Representing effects of aqueous-phase reactions in shallow cumuli in global models

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Beyond effects on dynamics, moist convection also affects atmospheric chemistry

- Vertical transport of chemical species (including scavenging)
- Turbulent mixing of chemical species
- Photochemistry by changing the radiation field
- Lightning production of NOx
- Aqueous phase reactions

Aqueous phase oxidation of SO_2 accounts for a majority of sulfate production

Table 2. GEOS-CHEM Global Budgets for Sulfate Produced by Different Oxidation Pathways

	Source, Tg S yr^{-1}
Total sulfate	31.0
SO_2 + OH (gas phase)	8.2
S(IV) + H_2O_2 (in cloud)	15.7
S(IV) + O_3 (in cloud)	2.3
S(IV) + O_3 (fine sea salt)	0.4
S(IV) + O_3 (coarse sea salt)	2.3
Primary anthropogenic	2.0

Alexander et al., 2005, JGR

It also increases the scattering efficiency of sulfate aerosols (Lelieveld and Heintzenberg, Science, 1992)

The reactions

$$\mathrm{SO_2(g) \Leftrightarrow SO_2 \cdot H_2O}$$

$$\mathrm{SO_2 \cdot H_2O \Leftrightarrow HSO_3^- + H^+}$$

$$\mathrm{H_2O_2}(g) \Leftrightarrow \mathrm{H_2O_2}(aq)$$

$$\mathrm{HSO_3^- + H^+ + H_2O_2}(aq) \rightarrow \mathrm{SO_4^{2-} + 2H^+ + H_2O}$$

Seinfeld and Pandis, 2006

Sulfate production rate in mixing ratio relative to air:

$$\frac{\mathrm{d}\left[\mathrm{SO_4^{2-}}\right]}{\mathrm{dt}} = \mathrm{k}\left[\mathrm{SO_2}\right]_\mathrm{g}\left[\mathrm{H_2O_2}\right]_\mathrm{g}\mathrm{q_c}\, p_{air}\rho_{air}$$

q_c: cloud water content

$$\mathrm{k} \approx 2 \times 10^{-3} s^{-1} ppb^{-1} \left(g/kg\right)^{-1} \left(bar\right)^{-1} \left(kgm^{-3}\right)^{-1}$$

Currently, in global chemical transport models (CTM), SO_2 and H_2O_2 are titrated over a CTM time step within the cloudy volume.

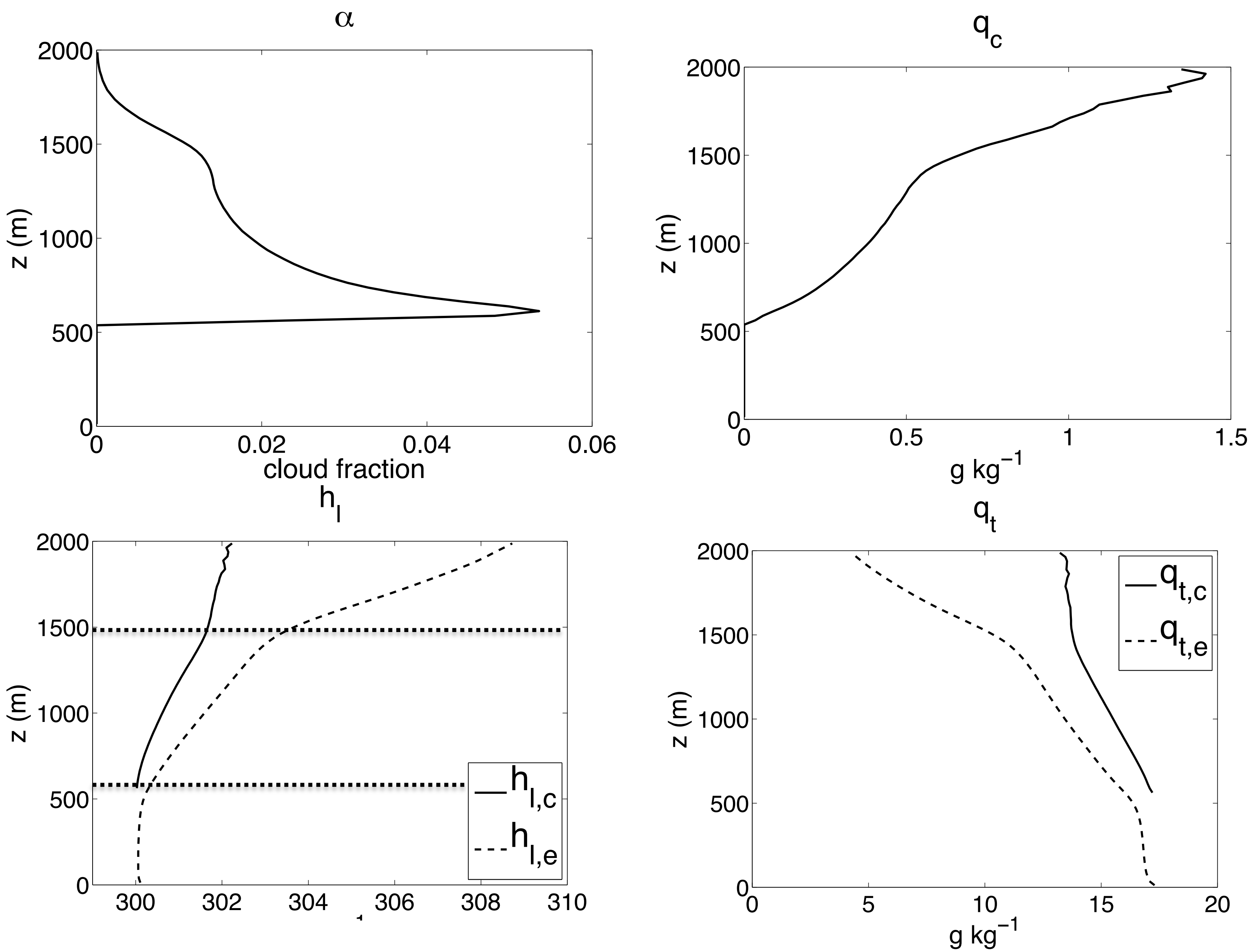
LES of SO_2 oxidation by H_2O_2

- Large-scale meteorological forcing from BOMEX
- 6.4kmX6.4kmX3km with a resolution of 25mX25mX25m

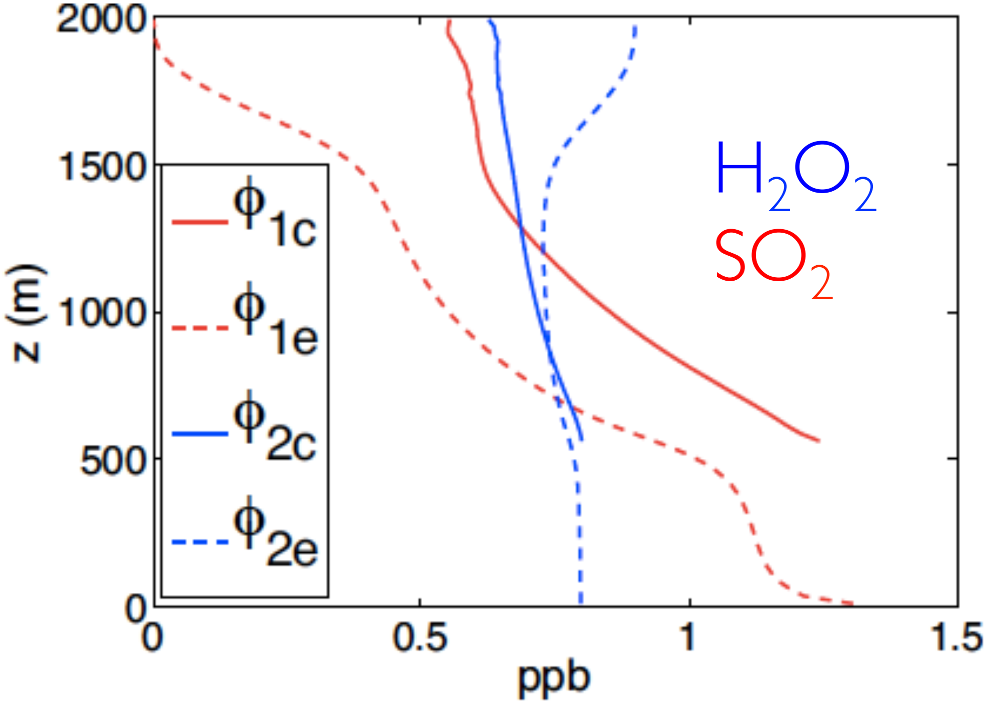
"Chemistry":

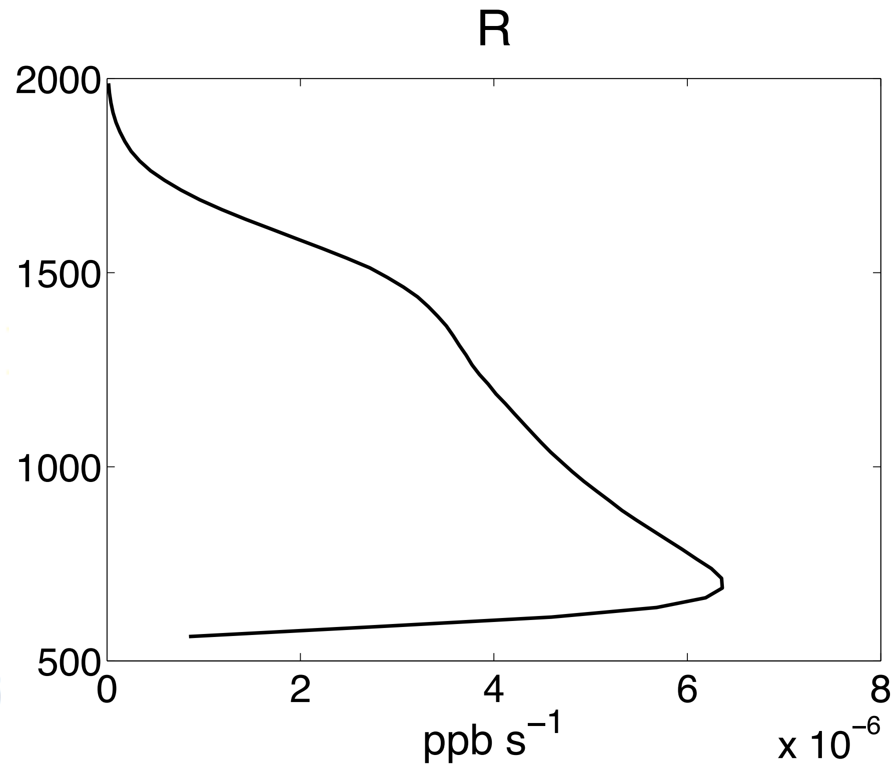
- Tracer 1 ("SO_2") is released from surface with a fixed flux,
- Tracer 2 ("H_2O_2") is relaxed to a constant reference profile over 1 day
- The two tracers react to form tracer 3 ("H_2SO_4") with a specified reaction rate k $\frac{d\left[SO_4^{\ 2-}\right]}{dt} = k\left[SO_2\right]_g \left[H_2O_2\right]_g q_c$
- An additional sink of tracer 1 with a timescale of one day (mimicking dry deposition and gaseous oxidation).

General characteristics of BOMEX



LES results on SO_2 oxidation





Reference case:

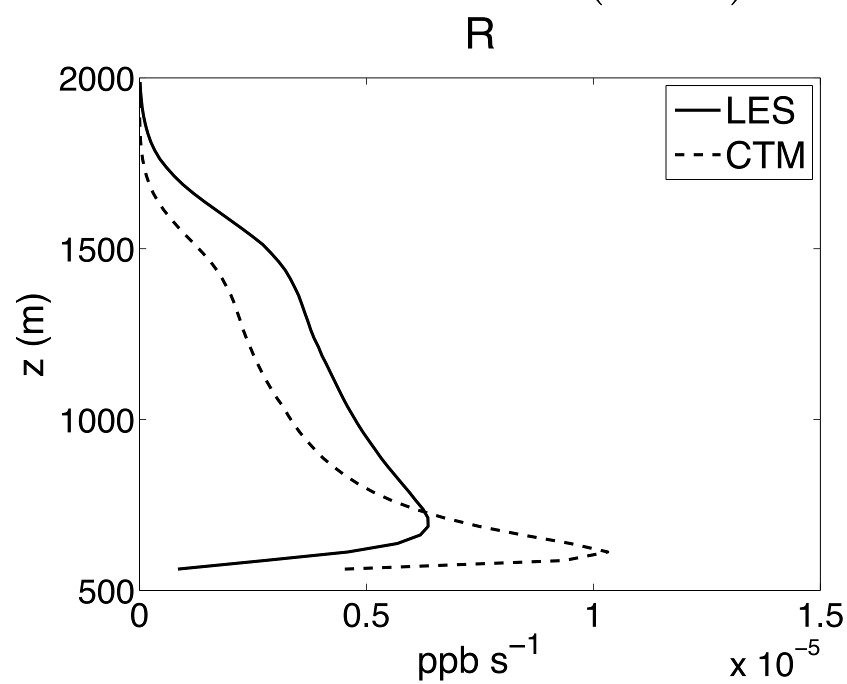
SO_2 flux: 0.024 ppb kg m^{-2} s^{-1}

H_2O_2 value: 0.9ppb

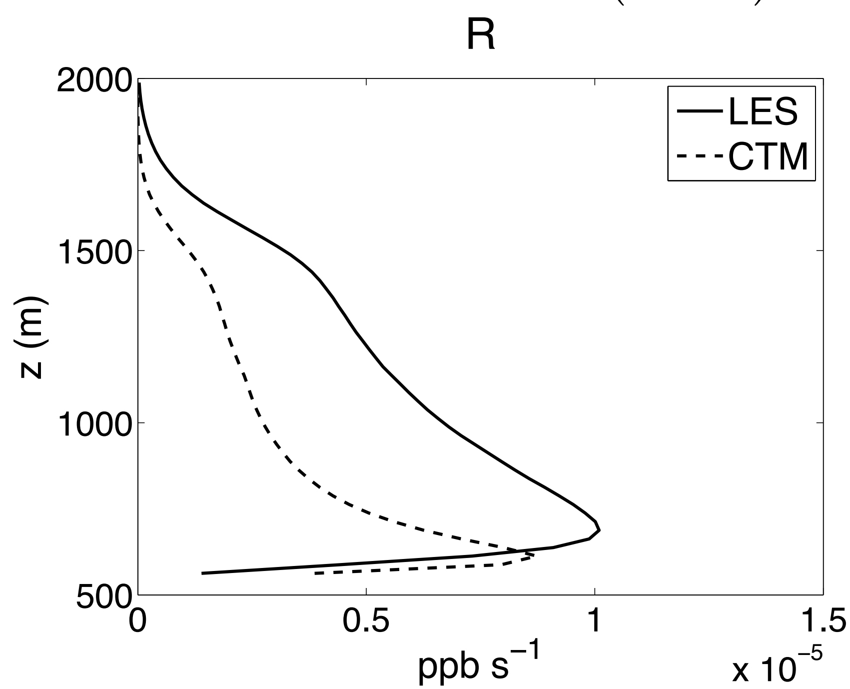
$$k = 1 \times 10^{-3} s^{-1} ppb^{-1} (g/kg)^{-1}$$

Performance of current chemical transport model treatment

$$k = 1\times10^{-3} s^{-1} ppb^{-1} (g/kg)^{-1}$$



$$k = 2\times10^{-3} s^{-1} ppb^{-1} (g/kg)^{-1}$$



Uses LES simulated cloud fraction and horizontal mean tracer values with a 1-hr global model time step.

How well can the eddy diffusivity and mass flux (EDMF) approach represent the aqueous phase reaction ?

Sub-grid scale transport

$$\overline{w'\phi'} \simeq -K\frac{\partial\overline{\phi}}{\partial z} + M(\phi_u - \overline{\phi})$$

Soares et al., QJ, 2004

where K is the eddy diffusivity and M is the updraft mass flux. The mass flux component is modeled with a bulk entraining/detraining plume

Reaction

$$k\overline{[\mathrm{SO_2}]}\,\overline{[\mathrm{H_2O_2}]}\,\overline{q_c}$$

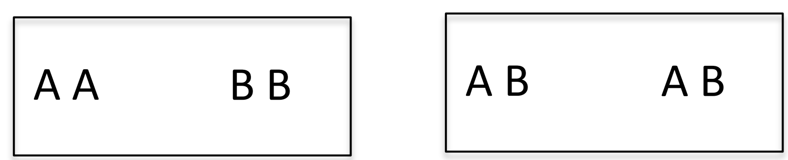
where over-bar indicates averages over cloudy updrafts

Effective entrainment/detrainment rates and eddy diffusivities are diagnosed using conserved tracers.

This approach isolates errors due to chemistry and can be used in a super-parameterized global model.

Potential errors:

1. Effective entrainment and detrainment rates are tracer-dependent
2. Segregation error



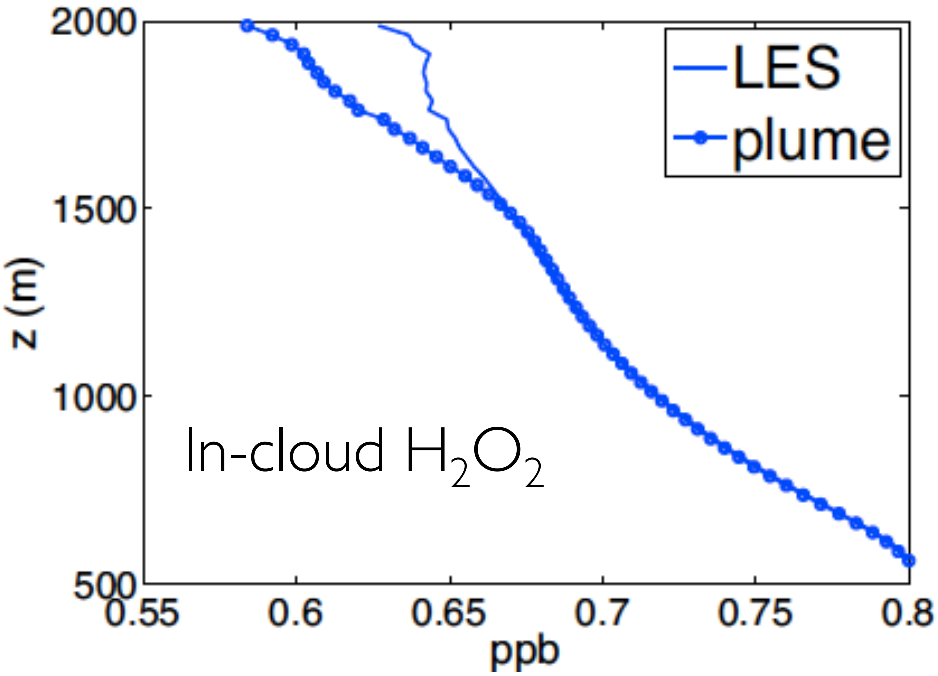
Single step errors

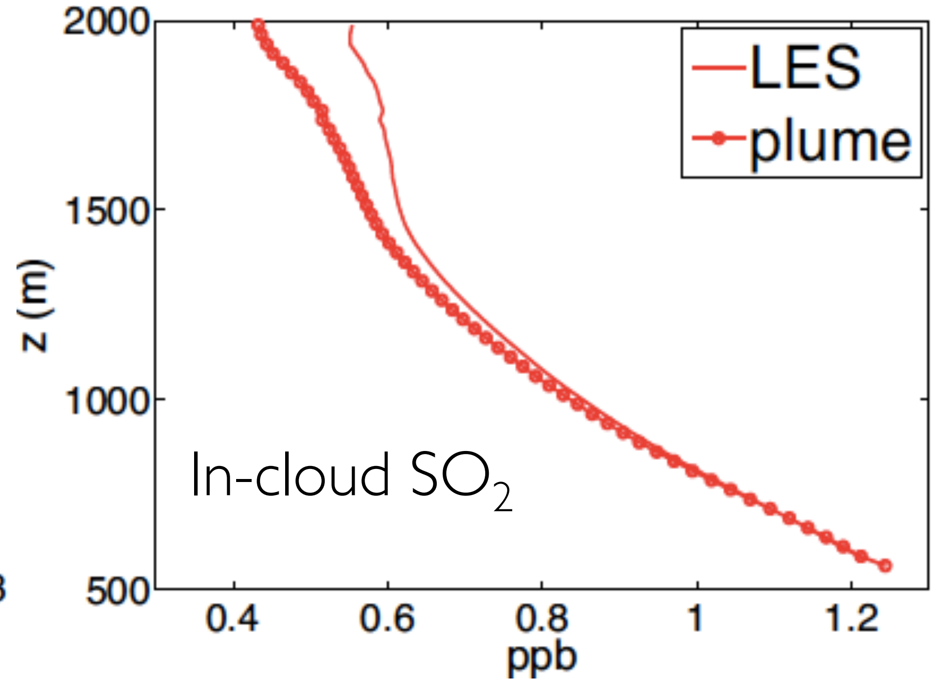
Reference case:

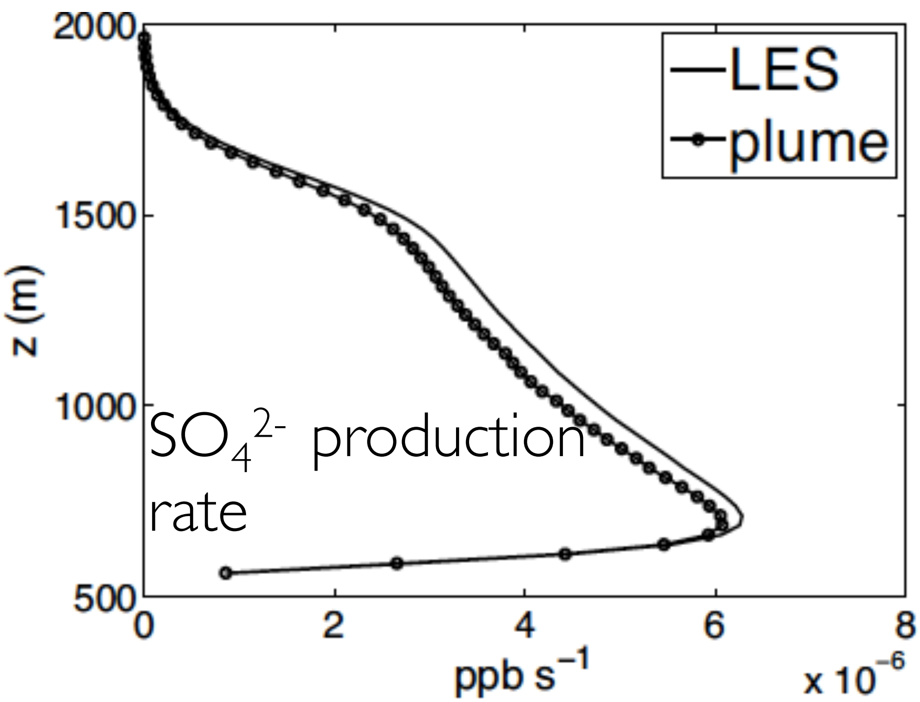
SO_2 flux: 0.024 ppb kg m^{-2} s^{-1}

H_2O_2 value: 0.9ppb

$$k = 1 \times 10^{-3} s^{-1} ppb^{-1} \left(g / kg \right)^{-1}$$





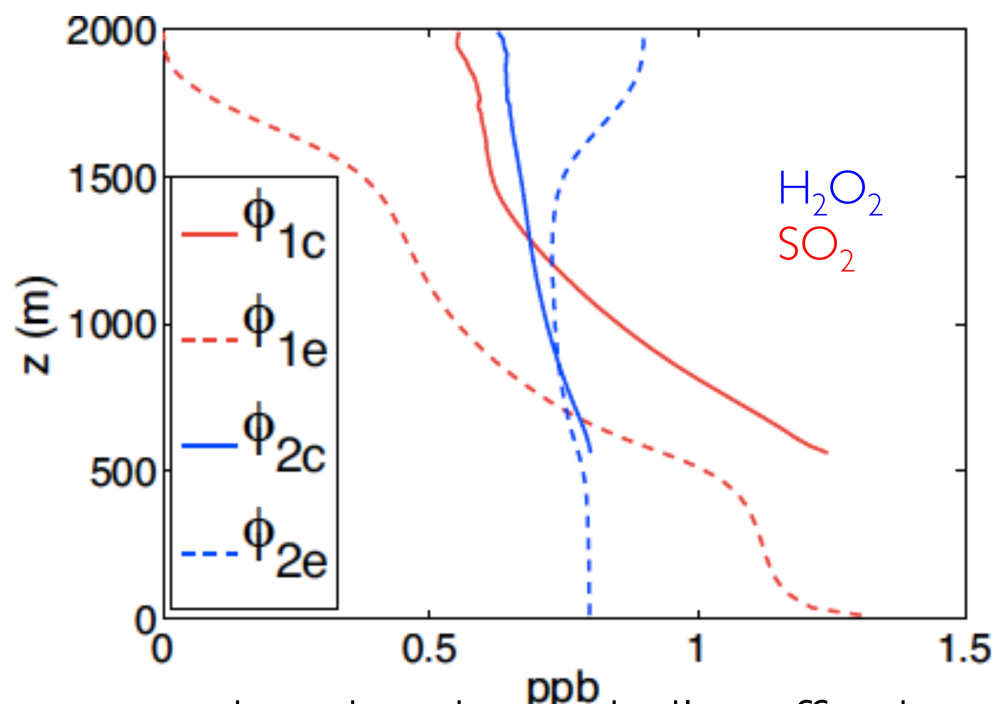


In-cloud tracer values are well represented below the inversion layer

The bulk plume underestimates the reaction rates by ~6%

Why are in-cloud tracer values well-modeled in the bulk plume?

While this reaction is considered fast from a global model perspective, it's relatively slow (tens of minutes) compared to the timescale of eddy mixing in cumulus clouds so that:



SO_2 is well correlated with total water so that they have similar effective entrainment/detrainment rates.

Because of the slow reaction and the small vertical gradient, H_2O_2 values in and out of clouds are similar so entrainment has less of an effect.

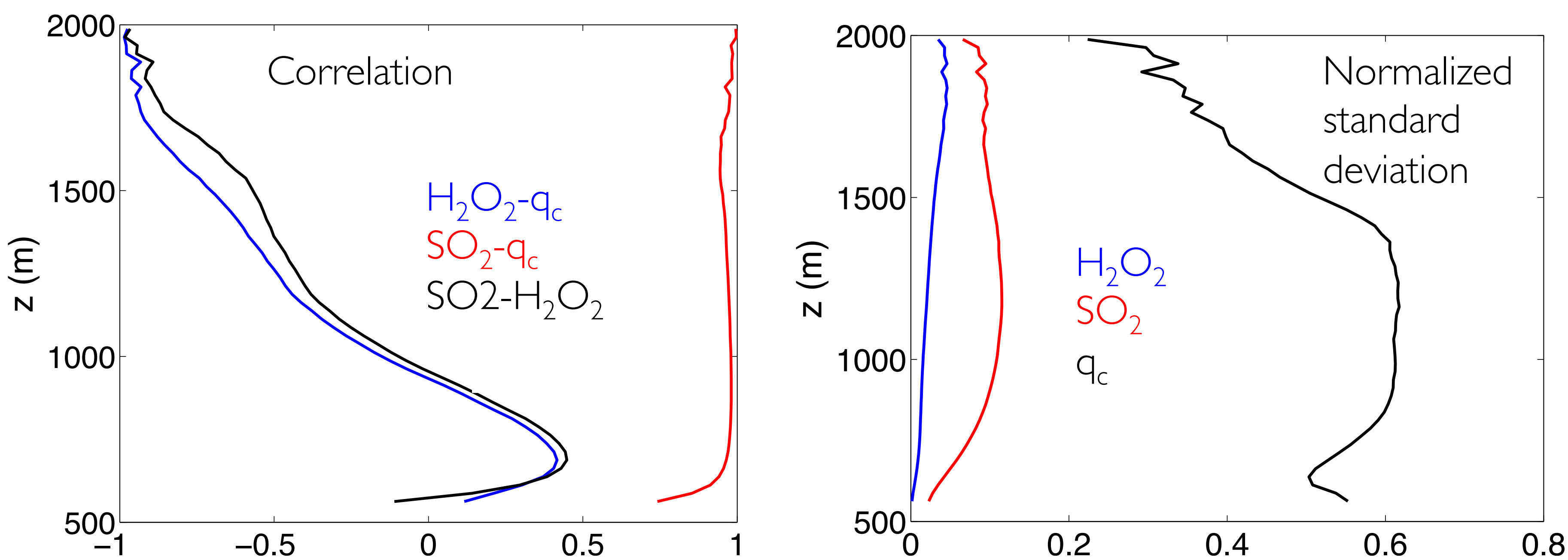
Why plume model underestimates the reaction rates

$$1-\frac{R_{LES}}{R_{plume}} \approx -c_{SO_2,q_c}\sigma_{SO_2}\sigma_{q_c} - c_{H_2O_2,q_c}\sigma_{H_2O_2}\sigma_{q_c} - c_{H_2O_2,SO_2}\sigma_{H_2O_2}\sigma_{SO_2}$$

$$\approx -\sigma_{SO_2}\sigma_{q_c}$$

Where σ is the standard deviation divided by the mean

- The reaction is "slow" so that SO_2 is well correlated with cloud liquid water
- Fractional variance of H_2O_2 is small compared to that of SO_2

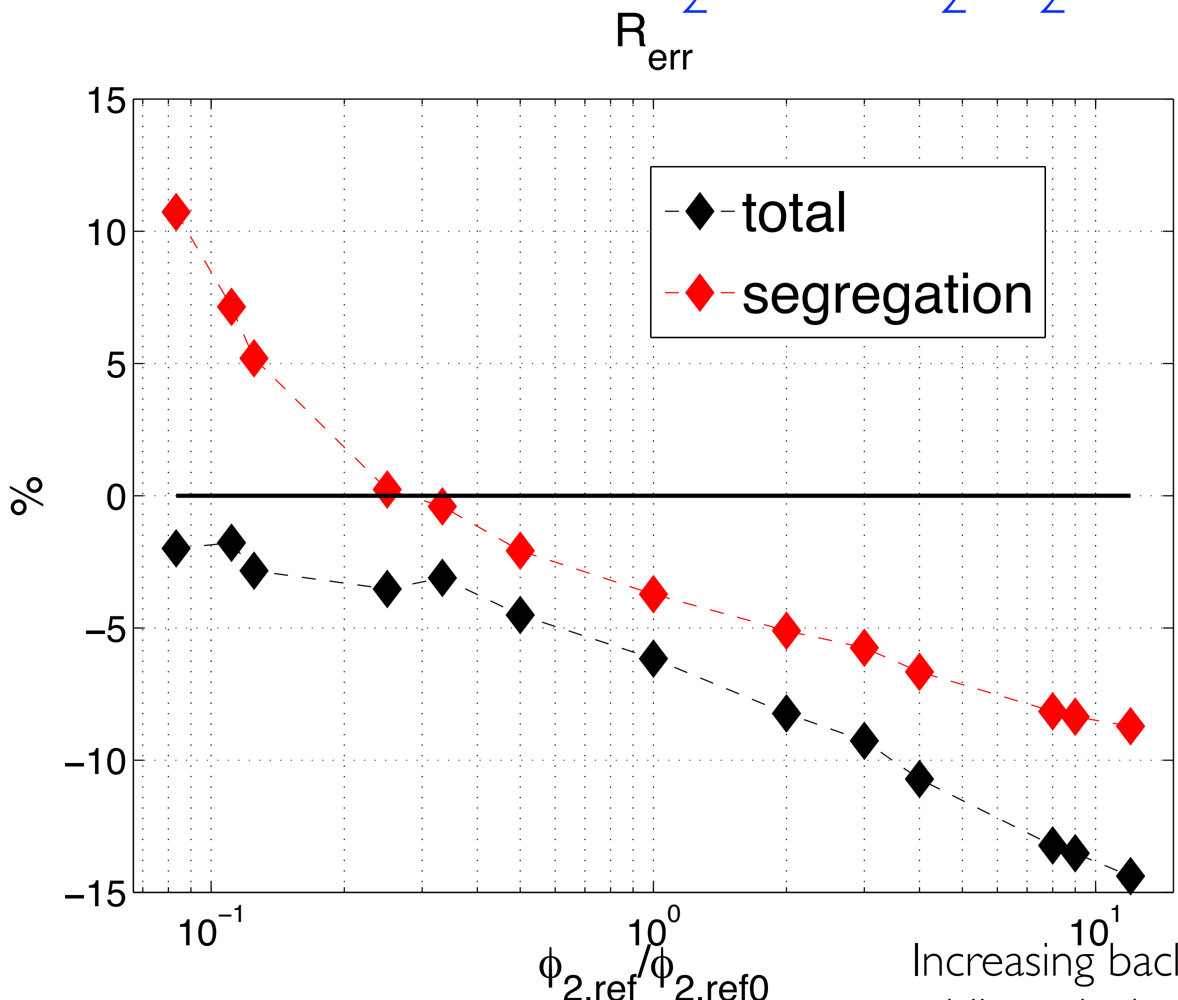


Varying two control parameters

Reaction rate constant: k

Relative magnitudes of sources of SO_2 and H_2O_2

Varying relative magnitudes of sources of SO_2 and H_2O_2



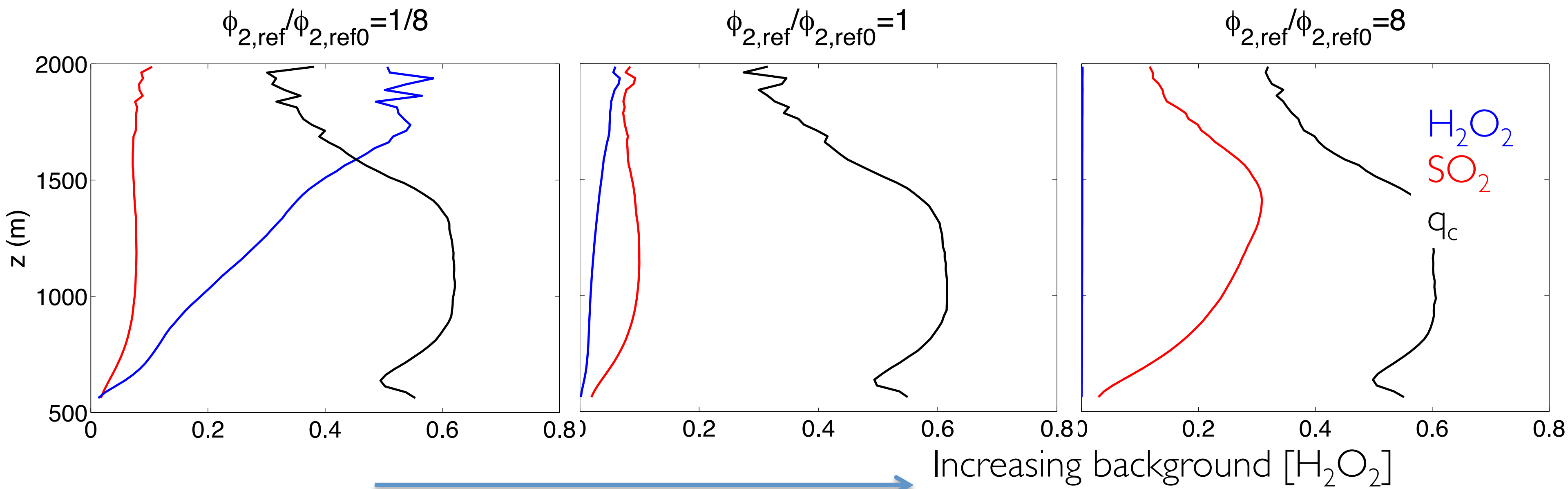
Increasing background $[H_2O_2]$ while reducing surface SO_2 flux by the same factor

Varying relative magnitudes of sources of SO_2 and H_2O_2

$$1-\frac{R_{LES}}{R_{plume}} \approx \boxed{-c_{SO_2,q_c}\sigma_{SO_2}\sigma_{q_c}} \boxed{-c_{H_2O_2,q_c}\sigma_{H_2O_2}\sigma_{q_c} - c_{H_2O_2,SO_2}\sigma_{H_2O_2}\sigma_{SO_2}}$$

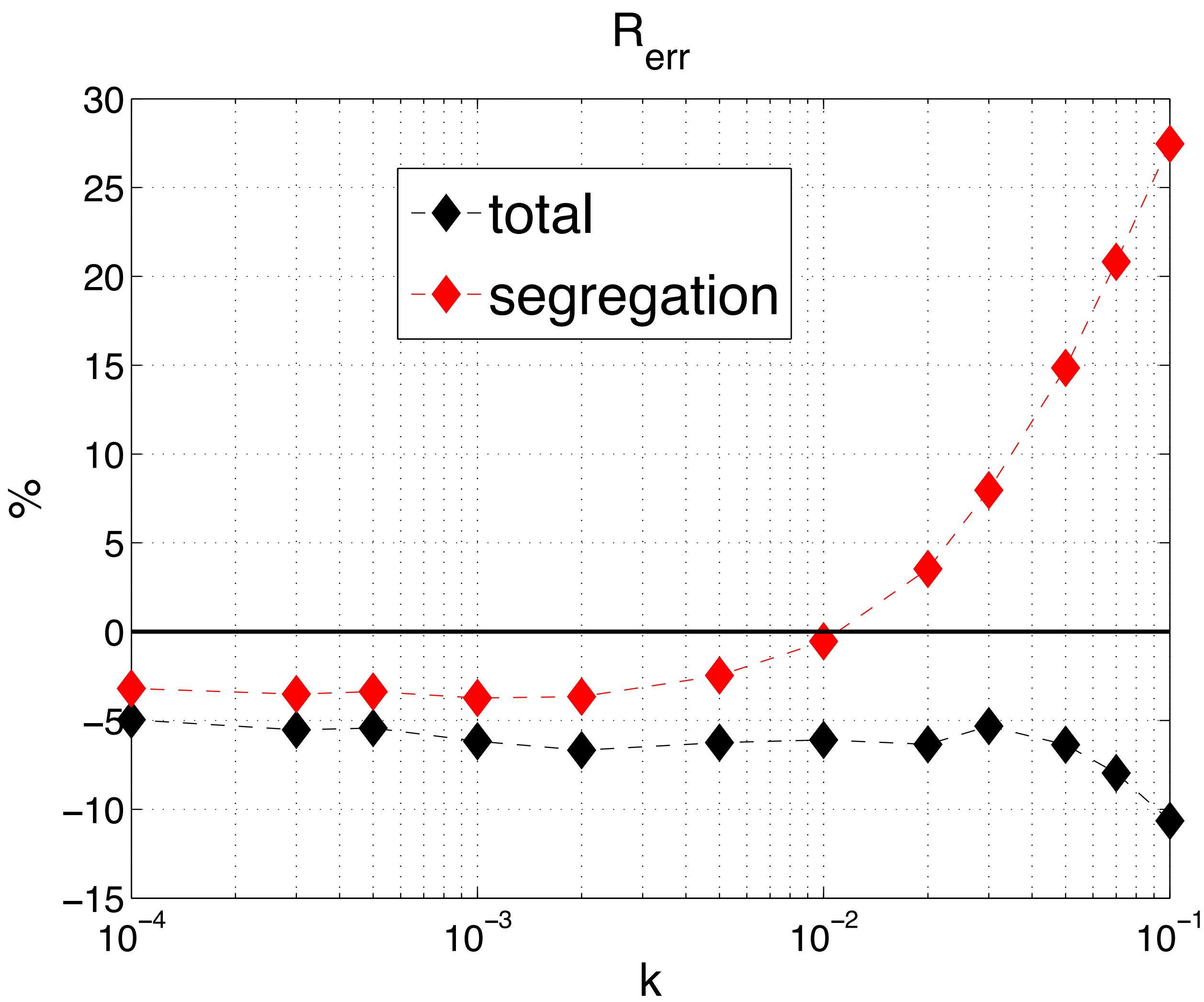
Negative Positive

Normalized standard deviation



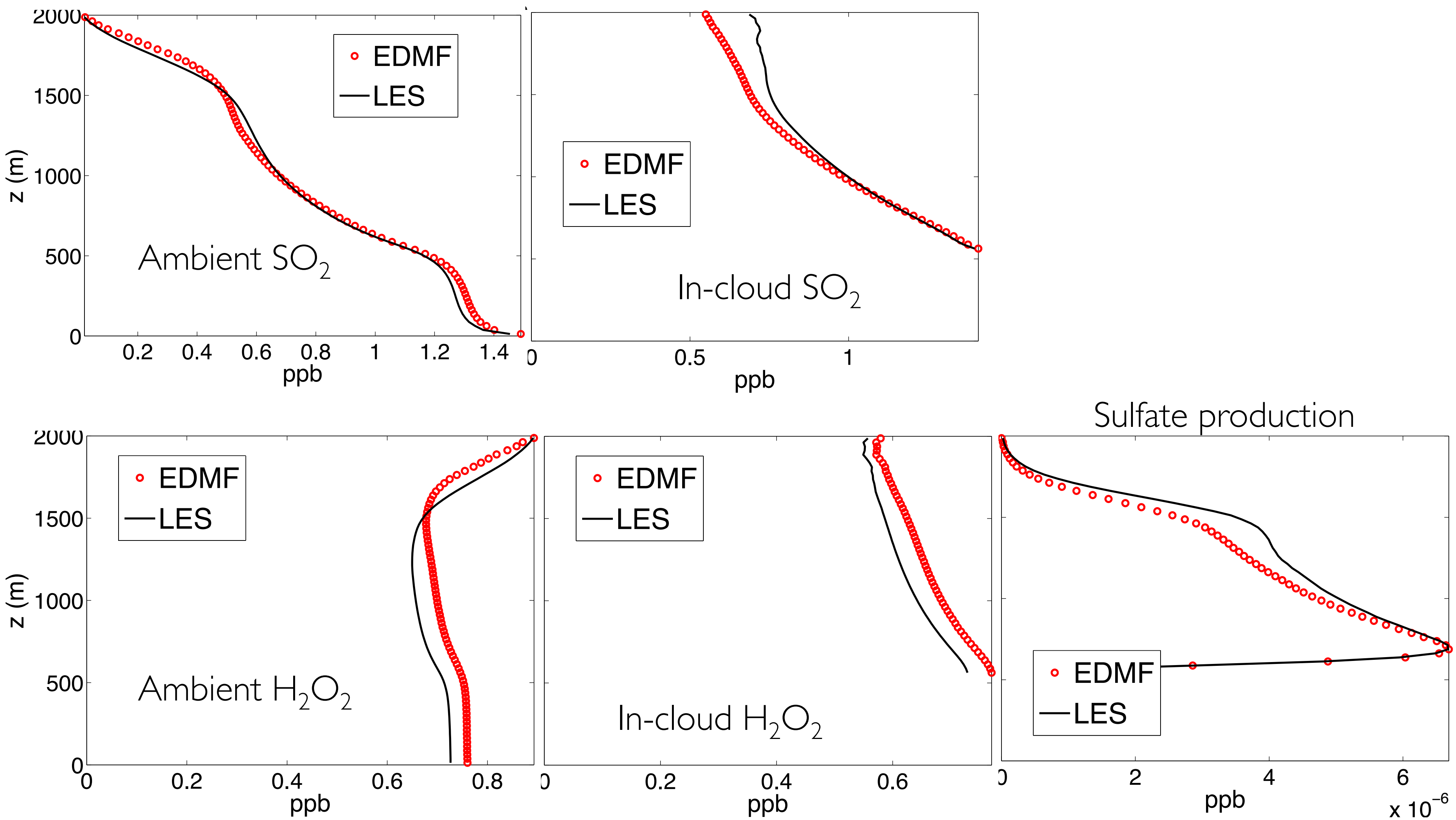
As H_2O_2 increases relative to SO_2, there is a stronger vertical gradient in SO_2 and stronger fractional in-cloud variance.

Varying the reaction rate constant



$s^{-1} ppb^{-1} (g/kg)^{-1}$

Equilibrium state using the EDMF

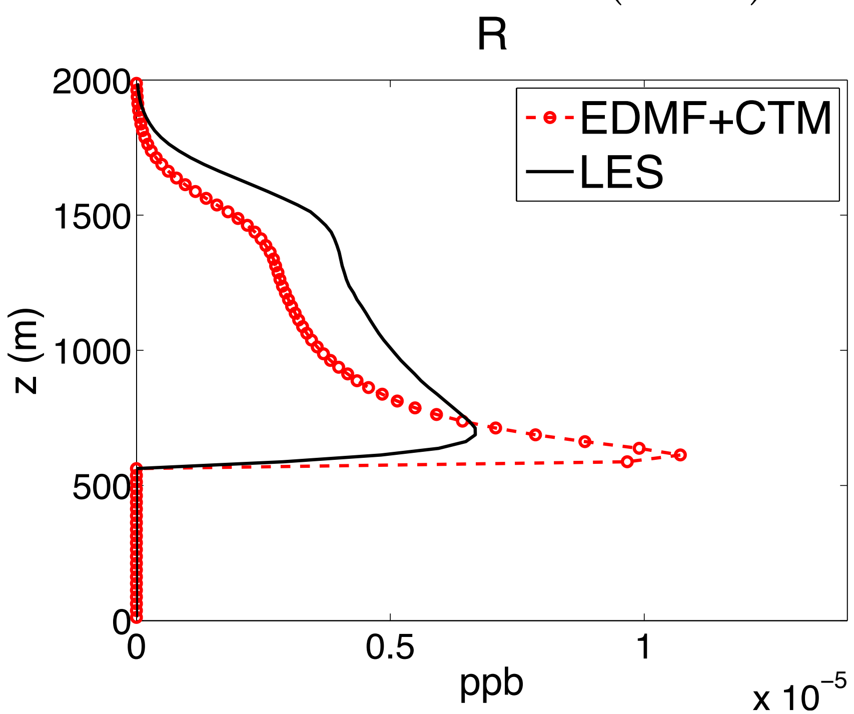


Conclusions

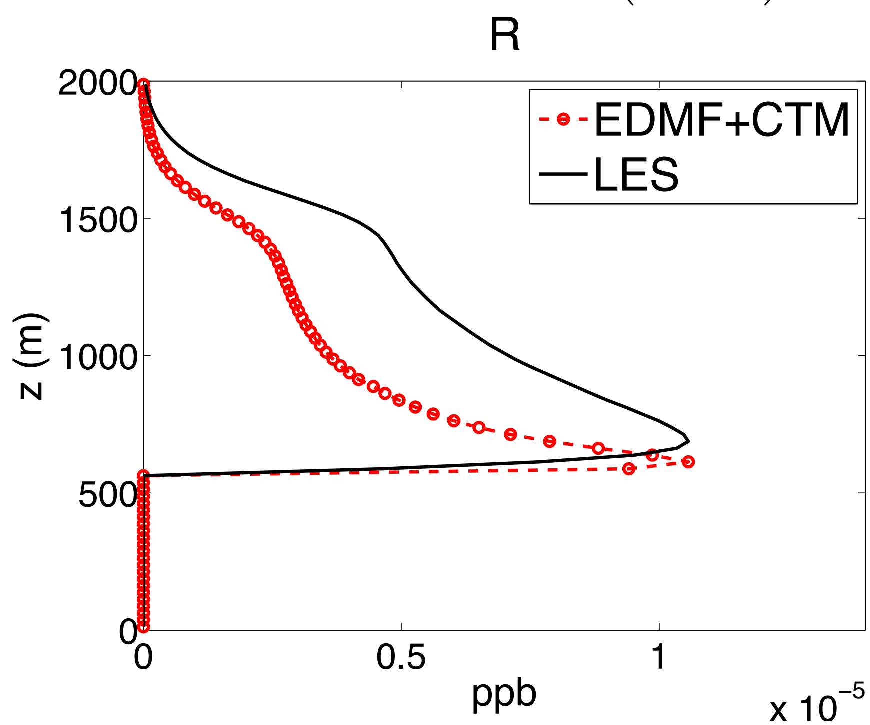
- The EDMF approach with a bulk plume can represent aqueous reaction in shallow cumuli quite well when entrainment/detrainment rates and eddy diffusivity are diagnosed using conservative tracers like total water.
- This is because the aqueous reactions are slow compared to eddy mixing timescale in shallow cumuli.
- The bulk plume underestimates the reaction rate by 5-10% and errors are larger with faster reactions and in H_2O_2 dominated cases (for understood reasons)
- This approach can be used with super-parameterization.

Performance of current chemical transport model treatment

$$k = 1\times10^{-3} s^{-1} ppb^{-1} (g/kg)^{-1}$$



$$k = 2\times10^{-3} s^{-1} ppb^{-1} (g/kg)^{-1}$$



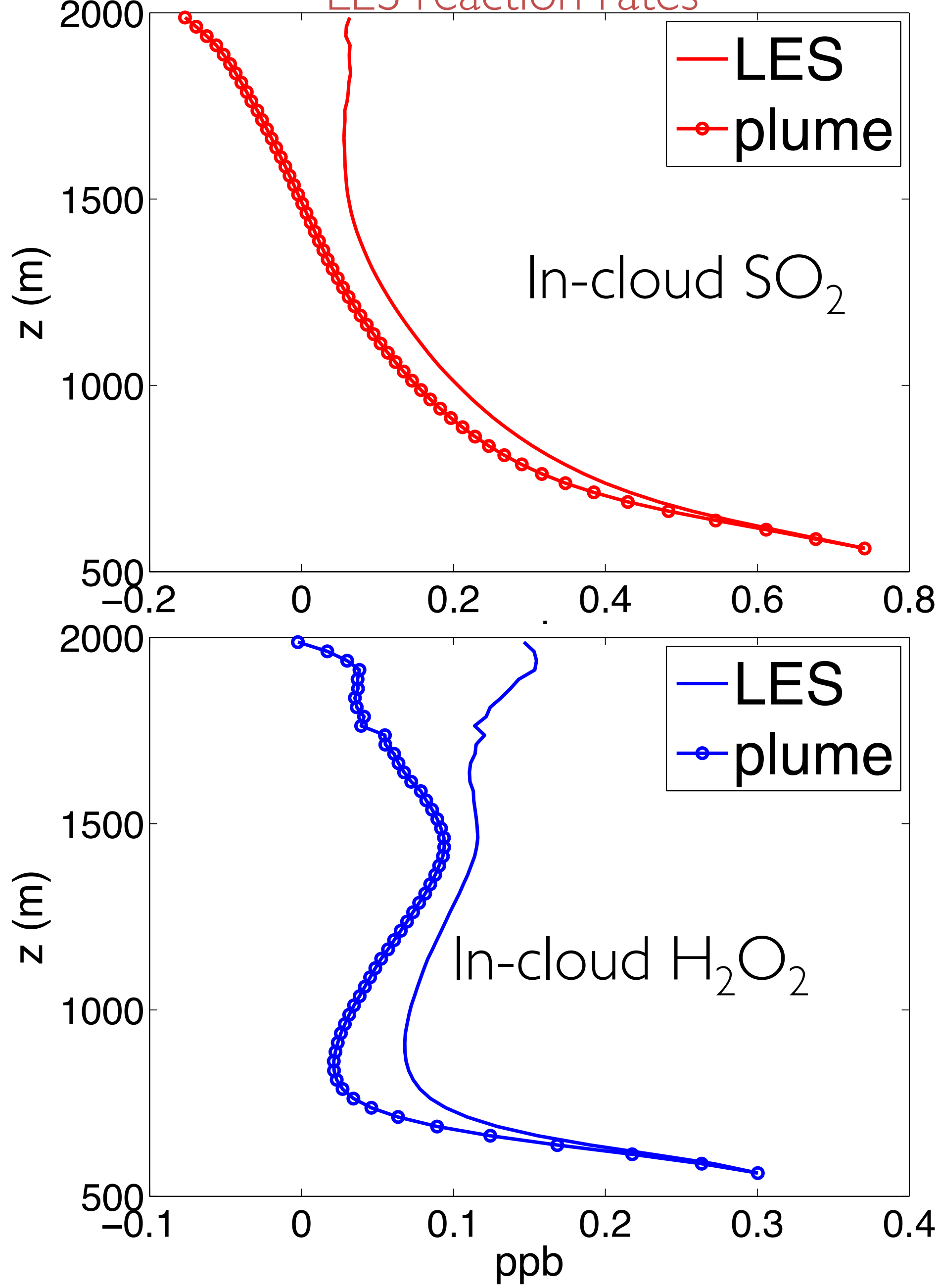
Uses cloud fraction and vertical tracer fluxes diagnosed from the LES with a 1-hr global model time step.

Errors in entrainment/ detrainment rates

$$k = 0.1 s^{-1} ppb^{-1} (g/kg)^{-1}$$

For large k, effective entrainment and detrainment rates for the tracers become more different from those for conserved variables.

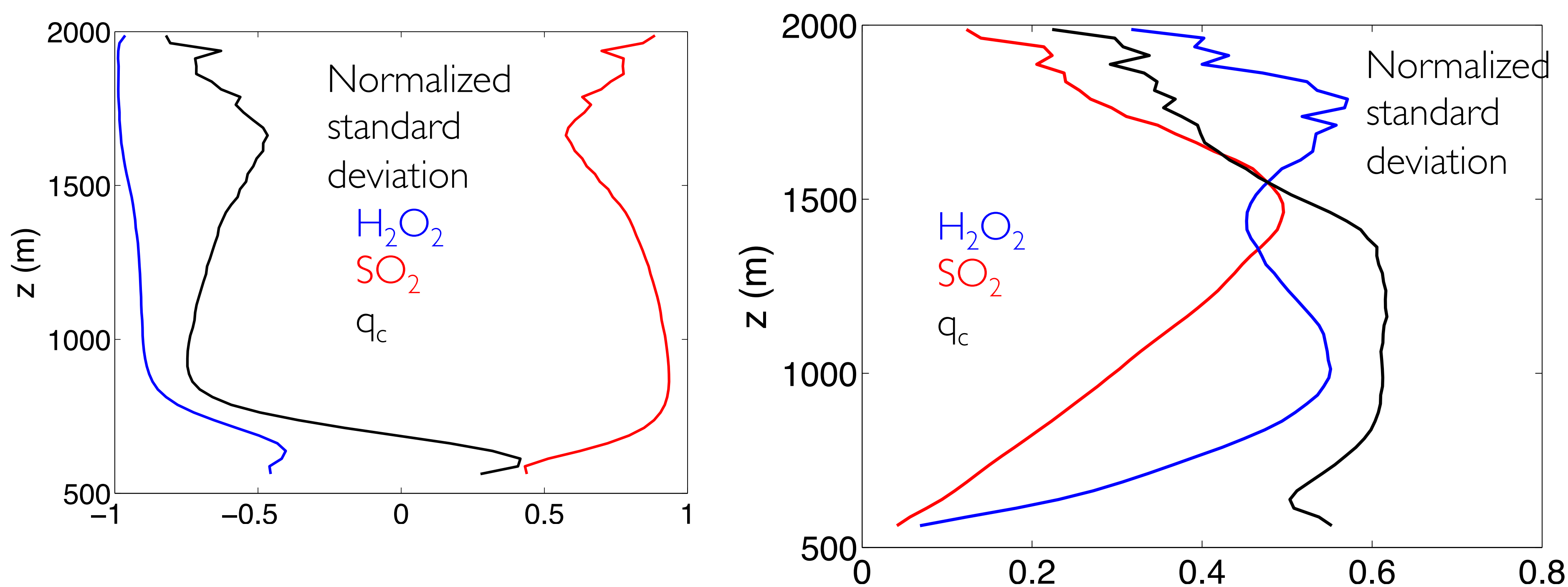
In-cloud tracer values assuming LES reaction rates



Segregation error $k = 0.1 s^{-1} ppb^{-1} (g/kg)^{-1}$

$$\frac{R_{LES}}{R_{plume}} - 1 \approx \sigma_{SO_2}\sigma_{q_c} - \sigma_{H_2O_2}\sigma_{q_c} - \sigma_{H_2O_2}\sigma_{SO_2}$$

As k increases, H_2O_2 becomes anti-correlated with SO_2 and cloud water, and fraction variance of H_2O_2 becomes large and the second and third terms become more dominant

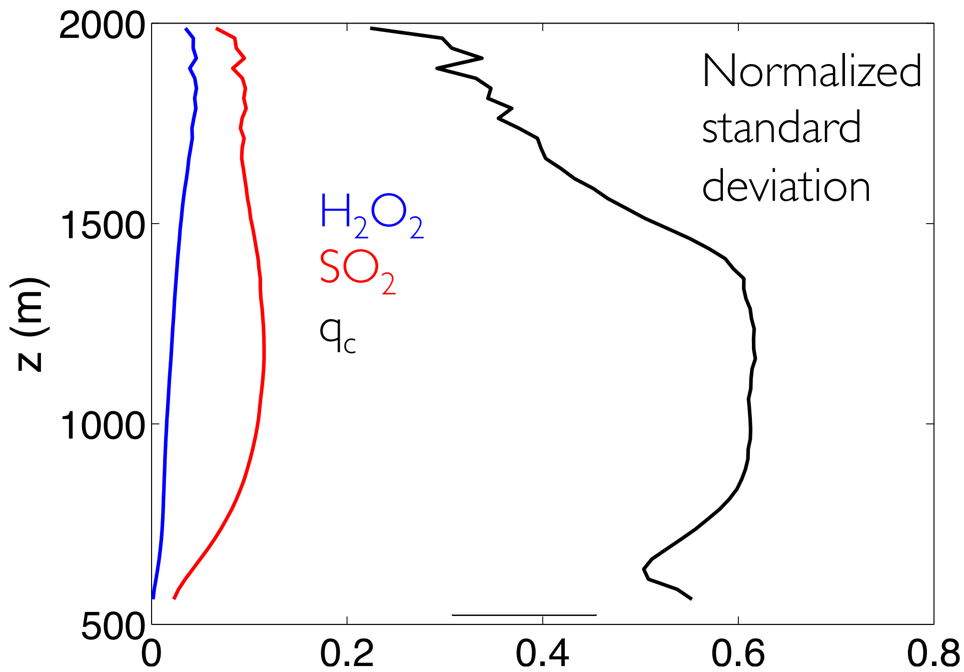


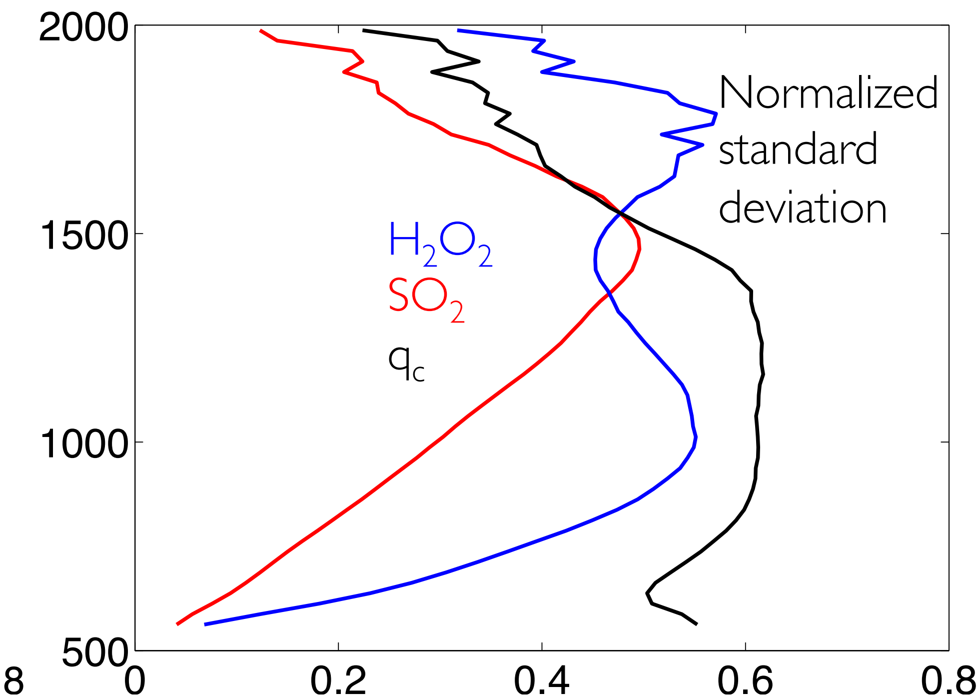
Segregation error

$$\frac{R_{LES}}{R_{plume}} - 1 \approx \sigma_{SO_2}\sigma_{q_c} - \sigma_{H_2O_2}\sigma_{q_c} - \sigma_{H_2O_2}\sigma_{SO_2}$$

$$k = 0.001 s^{-1} ppb^{-1} (g/kg)^{-1}$$

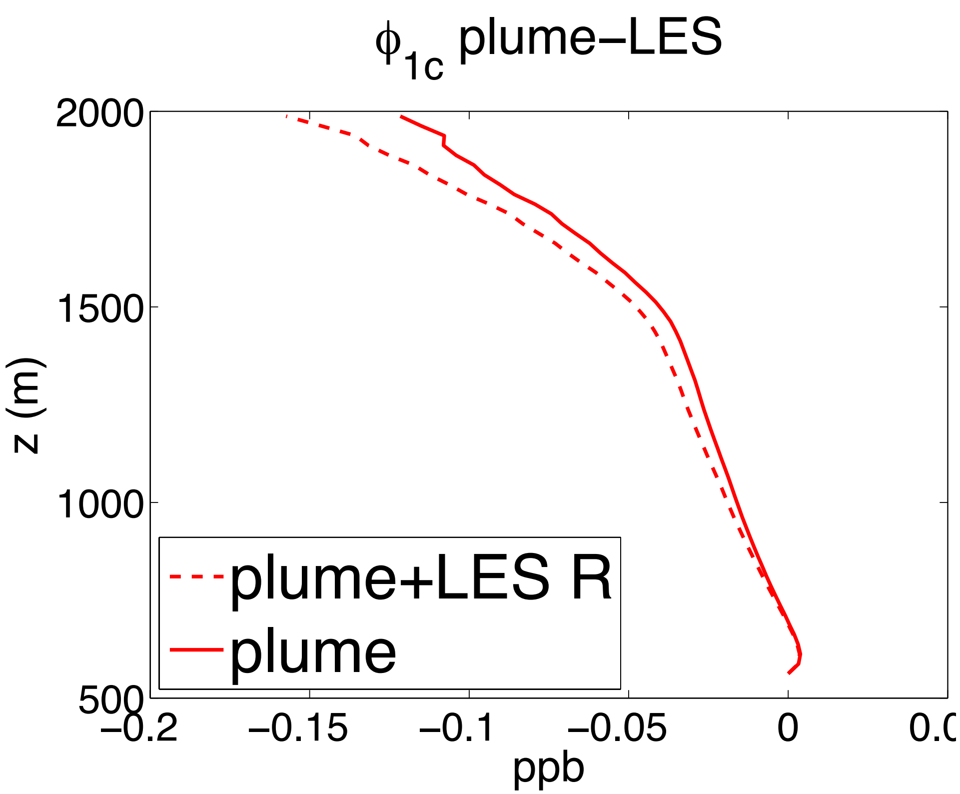
$$k = 0.1 s^{-1} ppb^{-1} (g/kg)^{-1}$$

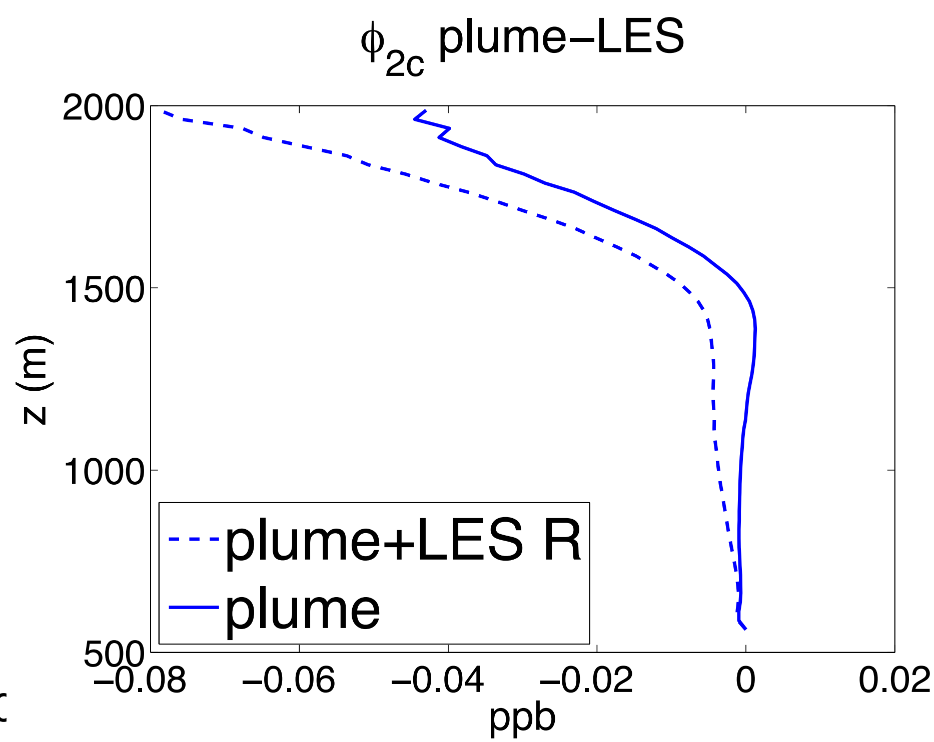




Why are in-cloud tracer values well-modeled with the bulk plume?

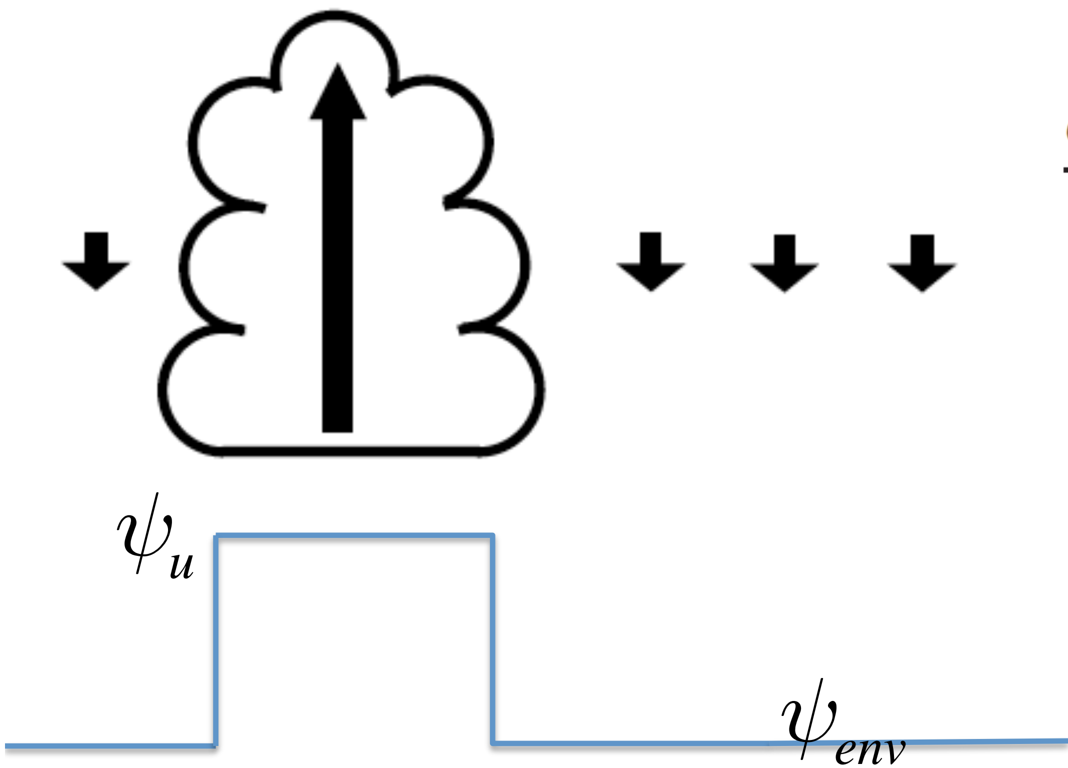
3. Error in reaction rates partly cancels error in entrainment





Bulk plume representation for mass flux

Assume clouds and environment at a given height have uniform properties within each category



$$\frac{\partial M_u}{\partial z} = M_u(\varepsilon - \delta),$$

$$\frac{\partial \psi_u}{\partial z} = \varepsilon(\overline{\psi} - \psi_u) + S_\psi.$$