



Global modeling of secondary organic aerosol with an explicit scheme

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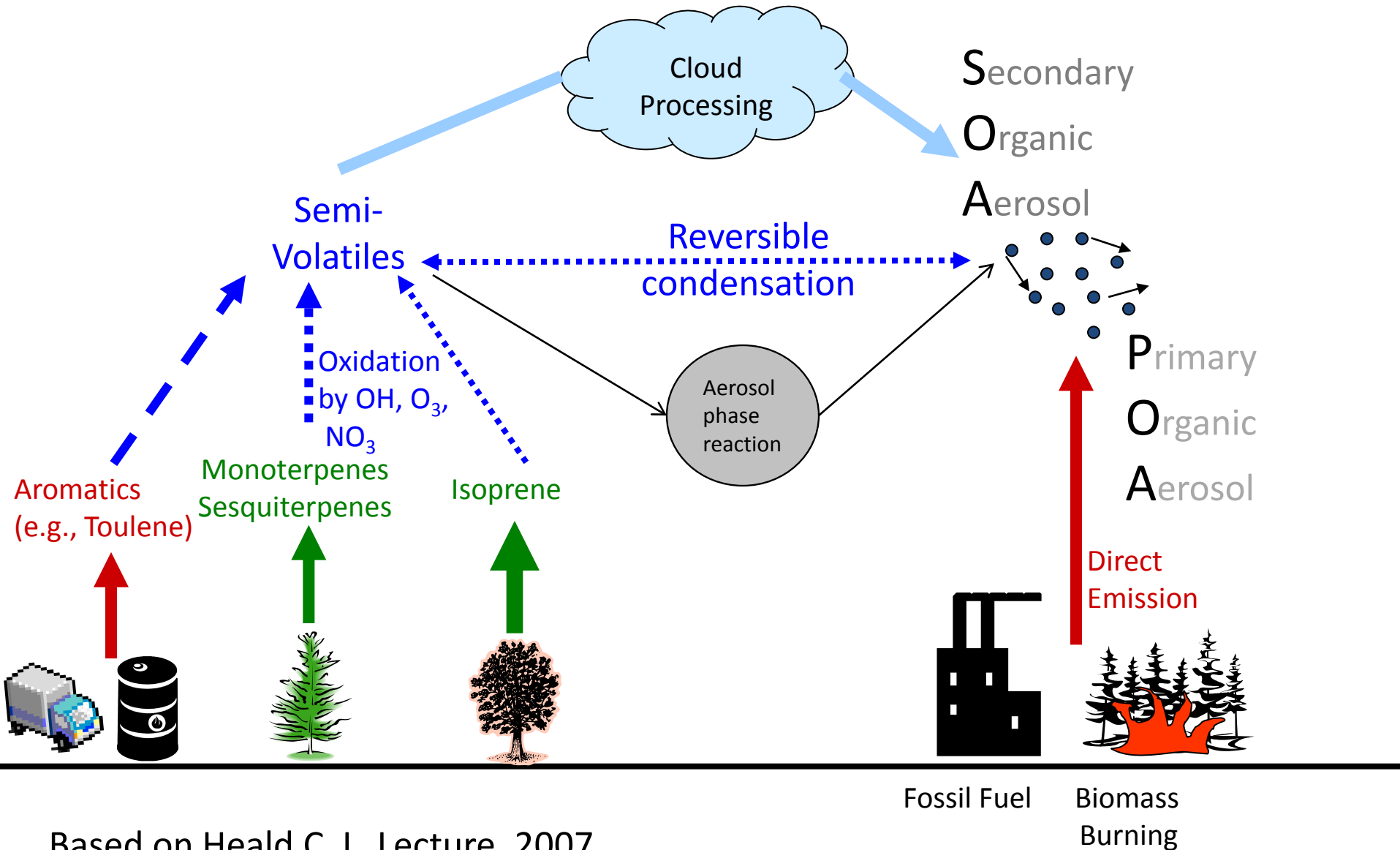
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Outline

- The effect of iron chemistry on SOA formation in cloud
- Radiative forcing of organic aerosol: effect of SOA and brown carbon (BrC)

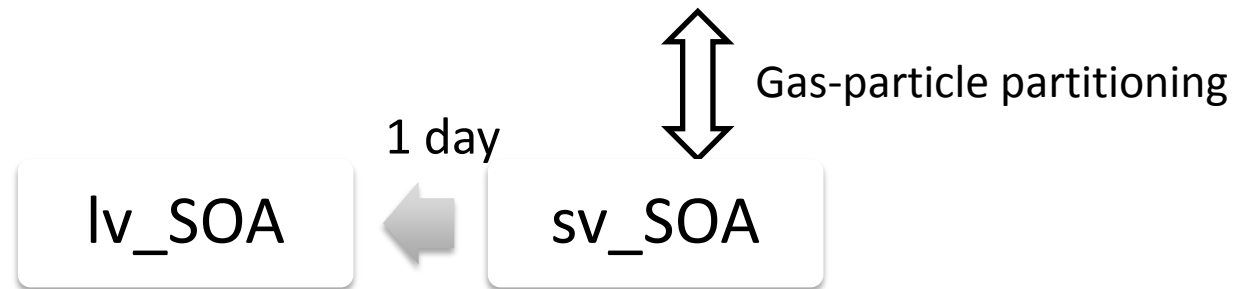
Introduction: How are organic aerosols formed?



Model description

3-D atmospheric chemical transport model (IMPACT)

- Microphysics of sulfate aerosol and the interactions between sulfate and non-sulfate aerosols (Liu et al., 2005).
- SOA formation from gas-particle partitioning of sVOCs (Lin et al., 2012). For example,



- Formation of SOA from reaction of glyoxal and methylglyoxal in cloud droplets and aqueous aerosols (Lin et al., 2013).
- Formation of non-evaporative SOA from epoxides (Lin et al., 2012).

Multiphase reaction scheme to simulate SOA formed in cloud

Representing all processes explicitly:

$$\frac{dC_{aq}}{dt} = R_{aq} + \frac{k_t}{RT} \cdot P_g - \frac{k_t}{HRT} Q \cdot C_{aq}$$

k_t : gas –transfer coefficient

P_g : gas phase partial pressure

Q : aqueous phase diffusion rate limitation factor

$$\frac{dC_g}{dt} = \frac{1}{4} \cdot \gamma \cdot A \langle v \rangle \cdot C_g$$

Oxalic acid is a major component of SOA formed in cloud

isoprene, benzene, toluene

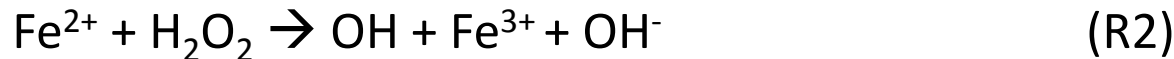
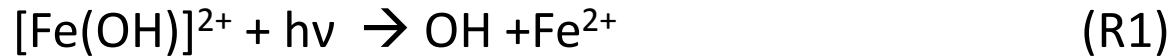
glyoxal, methylglyoxal, OH

organic acids
(glyoxylic acid,
oxalic acid,
pyruvic acid)

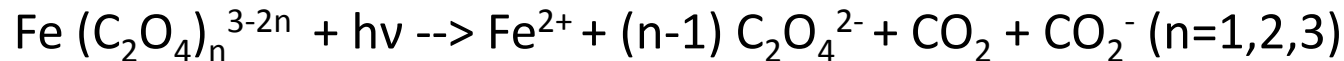
SOA

Iron (Fe) chemistry in cloud

- Contribute to the budget of OH radicals in cloud



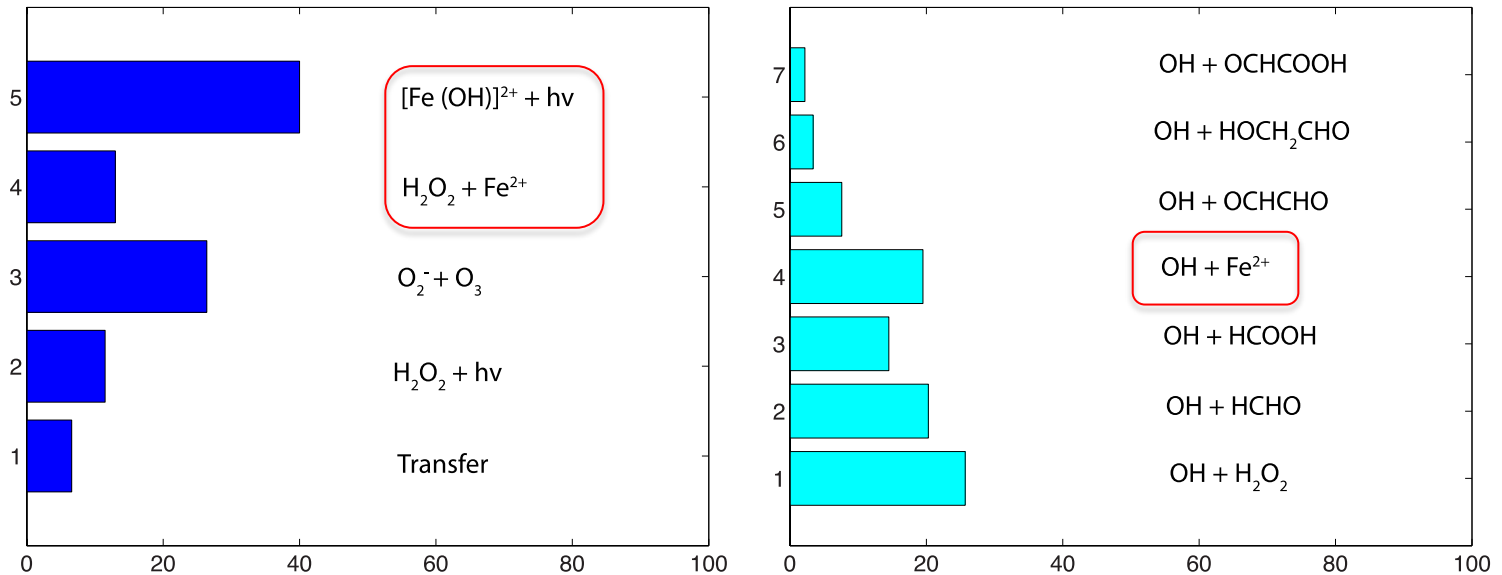
- A sink of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$)/oxalate ($\text{C}_2\text{O}_4^{2-}$)



But no global SOA models has included iron chemistry.

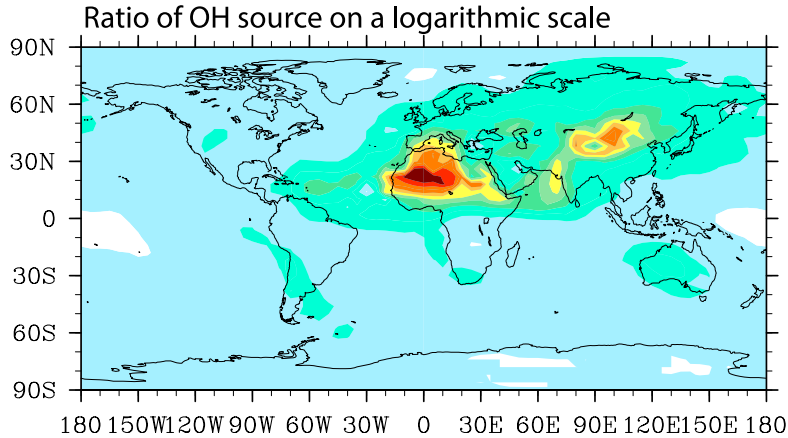
We assumed 3.5% mass of dust aerosol composed of Fe (Taylor and McLennan, 1985), only 5% of which could be dissolved into cloud water (Ito and Xu., 2013).

Predicted global budget of aqueous OH radical

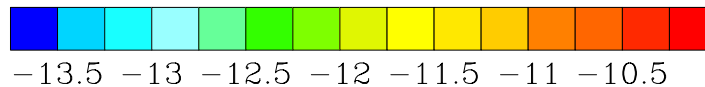
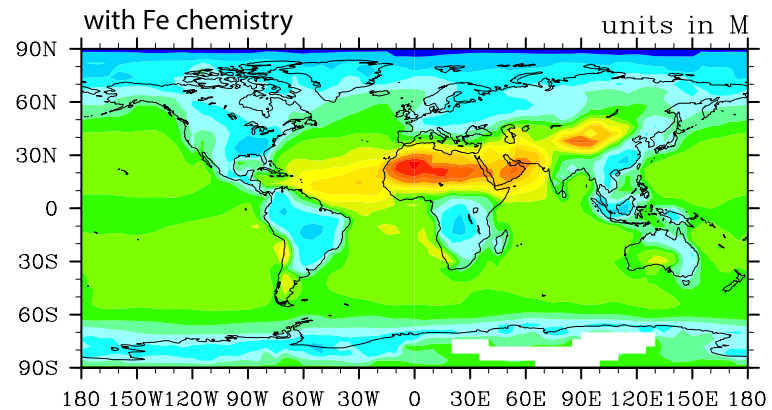
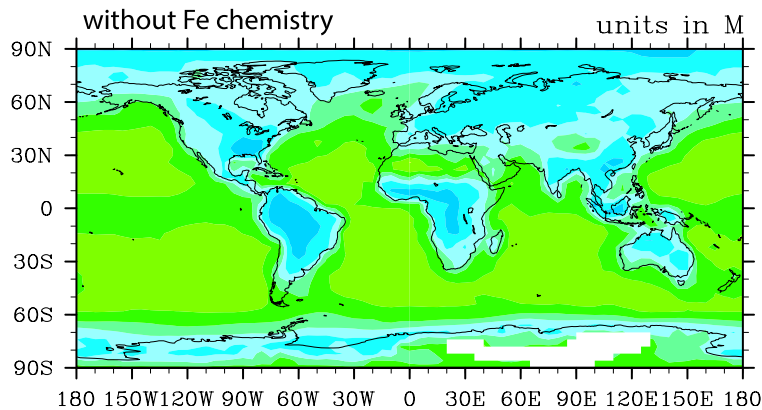


Globally, iron chemistry contribute over 50% of aqueous OH radical sources and over 20% of sinks

Iron chemistry increases the in-cloud OH radical

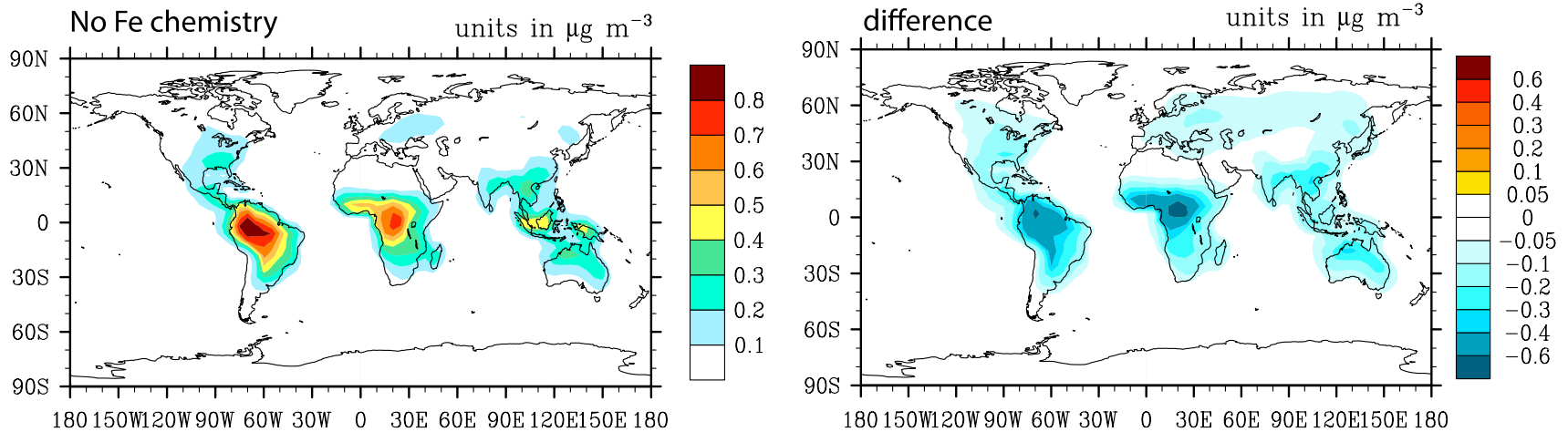


The ratio of annual mean in-cloud OH radical source in simulation with Fe chemistry to that in simulation without Fe chemistry.



Annual mean aqueous OH concentration at 971 hPa (units: mol/L)
Values are on a logarithmic scale.

Dissolved iron chemistry decreases oxalic acid/oxalate



Annual mean oxalate concentration at 971 hPa

Global change in oxalate reaction rates (Tg/yr)

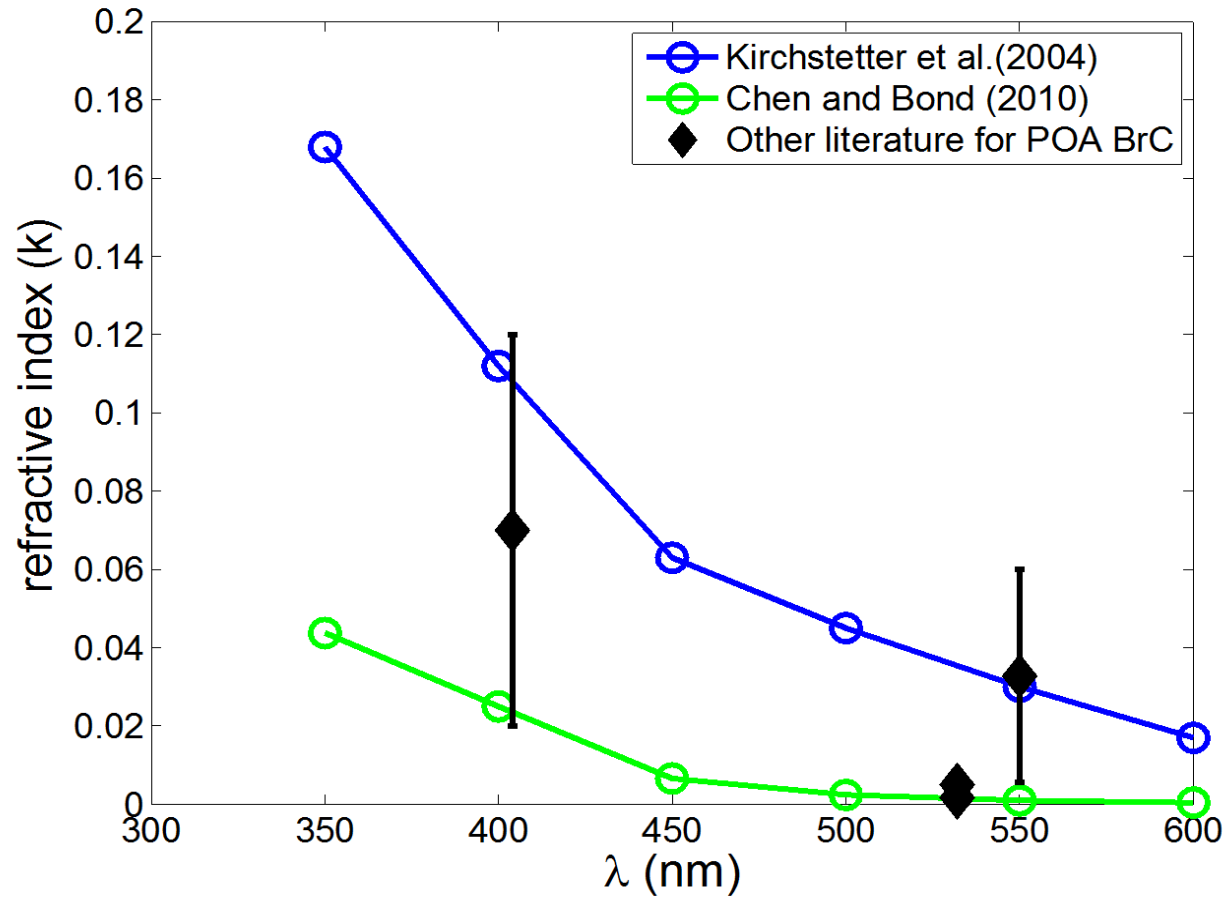
	Chemical production	Chemical destruction	Net production
Simulation without Fe chemistry	22.9	7.2	15.7
Simulation with Fe chemistry	32.2	27.8	4.4

Radiative forcing of OA: effect of SOA and brown carbon

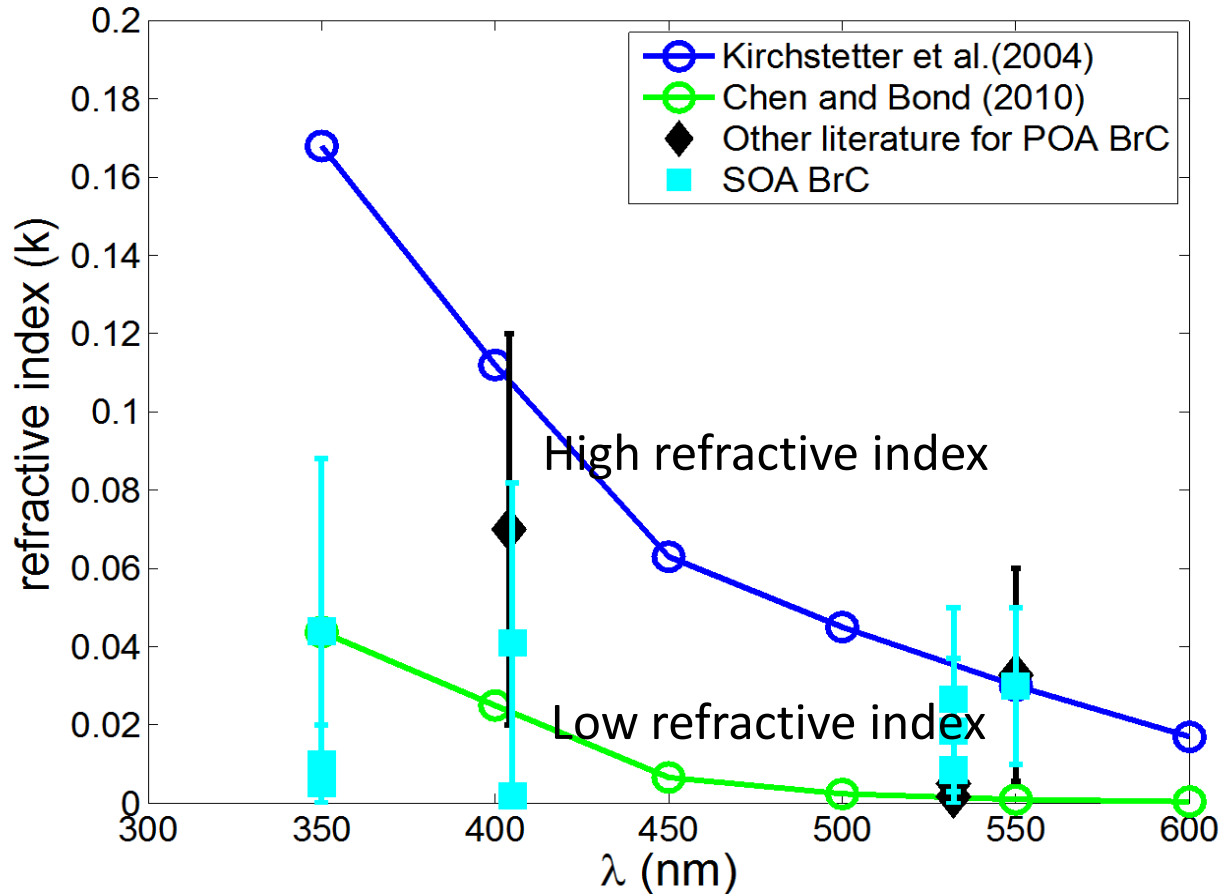
Motivation

- Very few global model SOA forcing estimates exist, although SOA is an important component of aerosol.
- The contribution of BrC absorption to total aerosol absorption could be significant. However, most of existing global models assume OA to be almost purely scattering.

Imaginary part of refractive index for POA BrC



Imaginary part of refractive index for SOA BrC



We use Kirchstetter et al. (2004) and Chen and Bond (2010) as potential limits of the light-absorbing properties of BrC.

Simulation set up

H-ABS (high-absorbing case)

L-ABS (low-absorbing case)

High refractive index

Low refractive index

Biomass burning POA

100% are BrC

Fossil fuel/biofuel POA

only biofuel and residential coal burning
POA can absorb sunlight

H-ABS

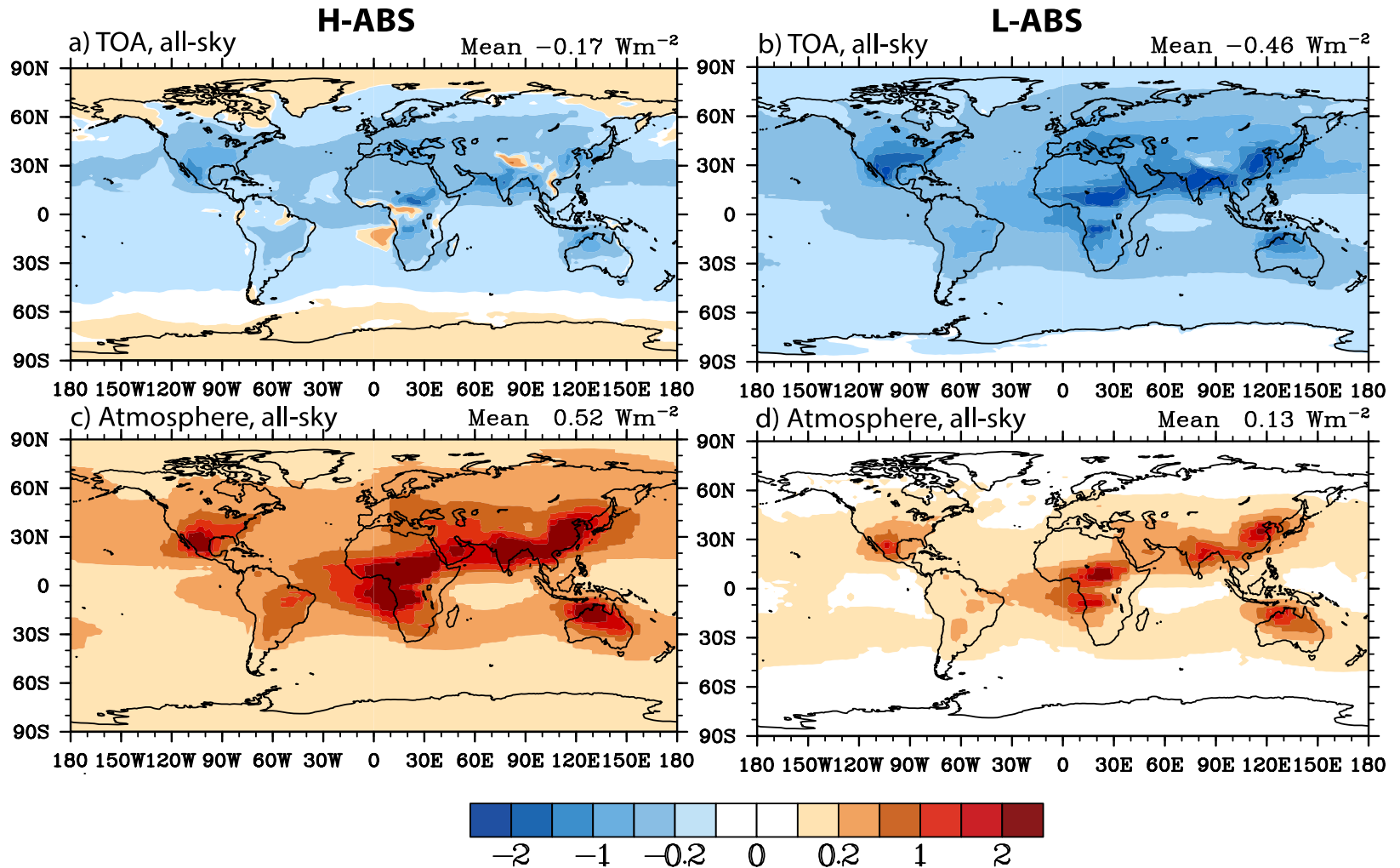
L-ABS

SOA

The same size distribution and BrC
fraction as biomass burning POA

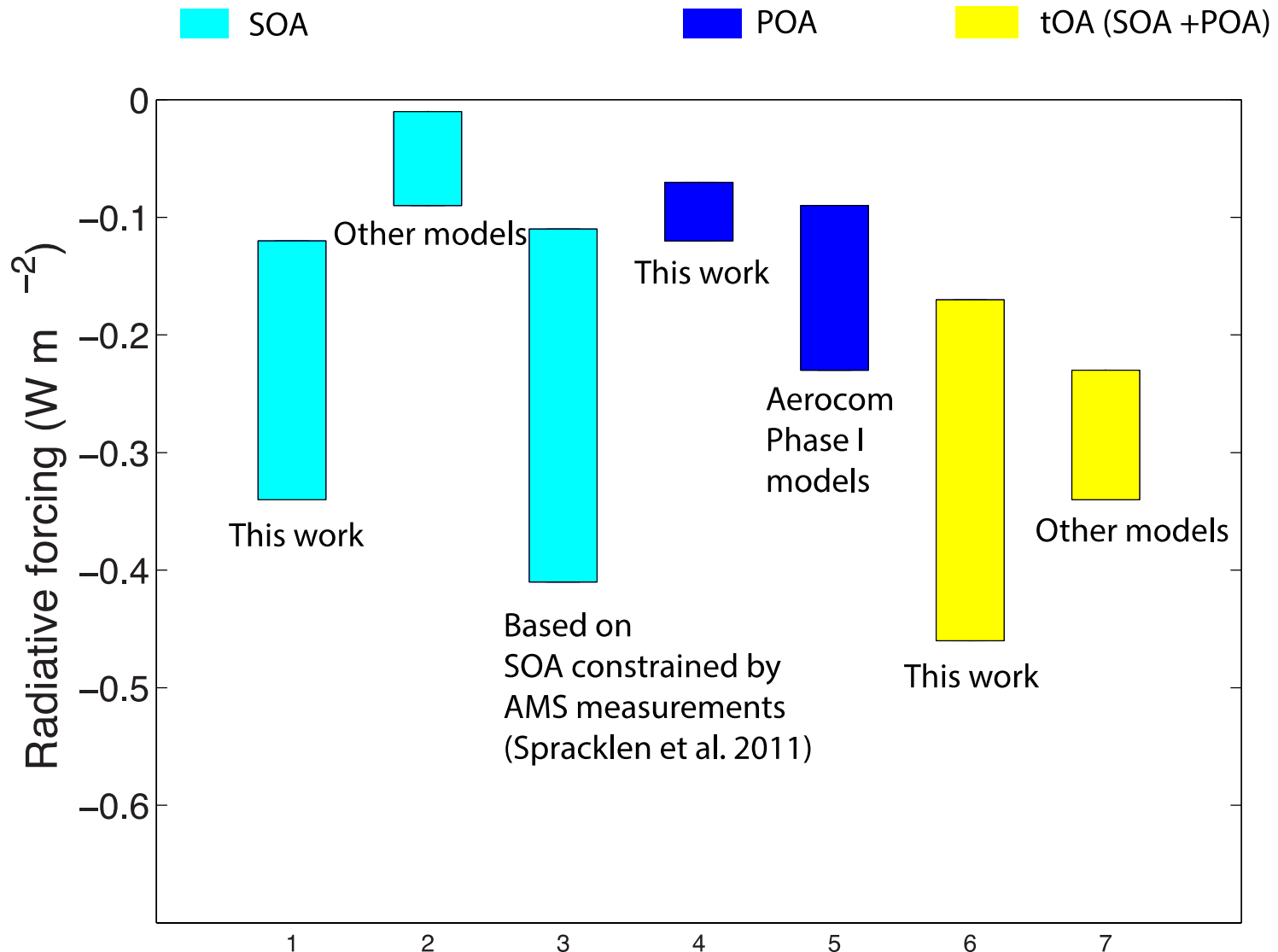
The same size distribution
and BrC fraction as fossil
fuel/biofuel POA

Direct radiative forcing of total OA (SOA+ POA)



BrC absorption: 14%~57% of BC absorption predicted in the model

Compare range of forcing to that estimated by others



Conclusion

- The inclusion of iron chemistry increases the aqueous OH radicals and decreases the oxalate concentration.
- The radiative forcing of SOA is predicted to range from -0.12 to -0.34 W m^{-2} .
- BrC leads to an atmospheric absorption of from 0.13 to 0.52 W m^{-2} .
- A large uncertainty of OA forcing associated with BrC and SOA.

Sources of brown carbon

Source of brown carbon

Primary source

Biomass and biofuel burning (Kirschstetter et al., 2004; Chen and Bond, 2010; Saleh et al., 2013).

Residential coal burning (Bond et al., 1999; Arola et al., 2011)

Secondary source

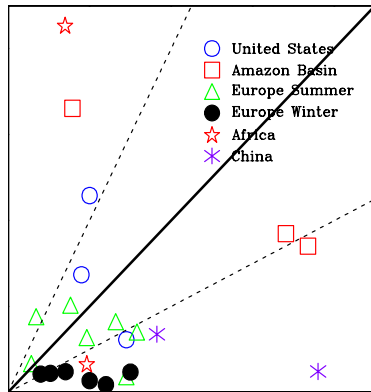
Formed in heterogeneous reactions from dienes (Limbeck et al., 2003)

generated from the photooxidation of α -pinene and toluene in the presence of NO_x (Jaoui et al., 2008)

Formed from the aqueous phase reactions involving glyoxal and methyglyoxal (Shapiro et al., 2009).

Other mechanisms

Comparison of Oxalate and OH



Marine

OH radicals in remote continental clouds

Arakaki et al.(2013)

North America

Measured average: $7.2\text{E-}15$ mol/L

Simulation

With Fe chemistry: $7.5\text{E-}14$

No Fe chemistry: $7.4\text{E-}14$

Global mean AAOD at 550 nm

Chung et al. (2012)	BC AAOD: 0.0077 (0.006 ~ 0.009) OM AAOD: 0.0018 (0.001 ~ 0.003)
Bond et al.(2013)	BC AAOD: 0.00605
This work	BC+OM AAOD 0.003000 (H-ABS) BC+OM AAOD 0.00224 0(L-ABS)

SOA from gas-particle partitioning

- Basic photochemistry of O_3 , OH, NO_x and VOCs (Ito et al., 2007)
- Epoxide formation from isoprene (Paulot et al., 2009)
- HO_x regeneration through isoprene oxidation proposed by Peeters et al. (2009) but with a recycled rate reduced by a factor of 10.

Select species that form SOA based on criteria from *Griffin et al. (2002)*.

Species vapor pressures estimated as in *Myrdal and Yalkowsky (1997)* with modifications from *Camredon and Aumont (2006)*.