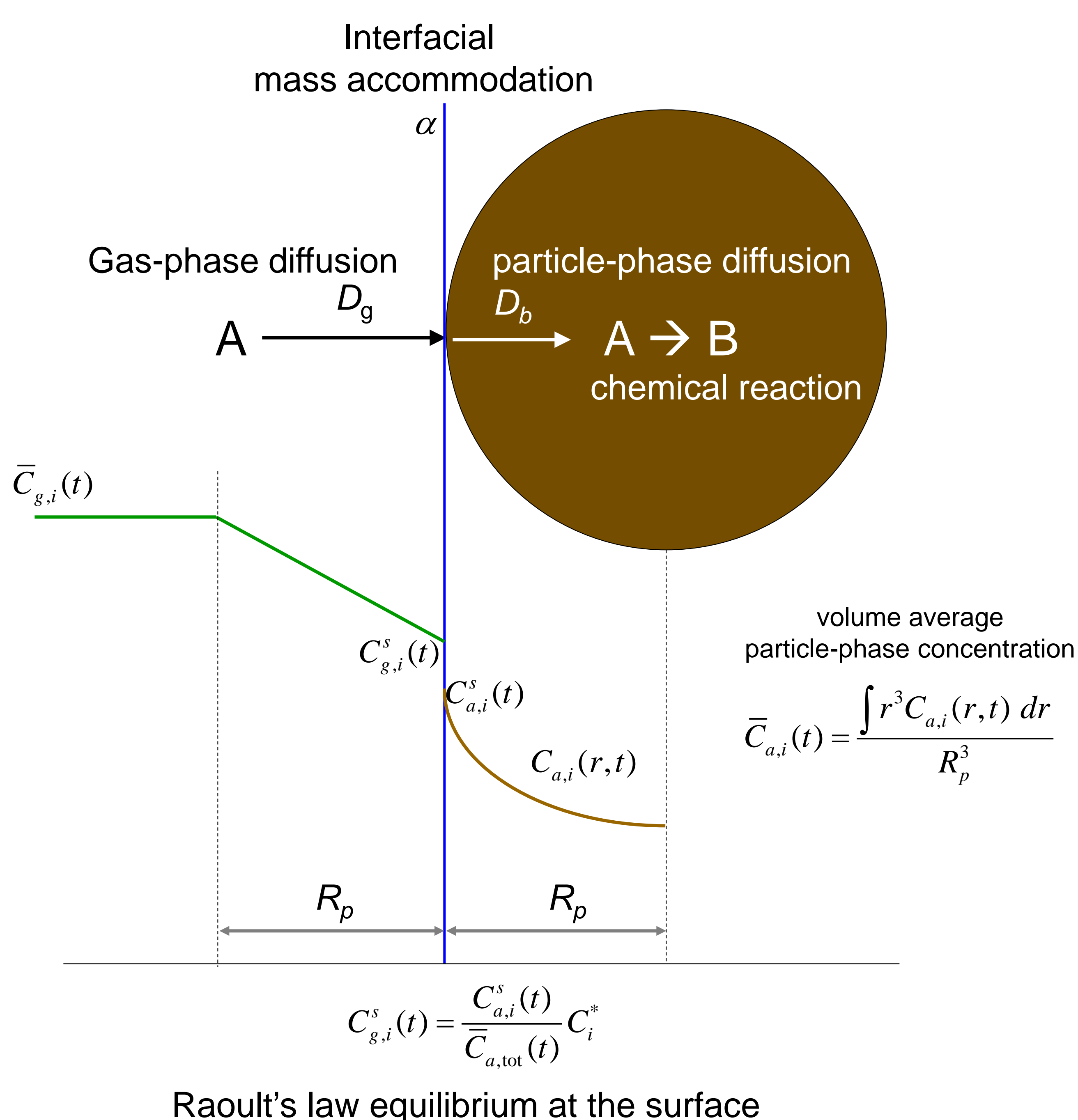**Pacific Northwest**
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1. Background

Several recent studies indicate that secondary organic aerosol (SOA) is a highly viscous liquid/semi-solid, with very low values of diffusivity in the particle phase (on the order 10^{-18} - 10^{-15} cm^2 s^{-1}), such that it evaporates very slowly (or not all) upon dilution. However, the mechanism of SOA formation itself remains poorly understood and inadequately represented in models.

In general, SOA can form via two possible mechanisms:

1) **Irreversible condensation** of non-volatile organic vapors formed from oxidation in the gas phase.

2) **Reversible absorption** of semi-volatile and volatile organic vapors according to Raoult's law, **with or without chemical reaction in the particle phase**.

The former is gas-phase diffusion limited and the growth will be controlled by pre-existing aerosol surface area. The growth characteristics in the latter depends strongly on the species' volatility as well as its diffusivity and reactivity in the particle phase. We have recently implemented these processes in the comprehensive aerosol model **MOSAIC** (Zaveri et al., 2008, JGR), which can then be applied to probe the mechanism of SOA formation from the observed evolution of aerosol size distributions in growth and evaporation experiments.

2. Schematic Process Representation

Interfacial mass accommodation
α

Gas-phase diffusion
D_g

particle-phase diffusion
D_b

$A \rightarrow B$ chemical reaction

$\overline{C}_{g,i}(t)$

$C_{g,i}^s(t)$

$C_{a,i}^s(t)$

$C_{a,i}(r,t)$

volume average particle-phase concentration
$$\overline{C}_{a,i}(t) = \frac{\int r^3 C_{a,i}(r,t)\, dr}{R_p^3}$$

R_p R_p

$$C_{g,i}^s(t) = \frac{C_{a,i}^s(t)}{\overline{C}_{a,\text{tot}}(t)} C_i^*$$

Raoult's law equilibrium at the surface

3. Model Development

Mass transfer of species i to spherical particles (size section m), with unsteady-state diffusion (D_b) and first-order reaction (k_{rxn}) inside the particle can be described by the following set of differential equations (based on work of Schwartz and Frieberg, 1981, Atmos. Environ.):

$$\frac{d\overline{C}_{a,i,m}}{dt} = k_{i,m}\left\{\overline{C}_{g,i} - \left(\frac{\overline{C}_{a,i,m}}{X_{i,m}}\right)\frac{C_i^*}{\overline{C}_{a,\text{tot},m}}\right\} - k_{rxn,i}\overline{C}_{a,i,m}$$

where

$$k_{i,m} = 4\pi R_{p,m}^2 N_m \left(\frac{R_{p,m}}{D_{g,i}} + \frac{4}{\alpha_i \overline{v}}\right)^{-1}$$ = gas-side mass transfer rate constant

$$X_i = 3\underbrace{\left(\frac{\coth q_i}{q_i} - \frac{1}{q_i^2}\right)}_{\text{steady-state term}} - \underbrace{\frac{6e^{-k_{rxn,i}^1 t}}{\pi^2}\sum_{n=1}^{\infty}\frac{\exp[-n^2\pi^2 D_{b,i}t/R_p^2]}{(q_i/\pi)^2 + n^2}}_{\text{unsteady-state term}}$$ = particle-phase reactive diffusion term
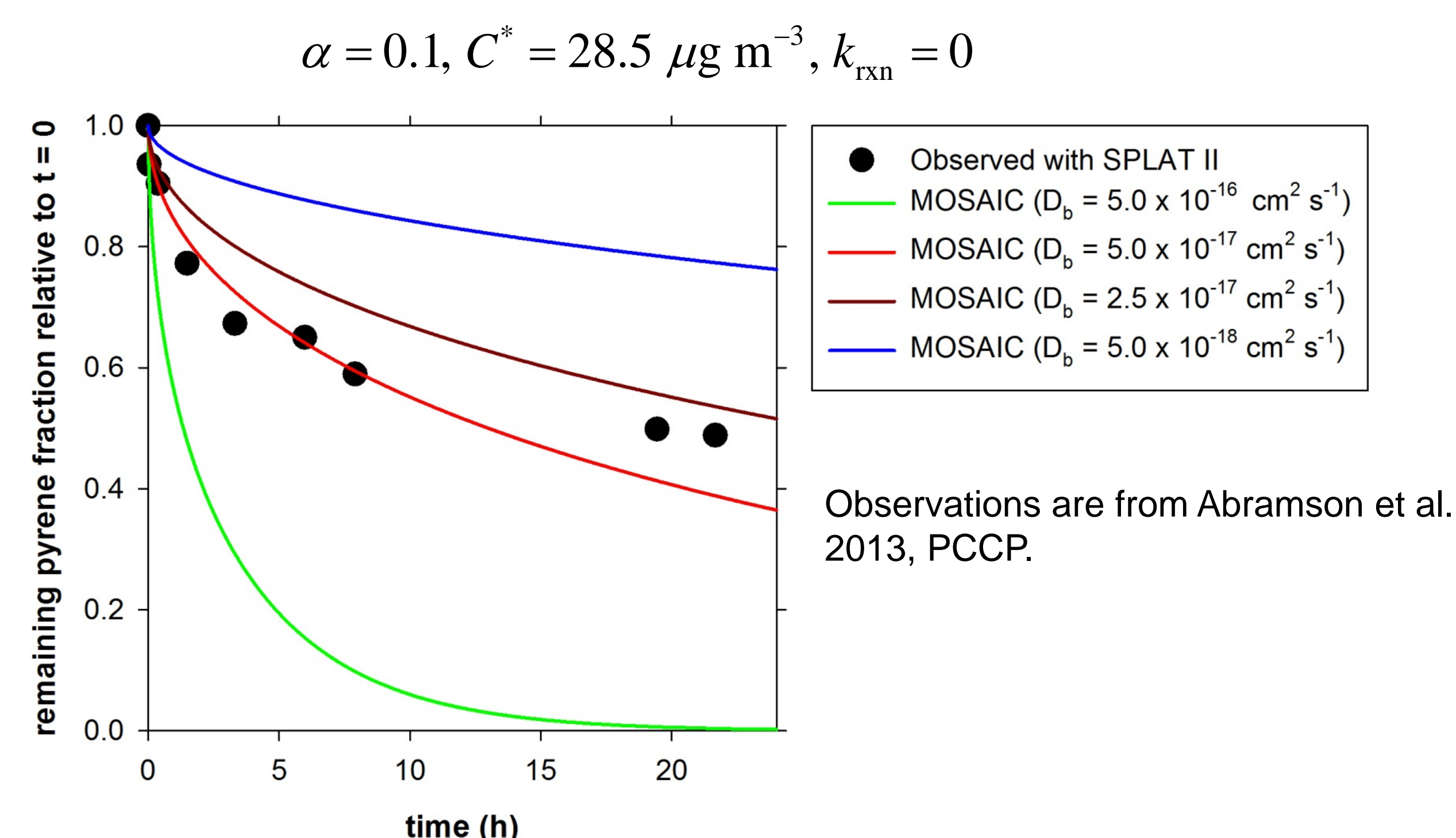
$$q_i = R_p\sqrt{\frac{k_{rxn,i}}{D_{b,i}}}$$ = diffuso-reactive parameter

$\overline{C}_{a,i,m}$ = average particle-phase concentration of species i in size bin m

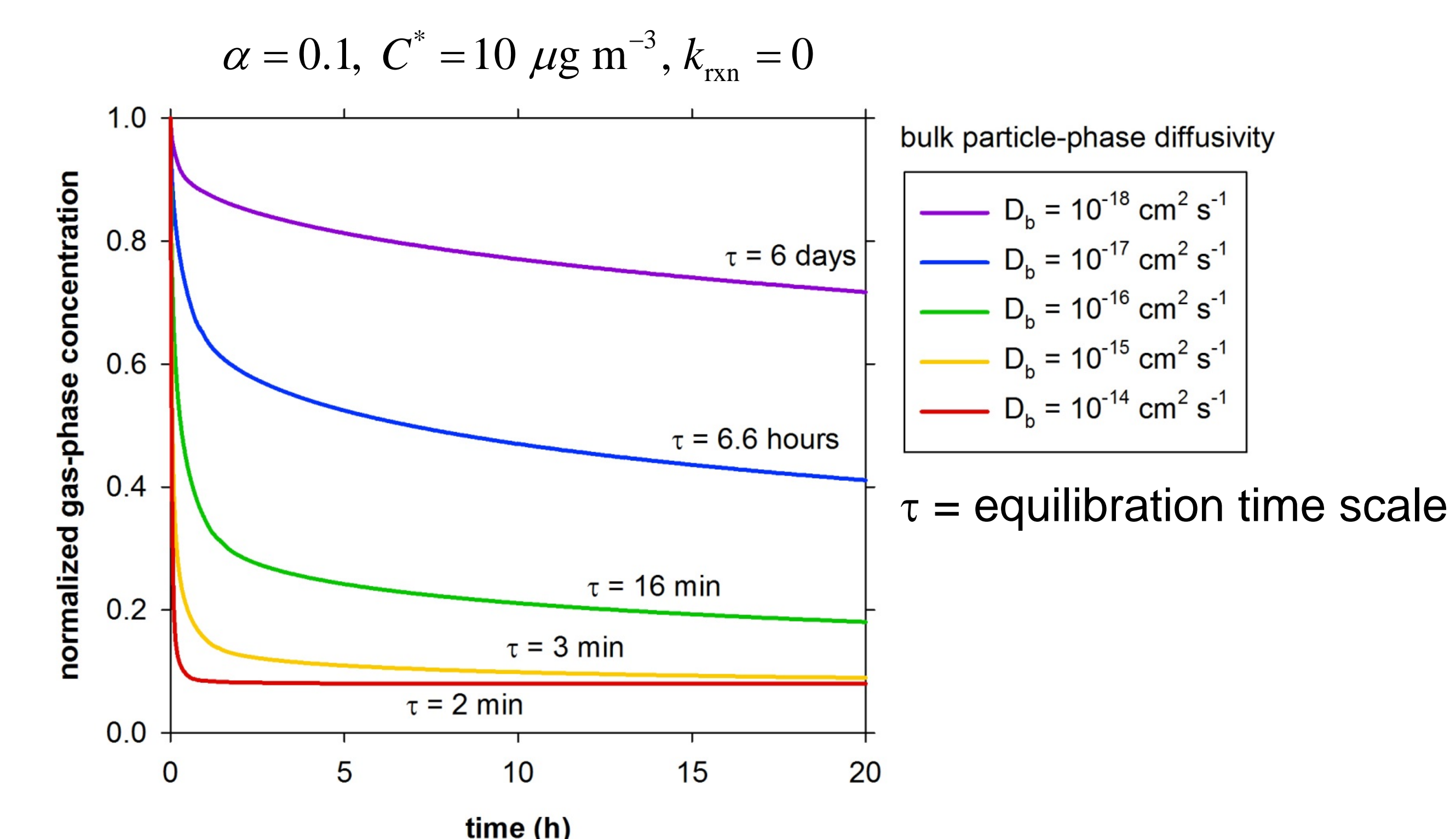$\overline{C}_{g,i}$ = average gas-phase concentration of species i

C_i^* = volatility of species i

4. Nonreactive Evaporation

$\alpha = 0.1,\ C^* = 28.5\ \mu g\ m^{-3},\ k_{rxn} = 0$

- ● Observed with SPLAT II
- MOSAIC ($D_b = 5.0 \times 10^{-16}$ cm^2 s^{-1})
- MOSAIC ($D_b = 5.0 \times 10^{-17}$ cm^2 s^{-1})
- MOSAIC ($D_b = 2.5 \times 10^{-17}$ cm^2 s^{-1})
- MOSAIC ($D_b = 5.0 \times 10^{-18}$ cm^2 s^{-1})
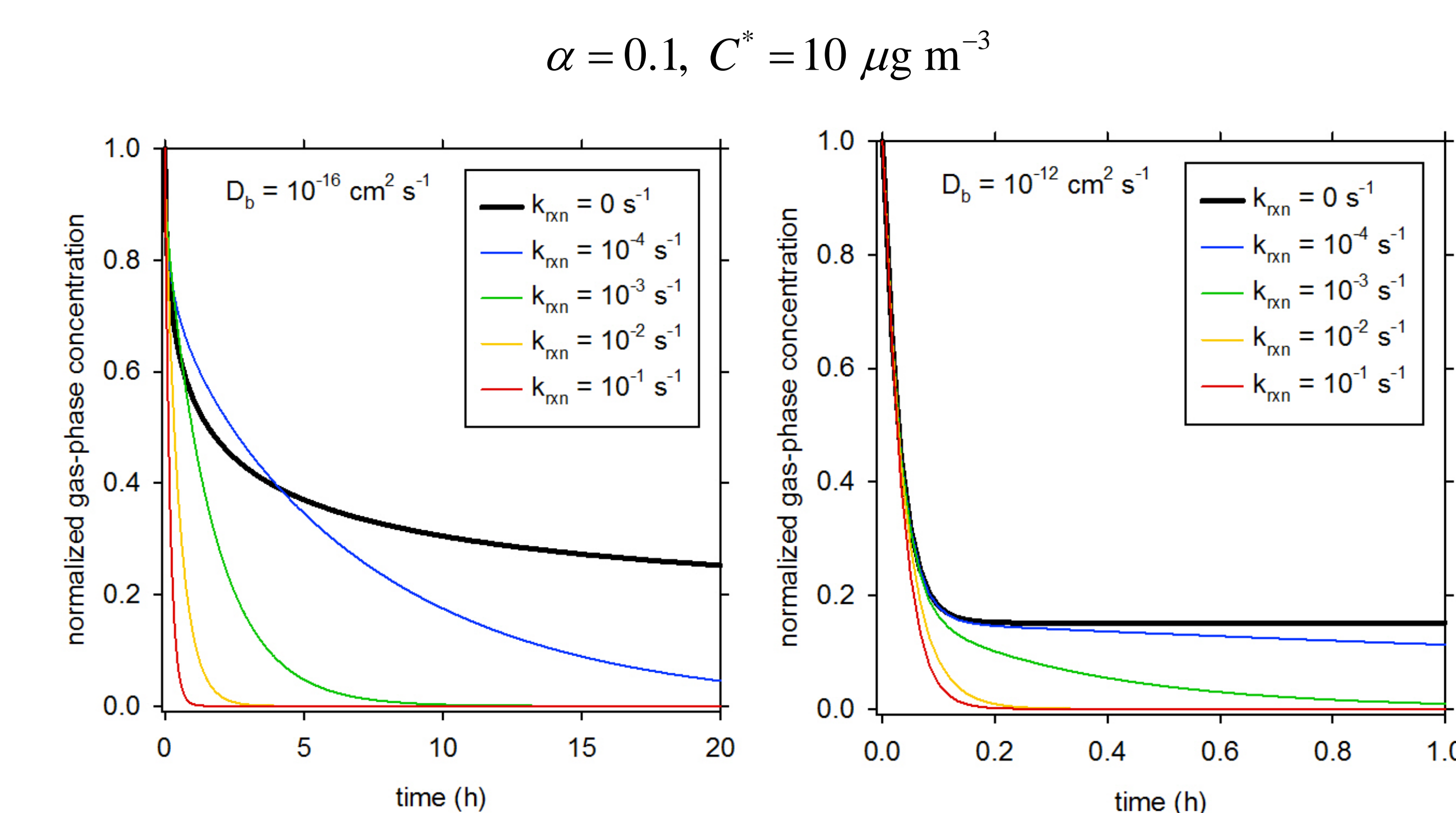
Observations are from Abramson et al., 2013, PCCP.

The model is successfully able to reproduce the observed evaporation of pyrene that was initially uniformly mixed in SOA particles of 0.175 μm diameter. Note that evaporation is rather slow, with ~40% remaining after 24 hours. The diffusivity in the bulk particle phase was determined to be 2.5 - 5.0 X 10^{-17} cm^2 s^{-1}.

5. Nonreactive Uptake

$\alpha = 0.1,\ C^* = 10\ \mu g\ m^{-3},\ k_{rxn} = 0$

bulk particle-phase diffusivity
- $D_b = 10^{-18}$ cm^2 s^{-1}
- $D_b = 10^{-17}$ cm^2 s^{-1}
- $D_b = 10^{-16}$ cm^2 s^{-1}
- $D_b = 10^{-15}$ cm^2 s^{-1}
- $D_b = 10^{-14}$ cm^2 s^{-1}

τ = 6 days
τ = 6.6 hours
τ = 16 min
τ = 3 min
τ = 2 min

τ = equilibration time scale

Decay of gas-phase concentration due to nonreactive mass transfer to a preexisting SOA (0.2 μm diameter) with different bulk particle-phase diffusivities $D_b = 10^{-14}$ to 10^{-18} cm^2 s^{-1}. The equilibration time scale (τ) ranges from ~2 min at $D_b = 10^{-14}$ to 6 days at $D_b = 10^{-18}$. These results are generally consistent with Shiraiwa and Seinfeld, 2012, GRL).

6. Reactive Uptake

$\alpha = 0.1,\ C^* = 10\ \mu g\ m^{-3}$

$D_b = 10^{-16}$ cm^2 s^{-1}
- $k_{rxn} = 0$ s^{-1}
- $k_{rxn} = 10^{-4}$ s^{-1}
- $k_{rxn} = 10^{-3}$ s^{-1}
- $k_{rxn} = 10^{-2}$ s^{-1}
- $k_{rxn} = 10^{-1}$ s^{-1}

$D_b = 10^{-12}$ cm^2 s^{-1}
- $k_{rxn} = 0$ s^{-1}
- $k_{rxn} = 10^{-4}$ s^{-1}
- $k_{rxn} = 10^{-3}$ s^{-1}
- $k_{rxn} = 10^{-2}$ s^{-1}
- $k_{rxn} = 10^{-1}$ s^{-1}

Decay of gas-phase concentration as the rate constant increases from 0 to 0.1 s^{-1} for two bulk diffusivity values: $D_b = 10^{-16}$ cm^2 s^{-1} (left) and $D_b = 10^{-12}$ cm^2 s^{-1} (right).

7. Ongoing and Future Work

- Analyze the behavior of reactive uptake for polydisperse aerosols
- Apply the model to interpret laboratory and field observations of aerosol growth and evaporation.
- Implement actual particle-phase reactions that produce oligomers, organosulfates, etc.

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