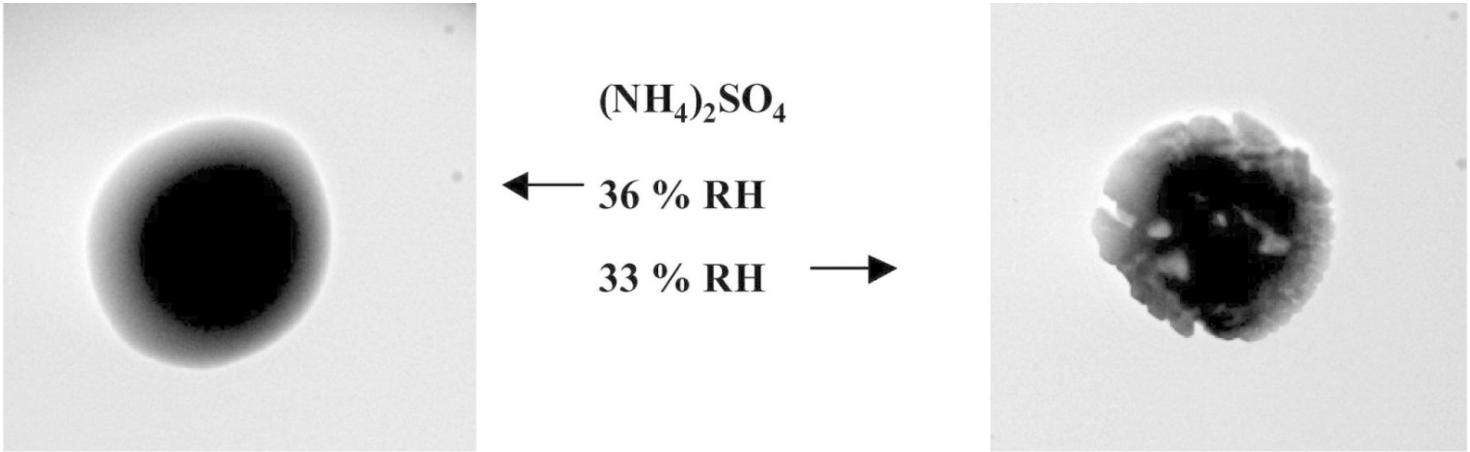

$(NH_4)_2SO_4$

← 36 % RH

33 % RH →

Sulfate Phase Transition in GEOS-Chem

University of Nebraska Lincoln

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University of Nebraska – Lincoln

NASA

Harvard University Atmospheric Chemistry Modeling Group

Scot Martin, Harvard; Daniel Jacob, Harvard;
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George Mason University

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Global distribution of solid and aqueous sulfate aerosols: Effect of the hysteresis of particle phase transitions

Jun Wang,[1,2] Andrew A. Hoffmann,[1] Rokjin J. Park,[1,3] Daniel J. Jacob,[1]
and Scot T. Martin[1]

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Sensitivity of sulfate direct climate forcing to the hysteresis of particle phase transitions

Jun Wang,[1,2] Daniel J. Jacob,[1] and Scot T. Martin[1]

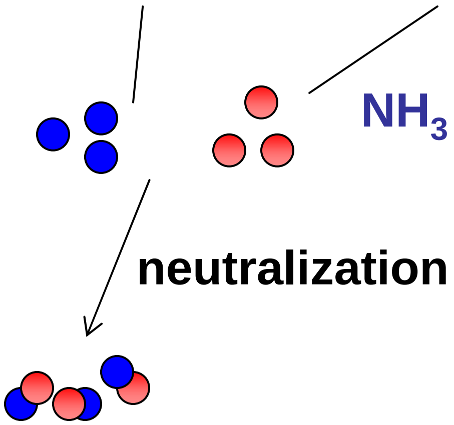
Received 9 September 2007; revised 5 February 2008; accepted 3 March 2008; published 10 June 2008.

FORMATION OF SULFATE PARTICLES

oxidization

$SO_2 \rightarrow H_2SO_4$

Industry



NH_3

neutralization

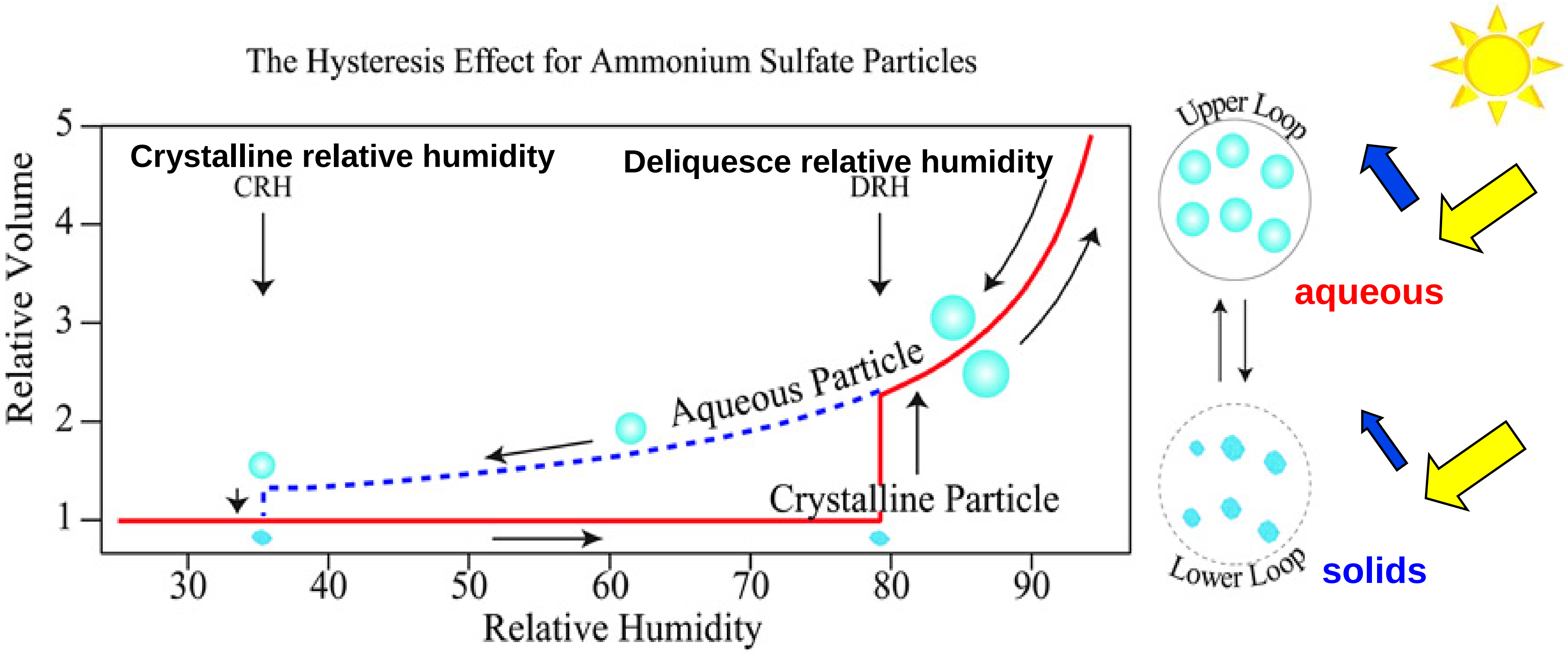
Sulfate Particle

Agriculture

Sulfate particles generally include pure sulfate acid particles (H_2SO_4) and those fully or partially neutralized sulfate particles such as $(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3HSO_4$.

THE HYSTERESIS OF SULFATE PHASE TRANSITION

Aerosol phase transition → Aerosol direct forcing on climate?



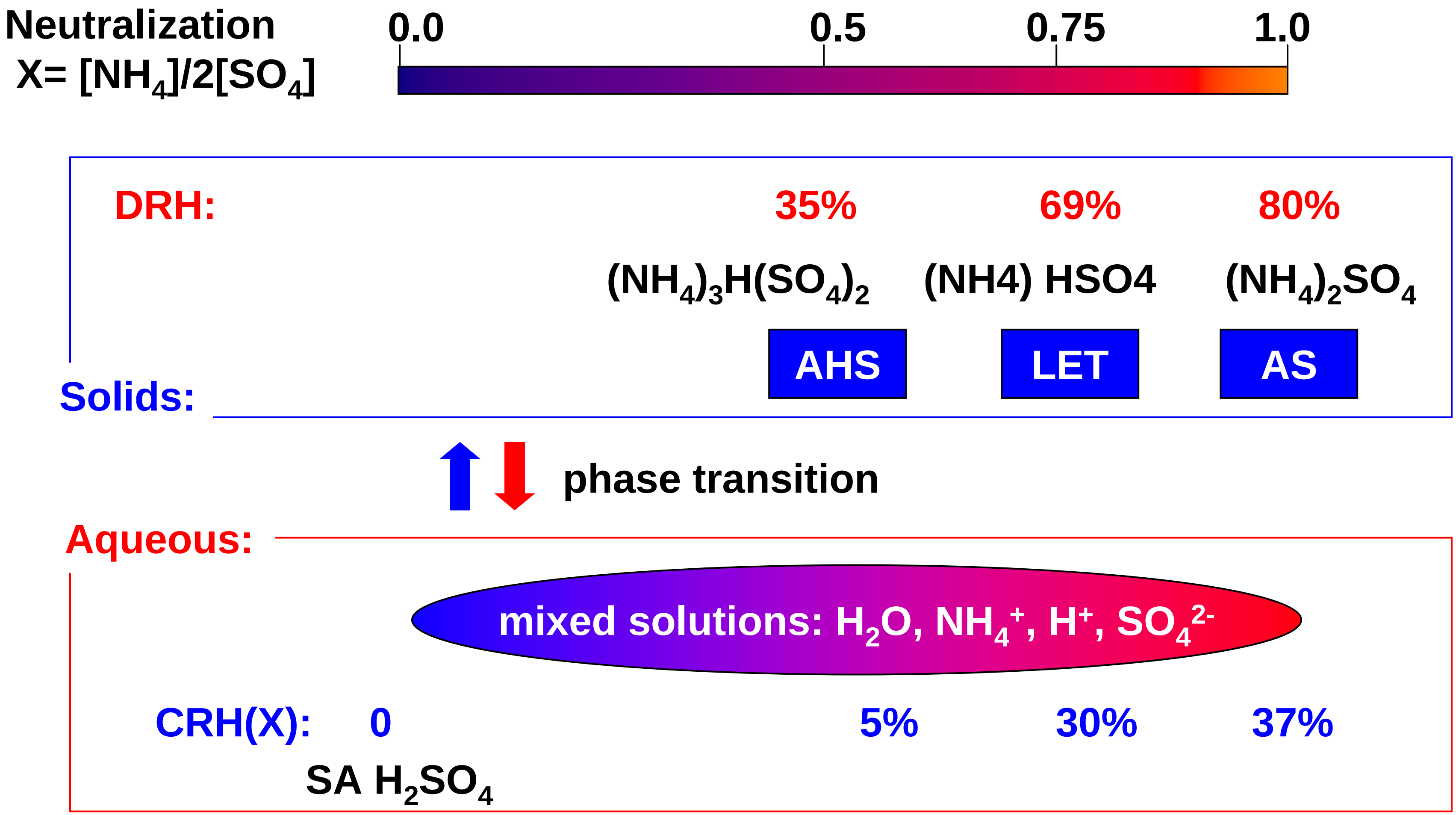
To predict the phase transition requires:

(a) Current phase (RH back-trajectory) → which curve ?

(b) RH in current and next model time step → which direction?

(c) CRH(X) & DRH(X) → phase changes?

SULFATE PHASE, CRH, AND DRH



Neutralization
$X = [NH_4]/2[SO_4]$

0.0 0.5 0.75 1.0

DRH: 35% 69% 80%

$(NH_4)_3H(SO_4)_2$ (NH4) HSO4 $(NH_4)_2SO_4$

AHS LET AS

Solids:

phase transition

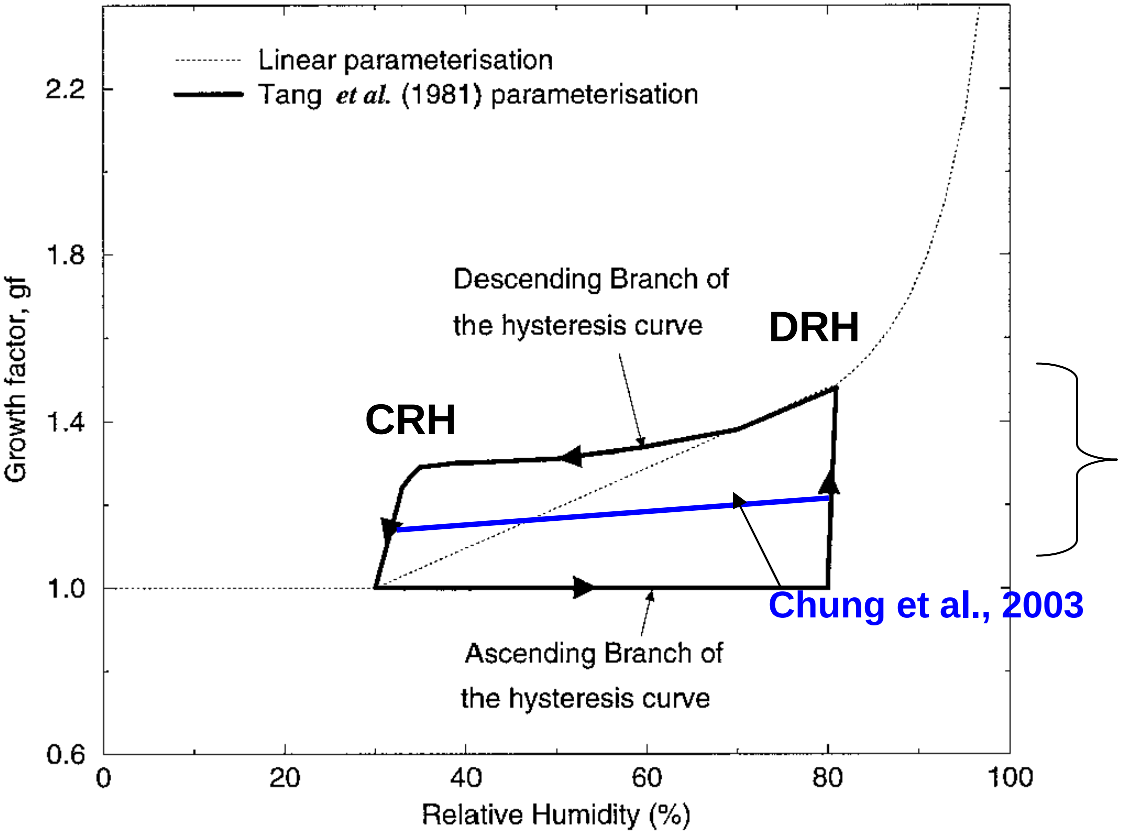
Aqueous:

mixed solutions: H_2O, NH_4^+, H^+, SO_4^{2-}

CRH(X): 0 5% 30% 37%

SA H_2SO_4

HYSTERESIS EFFECT IN PREVIOUS CTMS



Limiting case studies

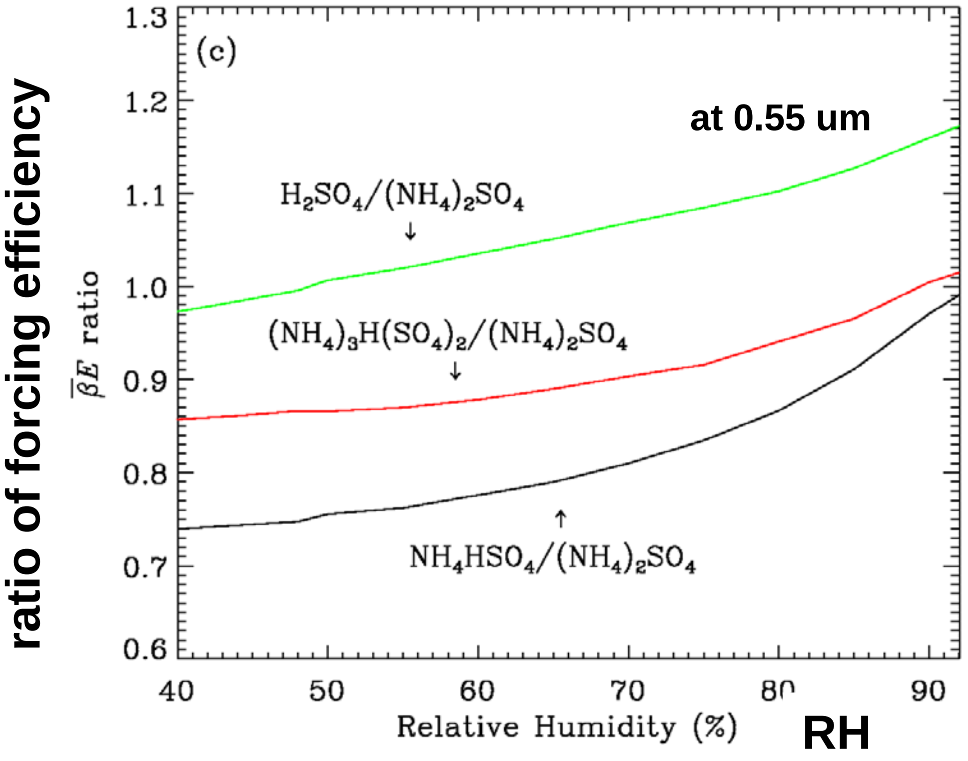
ΔF:

18%, Haywood et al., 1997

24%, Martin et al., 2004

A full consideration of the hysteresis effect has not been made in the past estimate of sulfate climate forcing.

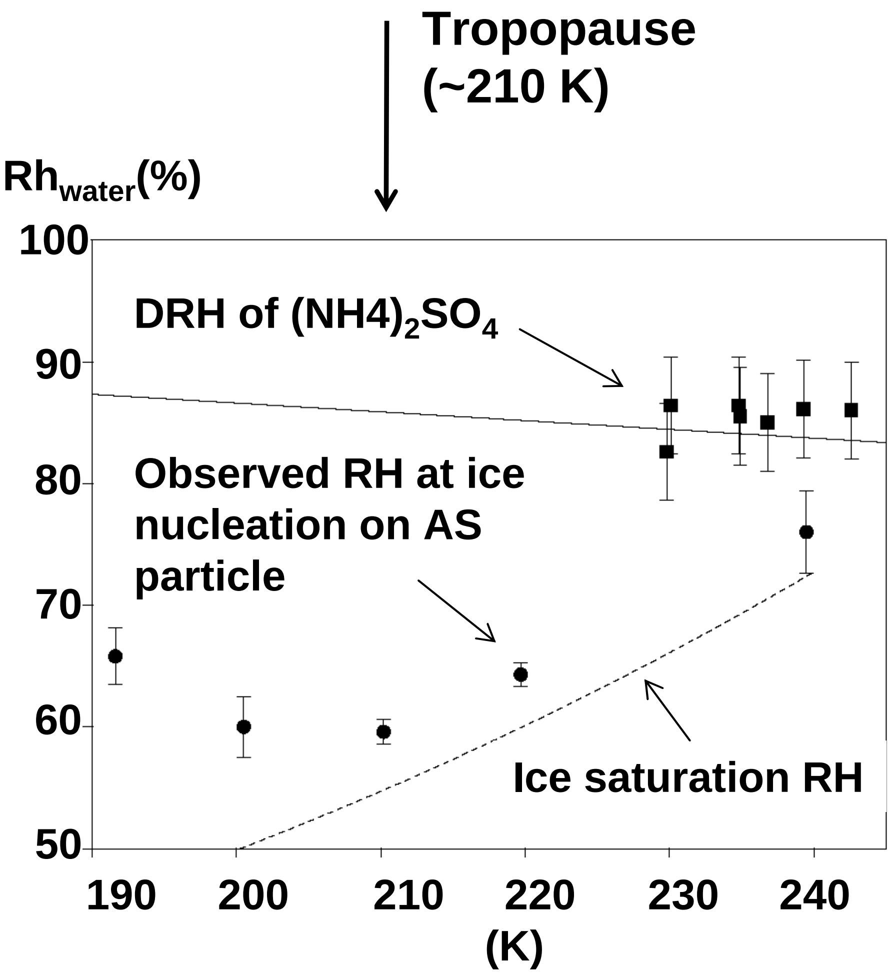
IMPACT OF SULFATE COMPOSITION ON THE FORCING EFFICIENCY OF SULFATE PARTICLES



At the same RH > 40%, sulfate particle composition can result in 20-30% differences in forcing efficiency (per unit mass burden).

Forcing efficiency = mass extinction efficiency (m^2/g) × daytime-averaged backscattering fraction.
Refractive index and hygroscopic growth from Tang et al (1996); lognormal distribution of dry particles rg=0.07um, sigmag=1.8.

LAB EVIDENCE FOR DEPOSITION NUCLEATION OF ICE ON SOLID AMMONIUM SULFATE



Shilling et al., 2006, Depositional ice nucleation on crystalline organic and inorganic solids, JGR, 2006.

Solid Ammonium Sulfate Aerosols as Ice Nuclei: A Pathway for Cirrus Cloud Formation

J. P. D. Abbatt,[1*] S. Benz,[2] D. J. Cziczo,[3] Z. Kanji,[1] U. Lohmann,[3] O. Möhler[2]

22 SEPTEMBER 2006 VOL 313 SCIENCE

Table 1. Global annual mean shortwave, longwave, and net cloud forcing (difference between all-sky and clear-sky conditions) at the top of the atmosphere; ice water path; and vertically integrated ice crystal number concentration for the different model simulations. HOM: only homogeneous freezing; DU1 and DU10: heterogeneous freezing whenever the dust ice nuclei concentration exceeds 1 cm^{-3} or 0.1 cm^{-3}, respectively, and homogeneous freezing otherwise; AS1, AS10, and AS100: same categorization as DU1, but instead of dust, 1, 10, or 100% of the $(NH_4)_2SO_4$ concentration, respectively, serve as ice nuclei once the $(NH_4)_2SO_4$ number concentration exceeds 1 cm^{-3}.

	HOM	DU1	DU10	AS1	AS10	AS100
Shortwave cloud forcing (W m^{-2})	–48.2	–48.3	–47.0	–47.7	–47.7	–47.3
Longwave cloud forcing (W m^{-2})	29.5	29.3	25.8	29.0	28.7	28.4
Net cloud forcing (W m^{-2})	–18.7	–19.0	–21.2	–18.7	–19.0	–18.9
Ice water path (g m^{-2})	22.3	21.7	14.1	21.2	20.3	19.4
Ice crystal number (10^6 cm^{-2})	1.01	0.925	0.521	0.789	0.716	0.650

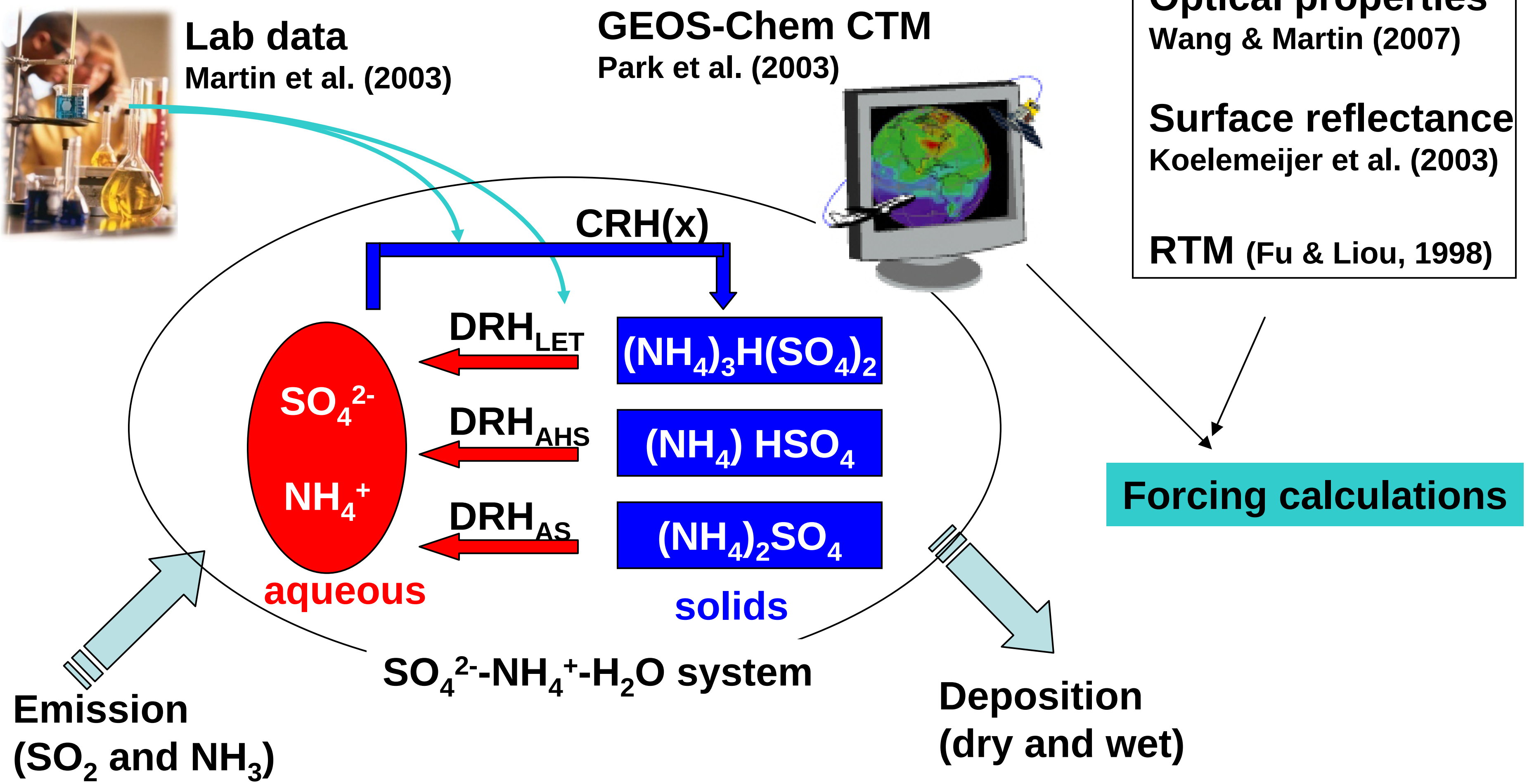
– (0 - 0.3) Wm^{-2}

Counteract ~20% of CO_2 forcing

One-sentence summary:

Knowledge of 4D distribution of the composition and **phase** of sulfate particles is needed to improve the estimate of anthorogogeic sulfate direct and indirect forcing.

APPROACH



Larger X, larger CRH

Lab data
Martin et al. (2003)

GEOS-Chem CTM
Park et al. (2003)

Optical properties
Wang & Martin (2007)

Surface reflectance
Koelemeijer et al. (2003)

RTM (Fu & Liou, 1998)

CRH(x)

DRH_{LET}

DRH_{AHS}

DRH_{AS}

SO_4^{2-}

NH_4^+

aqueous

$(NH_4)_3H(SO_4)_2$

$(NH_4)\ HSO_4$

$(NH_4)_2SO_4$

solids

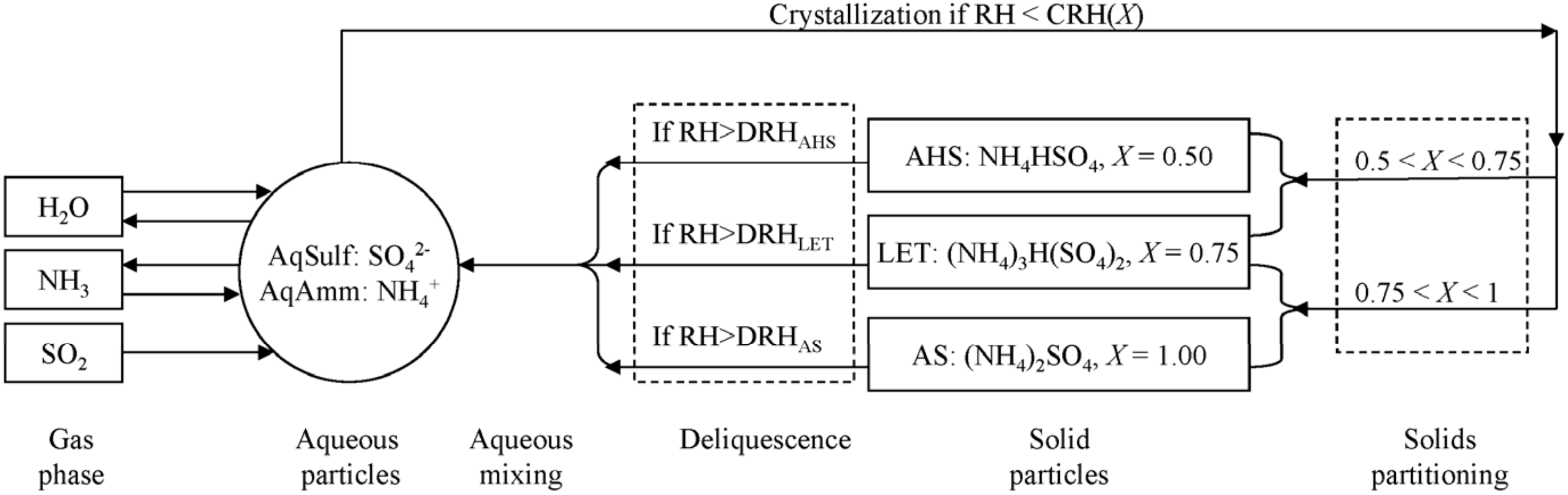
SO_4^{2-}-NH_4^+-H_2O system

Emission
(SO_2 and NH_3)

Deposition
(dry and wet)

Forcing calculations

SULFATE PHASE TRANSITION SCHEME: DETAILS



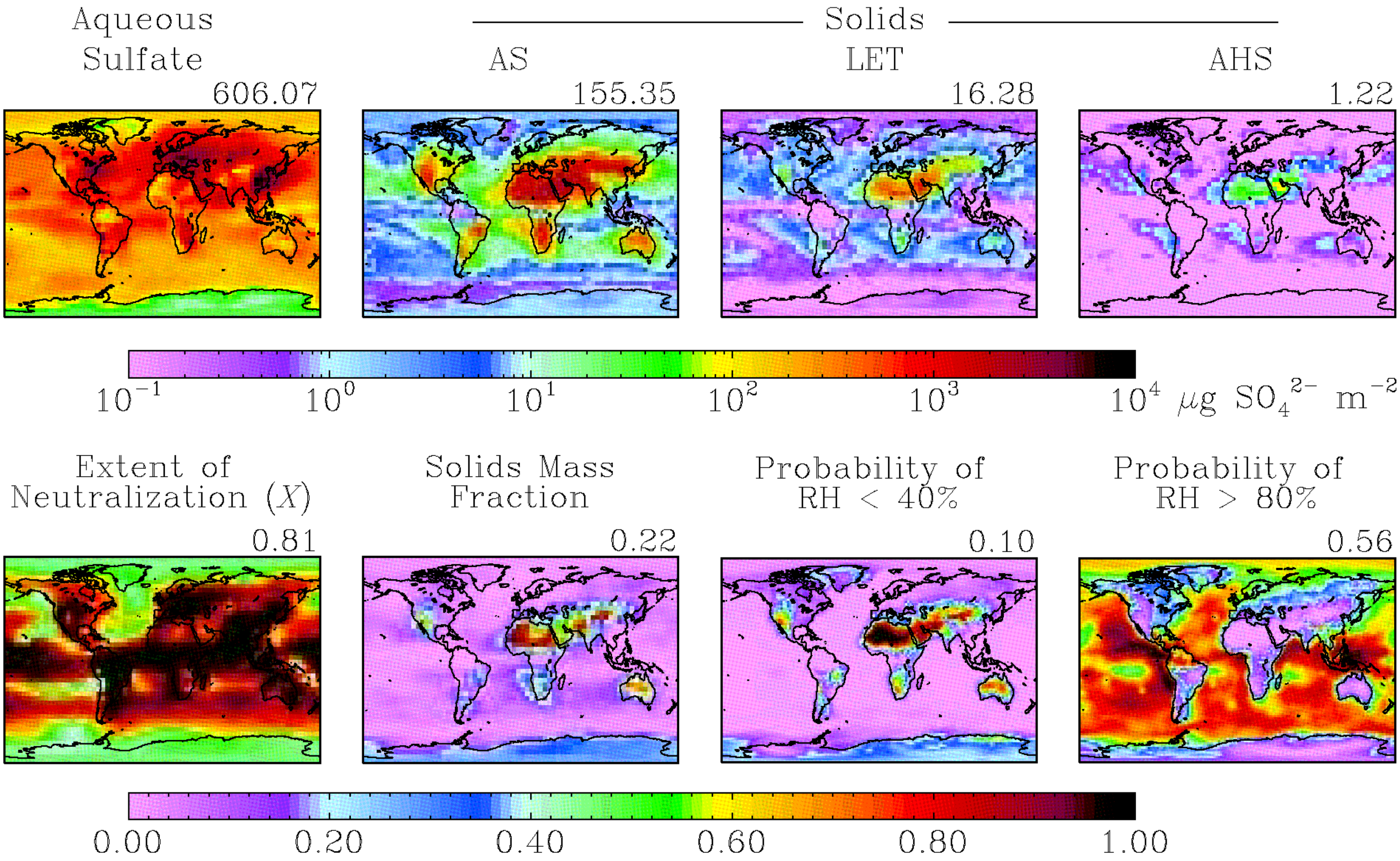
Parameterization of CRH of sulfate particles (from Martin et al., 2003, GRL):

$$CRH_0(X) = -71925 + 1690X - 139X^2 + \frac{1770760}{25 + 0.5(X - 0.7)}$$

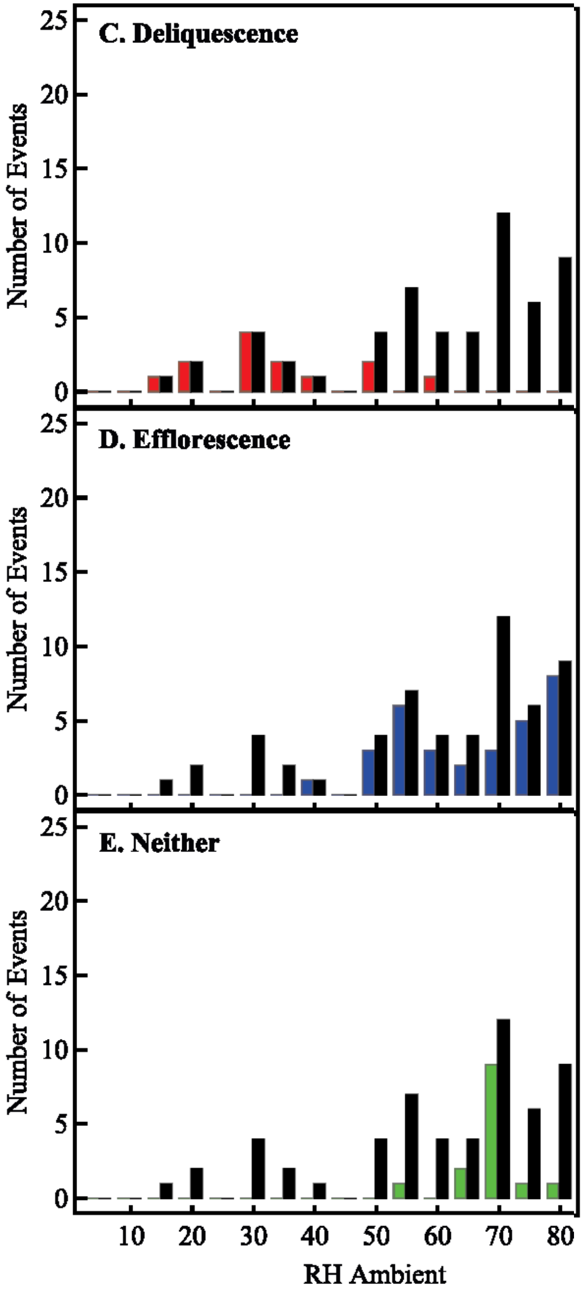
$$CRH_0(X) = 0$$

ANNUAL AVERAGES IN BOUNDARY LAYER

Burden (natural + anthropogenic)



Phase transition measured in SGP site



Legend

● Deliquescence
● Both deliq and effl
● Efflorescence
● No transitions observed

Black: total number of events

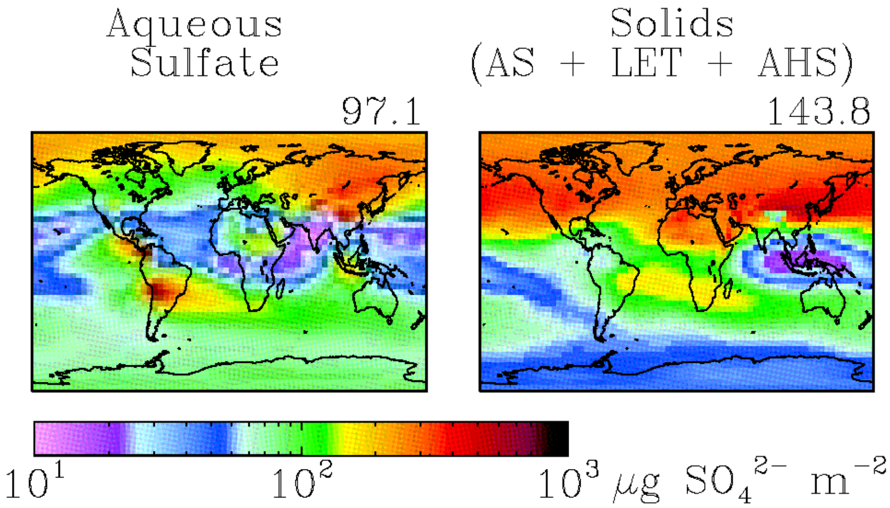
In 101 runs in June 2007, efflorescence occurred 72% of the time for particles sampled at ambient RH. Deliquescence occurred in 13% of the runs.

Martin et al., 2008, GRL.

ANNUAL AVERAGES IN UPPER TROPOSPHERE

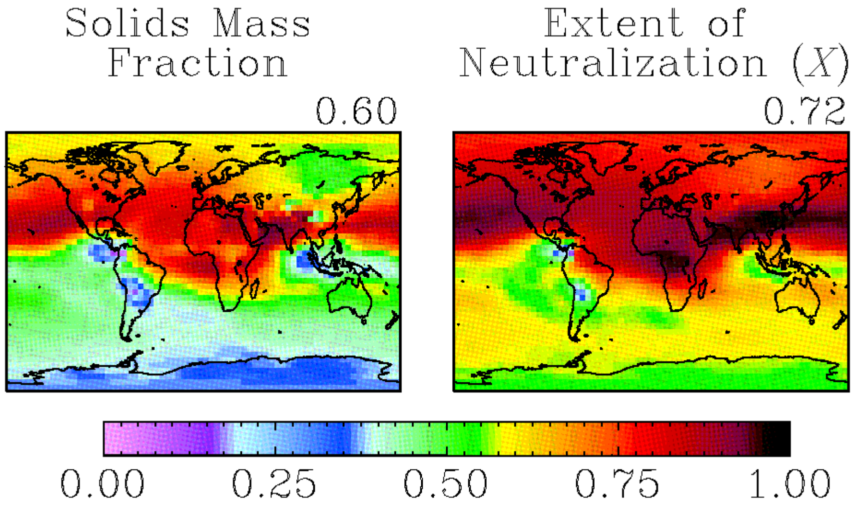
(above 500 mb)

Burden (natural + anthropogenic)



Aqueous Sulfate 97.1

Solids (AS + LET + AHS) 143.8



Solids Mass Fraction 0.60

Extent of Neutralization (X) 0.72

CONSISTENCY & DISCREPANCIES WITH PAST STUDIES

[NH_4] / [SO_4]

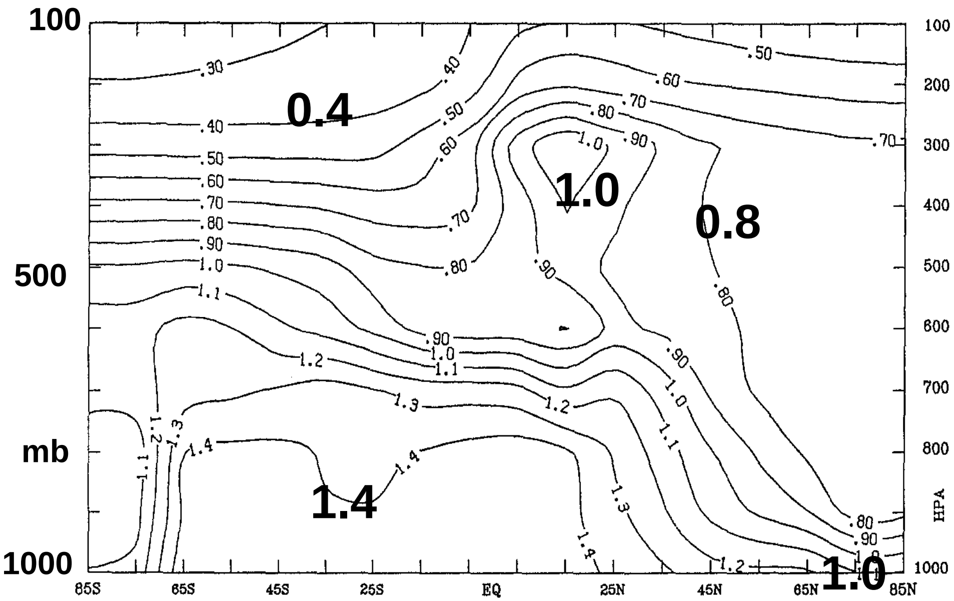


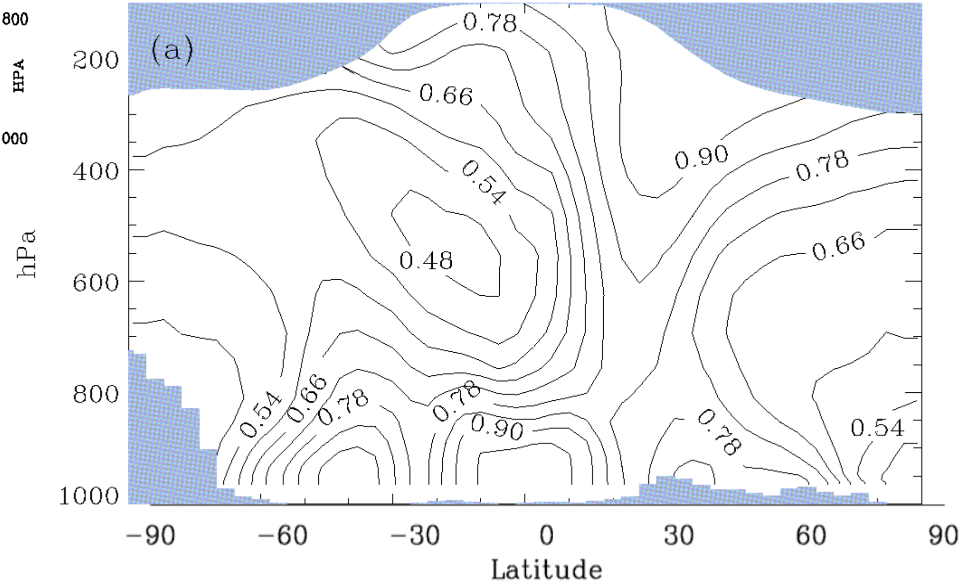
Fig. 4b.

(grids: 18 X 36 X 10)

Dentener and Crutzen, 1994.

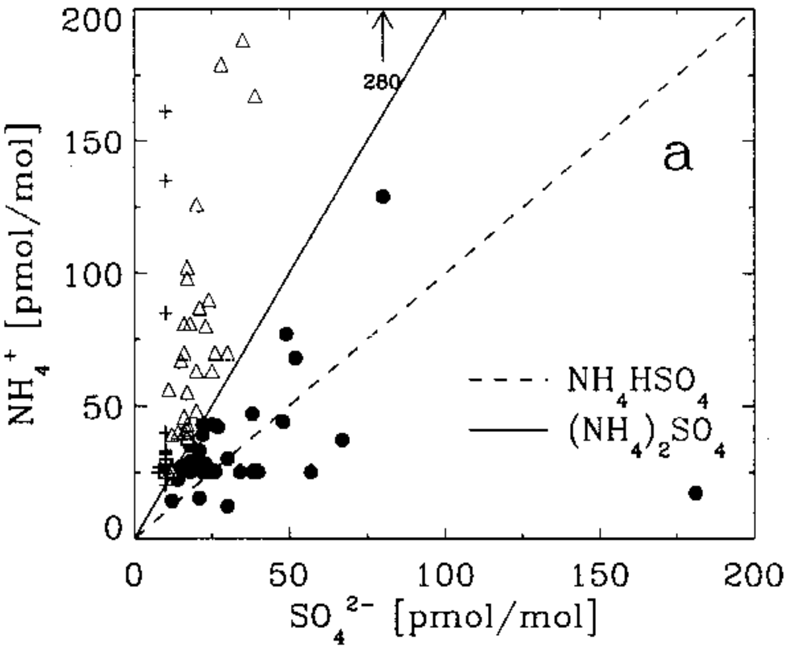
Our simulation is against the traditional view that sulfate should be less neutralized in upper troposphere due to efficient scavenging of NH_3.

X = [NH_4] / [SO_4] / 2



(grids: 46 X 72 X 30)

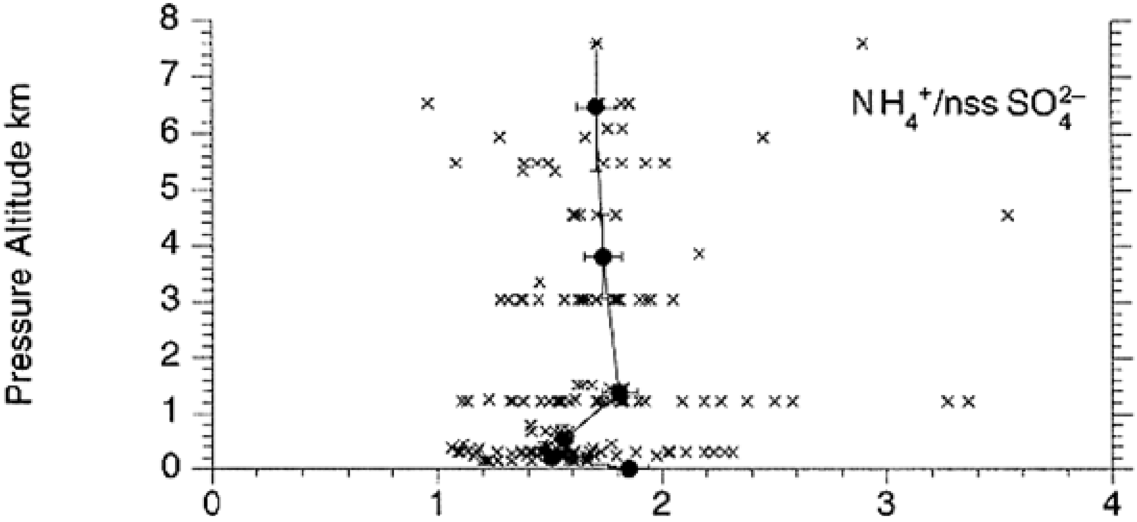
OBSERVATION DATA (S-Hemisphere)



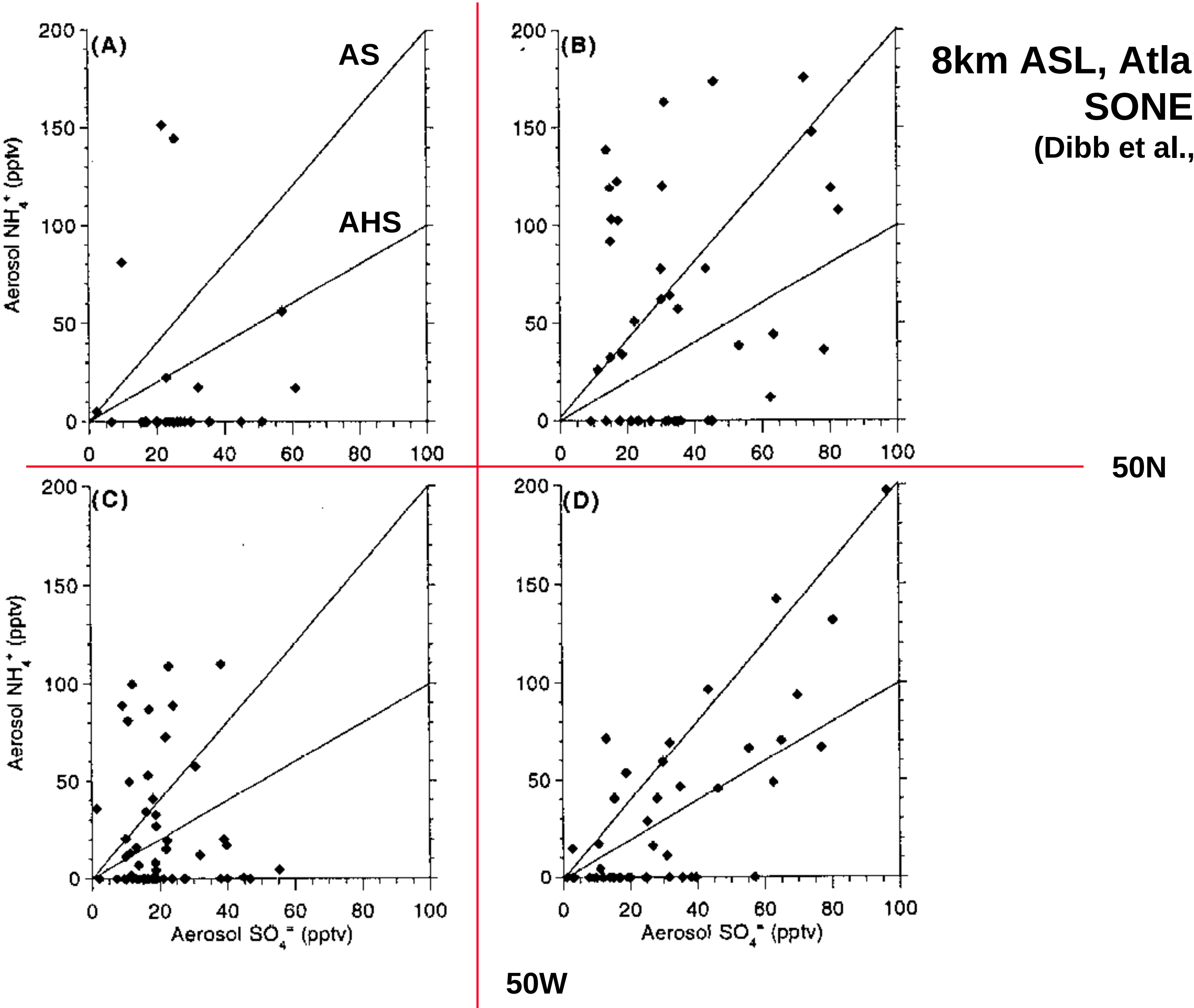
6-12km, southern Pacific
PEM-Tropics A
(Schultz et al., 2000)

NASA ER2, 65,000 feet (~20km) ASL

PEM-Tropics B
(Dibb et al., 2003)

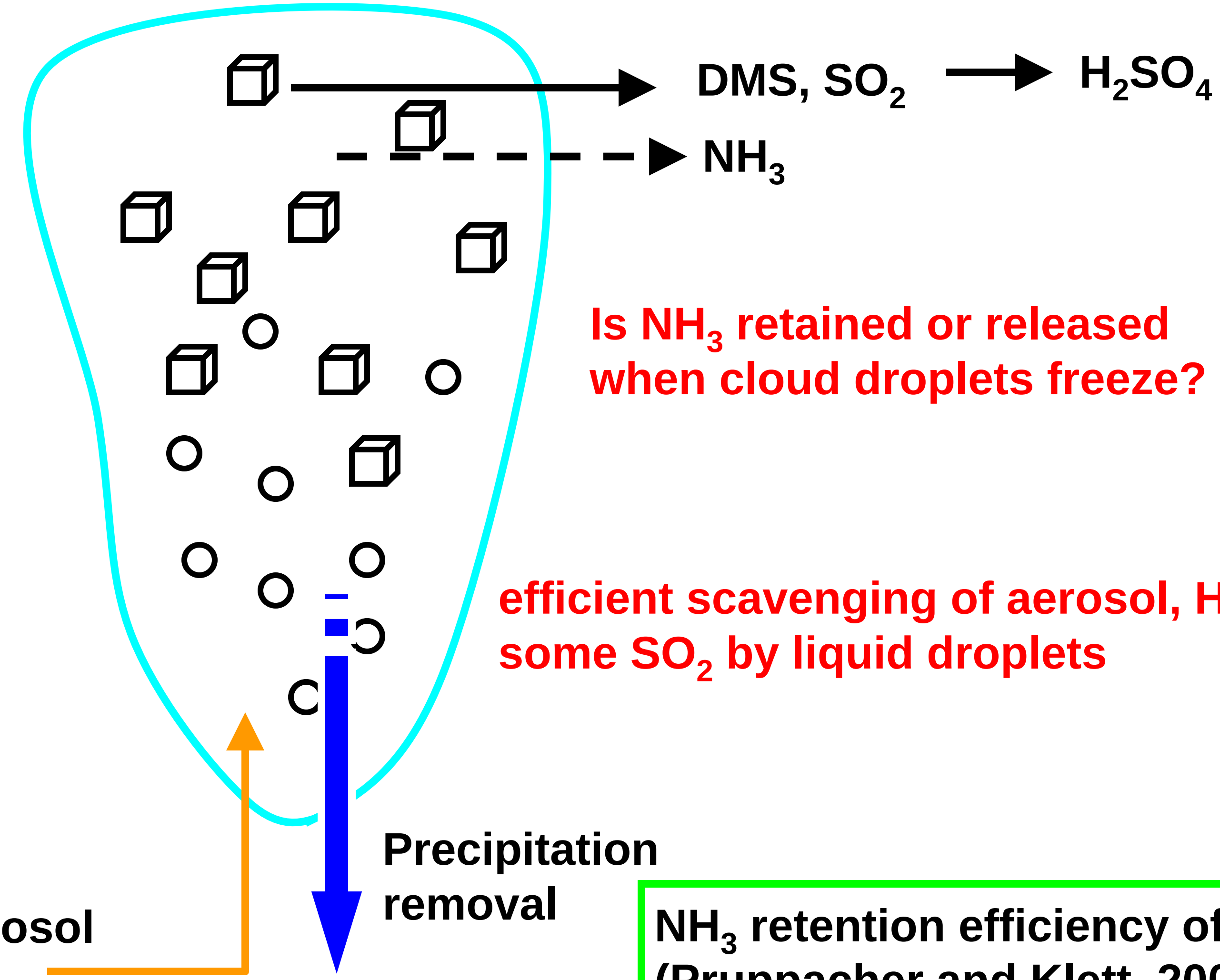


OBSERVATIONAL EVIDENCE (N-Hemisphere)



8km ASL, Atlantic ocean
SONEX
(Dibb et al., 2000)

EXPLAINING PERSISTENT OBSERVATIONS OF NEUTRALIZED SULFATE IN UPPER TROPOSPHERE



DMS, SO_2 → H_2SO_4

NH_3

Is NH_3 retained or released when cloud droplets freeze?

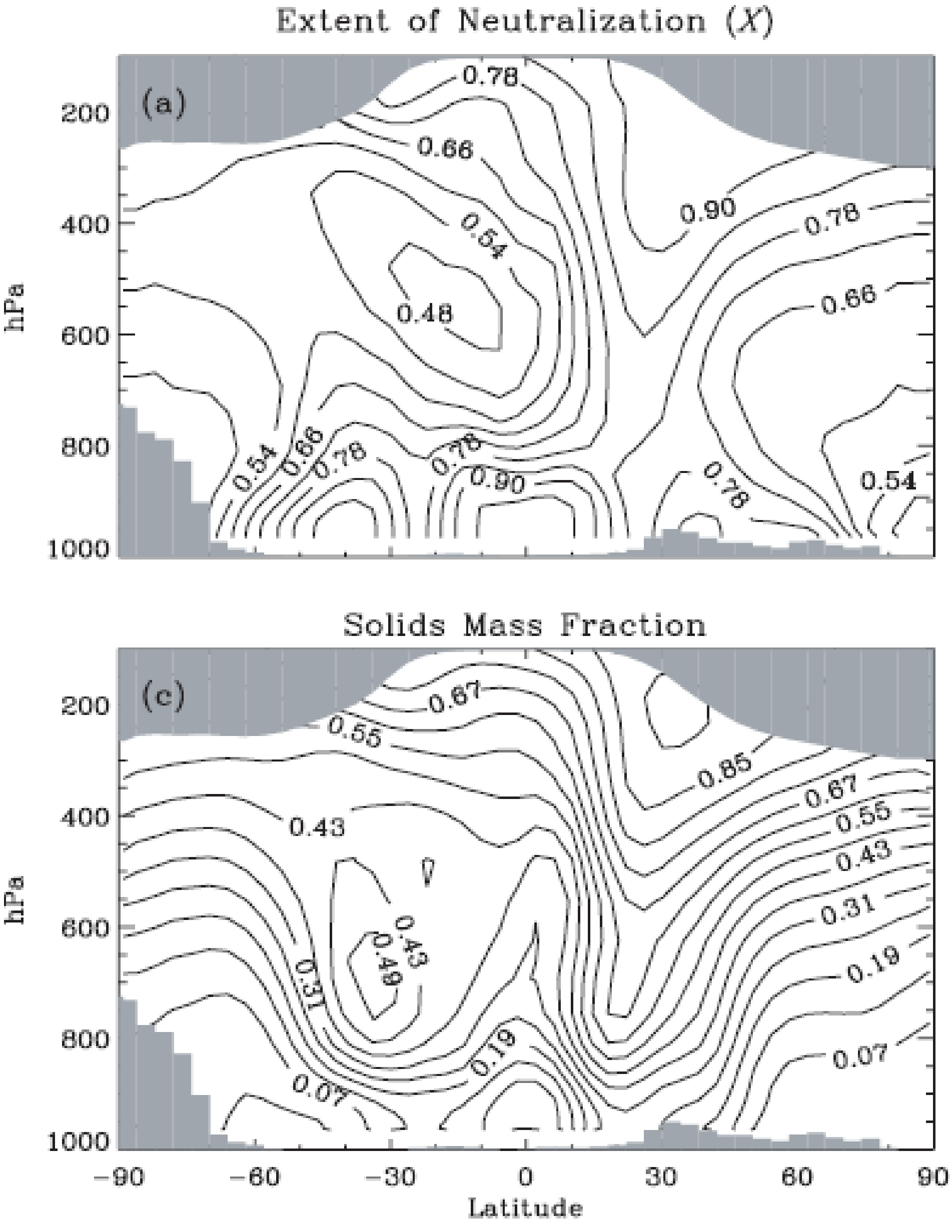
efficient scavenging of aerosol, HNO_3, NH_3, some SO_2 by liquid droplets

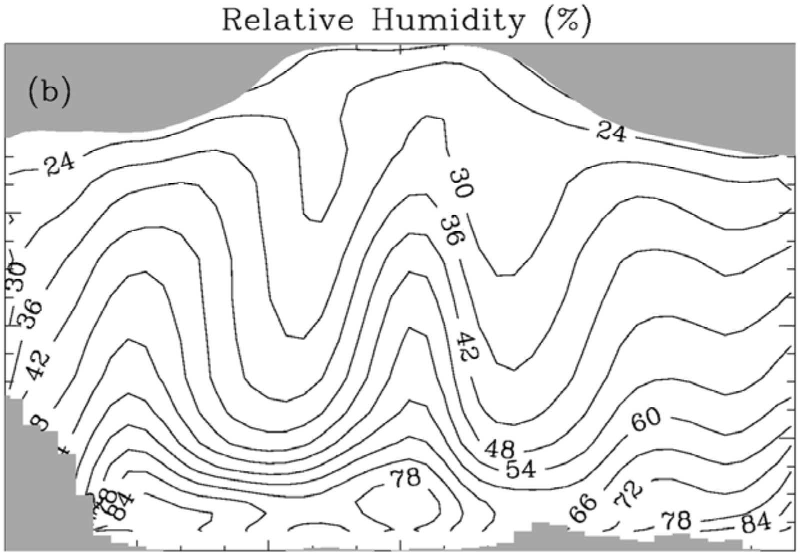
DMS, SO_2
Sulfate aerosol
NH_3
HNO_3

Precipitation removal

NH_3 retention efficiency of 10^{-4}-10^{-2} (Pruppacher and Klett, 2003), would allow efficient release of NH_3 to neutralize upper tropospheric aerosol

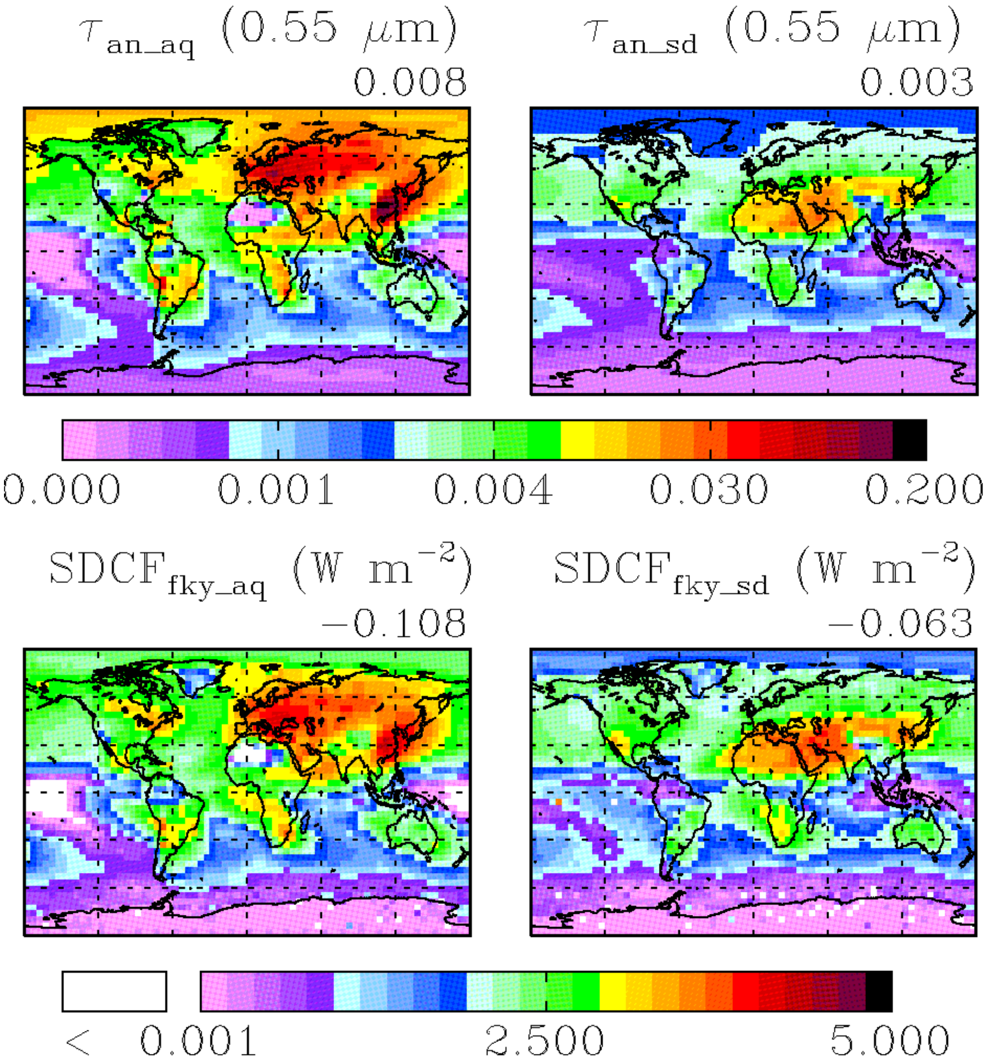
SIMULATED IMPACT OF SULFATE NEUTRALIZATION (X) AND SULFATE PHASE

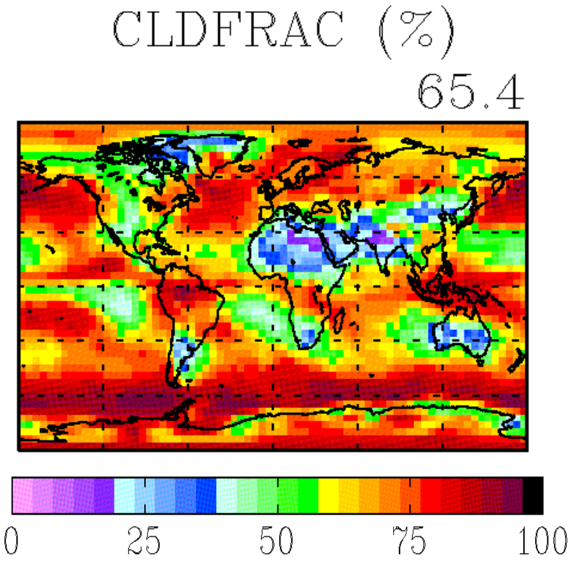




Upper tropospheric sulfate is mostly neutralized and solid! Implications for atmospheric chemistry, cirrus formation…

ANTHROPOGENIC SULFATE AOT & DIRECT FORCING



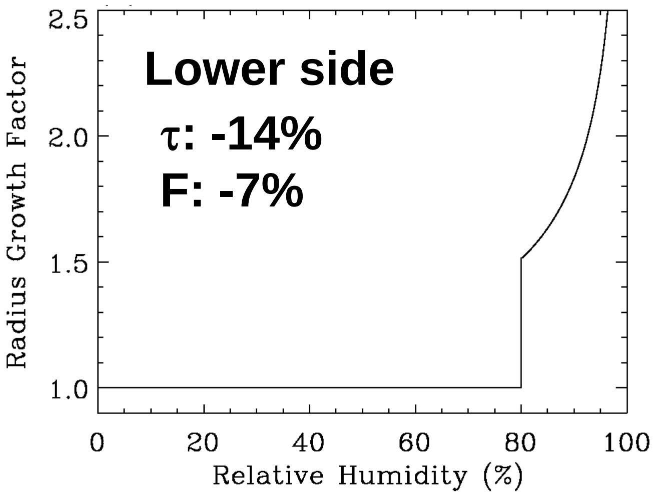


Sulfate forcing: -0.17 Wm^{-2}
CO_2 warming: 1.6 Wm^{-2}

Solids: 41% in burden, 26% in optical thickness, 37% in full-sky forcing; negative correlation between solids fraction and cloud fraction solids sulfate forcing.

SENSITIVITY ANALYSIS TO THE HYSTERESIS EFFECT

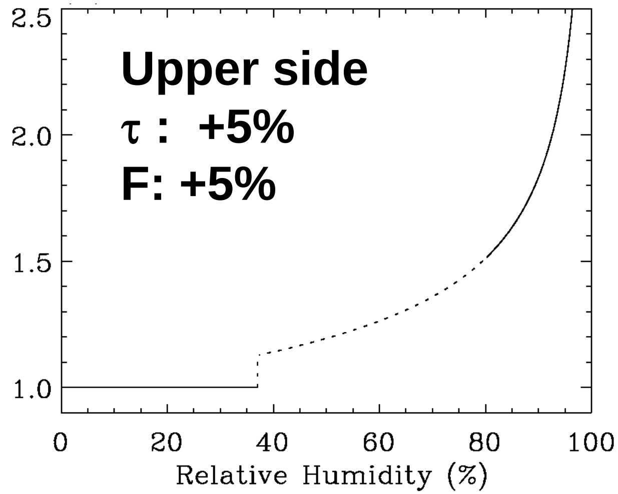
(compared to the base case; anthropogenic component only)



Lower side

τ: -14%

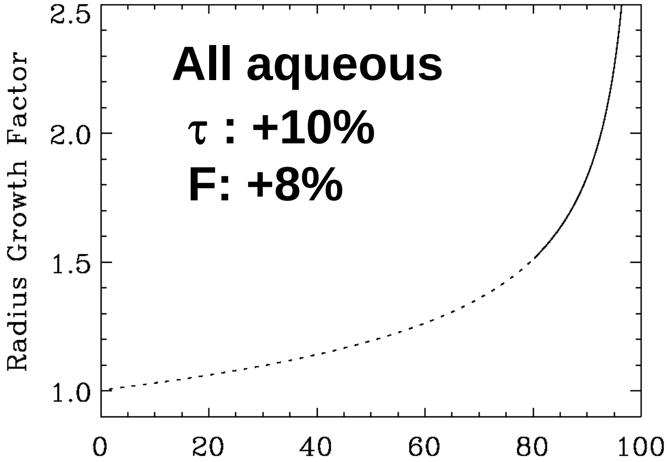
F: -7%



Upper side

τ : +5%

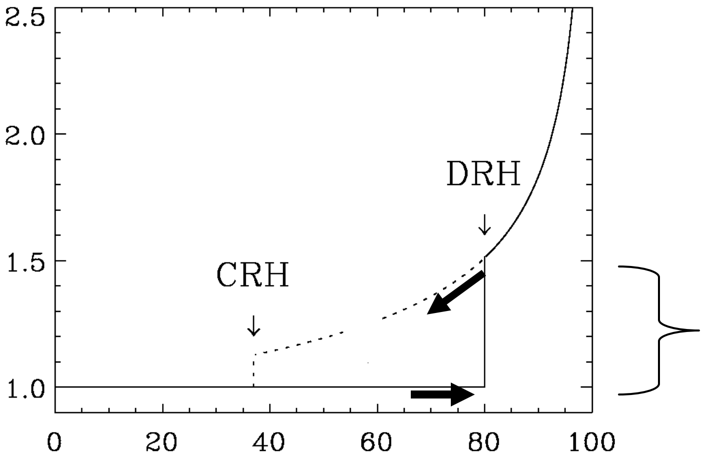
F: +5%



All aqueous

τ : +10%

F: +8%

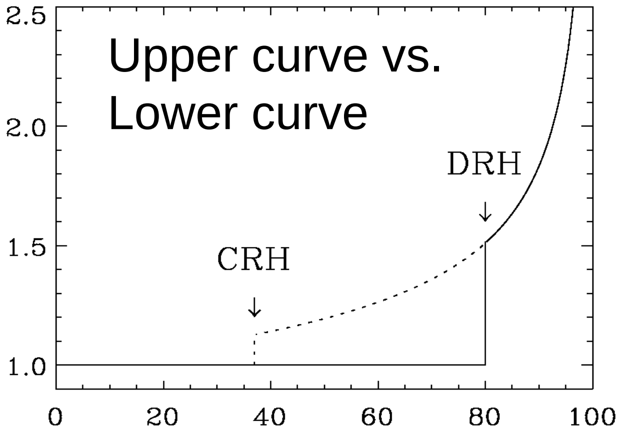


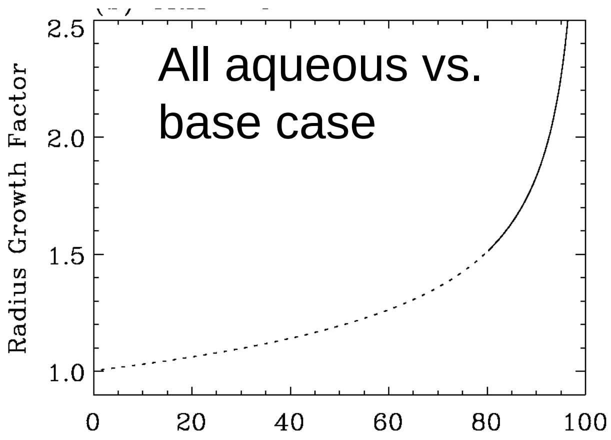
Δτ : 19%

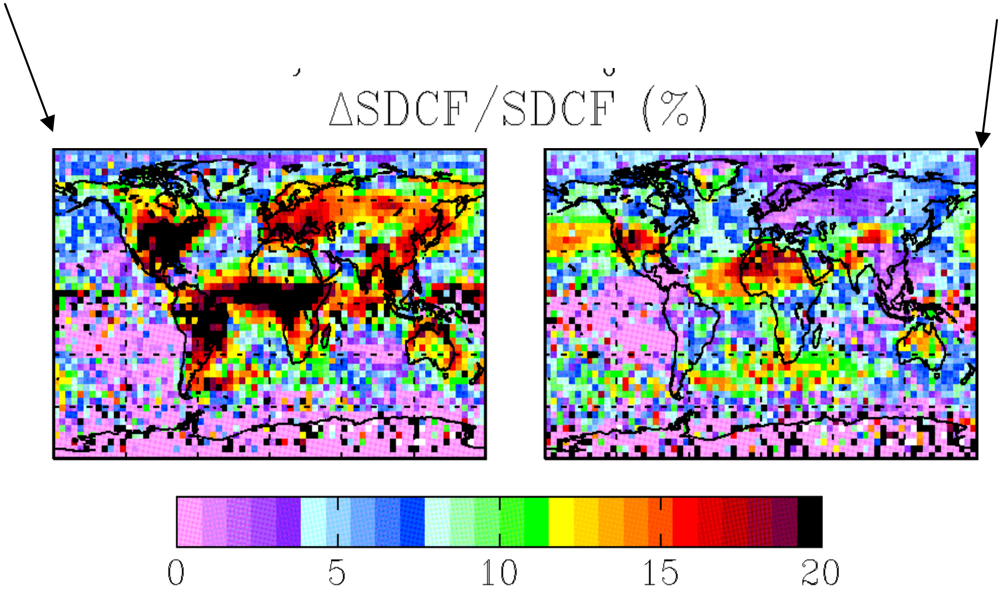
ΔF: 12%

“lower side” and “upper side” difference

FORCING DIFFERENCE DUE TO HYSTERESIS IN DIFFERENT REGIONS


Upper curve vs.
Lower curve


All aqueous vs.
base case



Regional difference due to hysteresis can be as large as ~20%. Those are systematical biases.

Summary

- The dominance of solids in the upper troposphere arises in part from high sulfate neutralization, reflecting in our simulation a low retention efficiency of NH_3 upon cloud freezing.

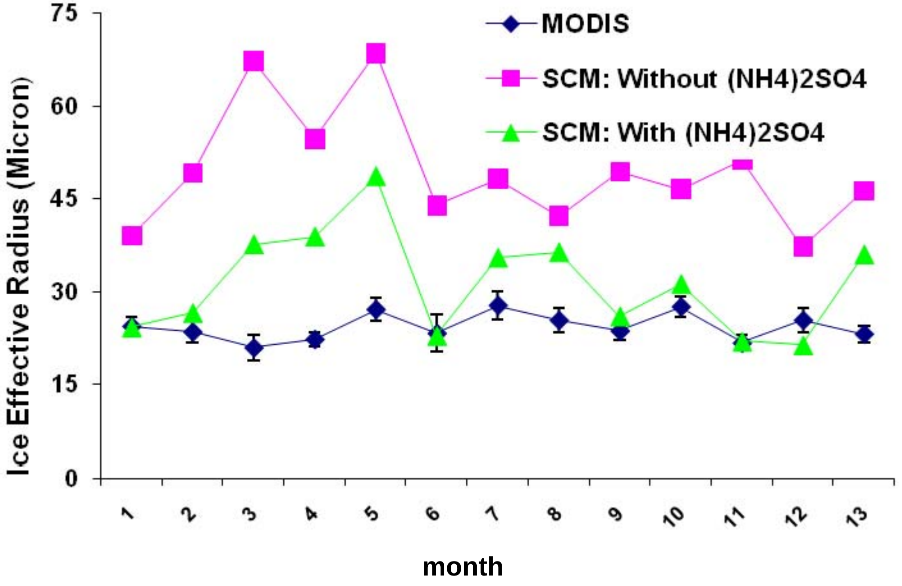
- Anthropogenic sulfate particles in solid phase contributes 41% in burden, 26% in optical thickness, and 37% in full-sky direct climate forcing of sulfate.

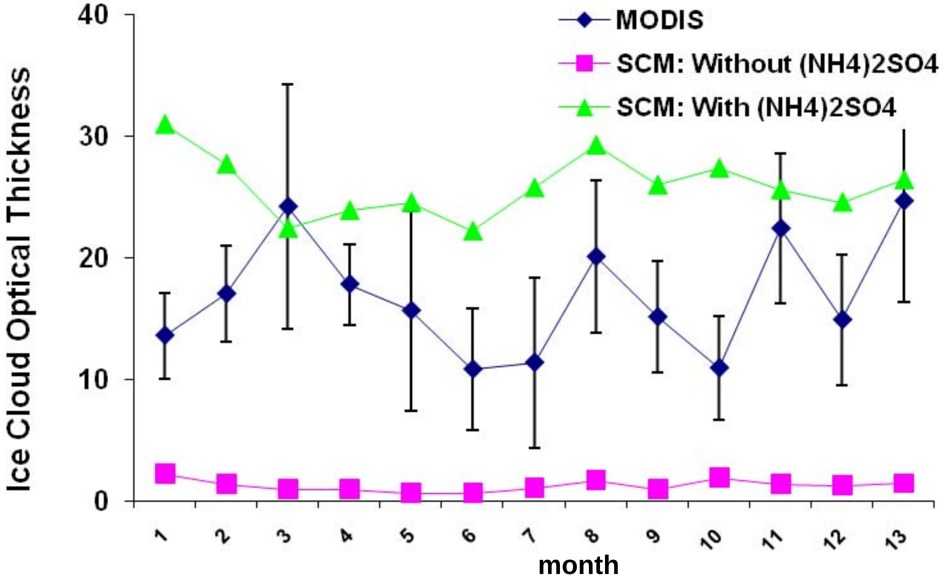
- Hysteresis can result in the uncertainty in the estimate of sulfate forcing by 12% (-7% – +5%) in global average and 20% in various regions.

- More percentage of solids is expected as the industrial emission of sulfate is decreasing in U.S. and Europe.

- Normalized growth factor of optical thickness should be considered as a standard output to facilitate meaningful intercomparisons among different forcing calculations.

PRELIMINARY STUDY USING A SINGLE COLUMN MODEL AT ARM SGP SITE

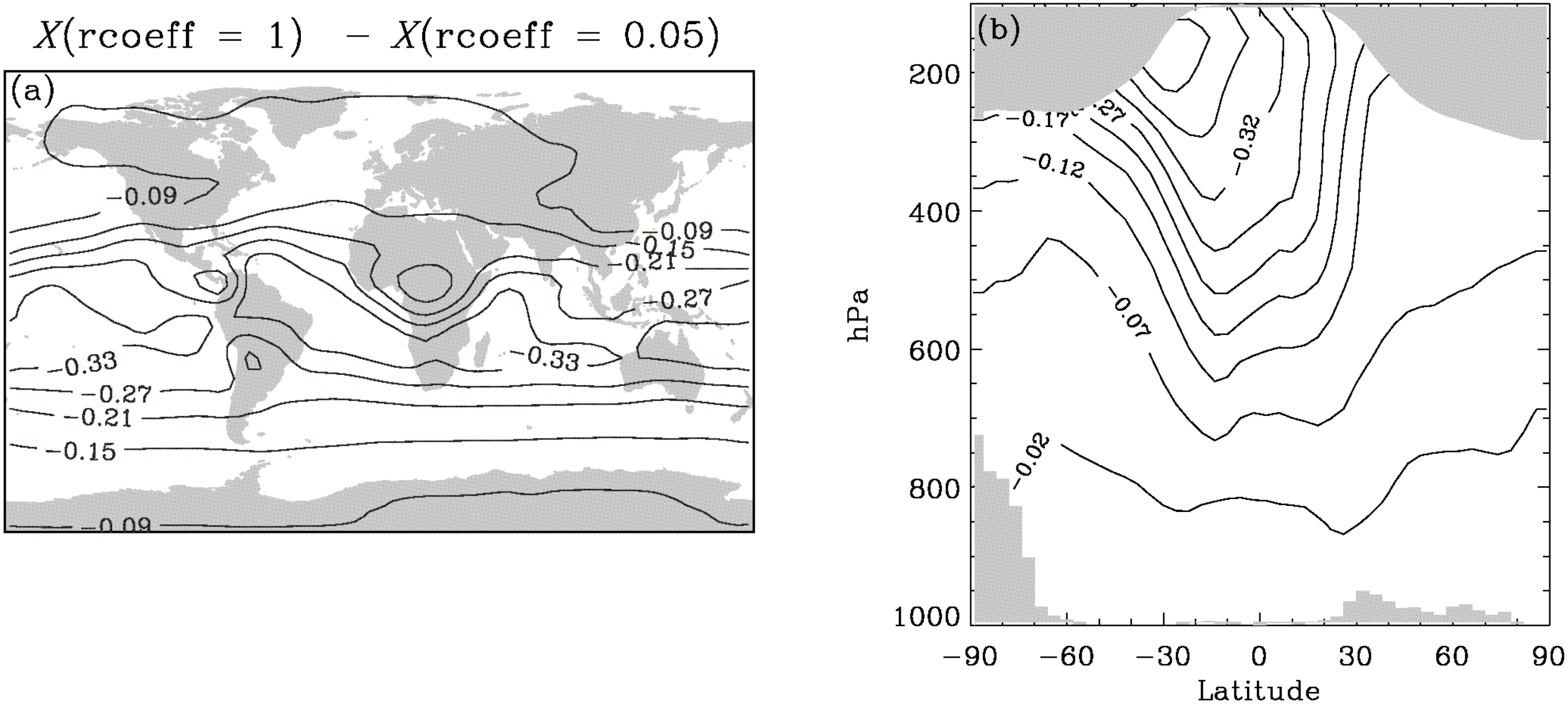




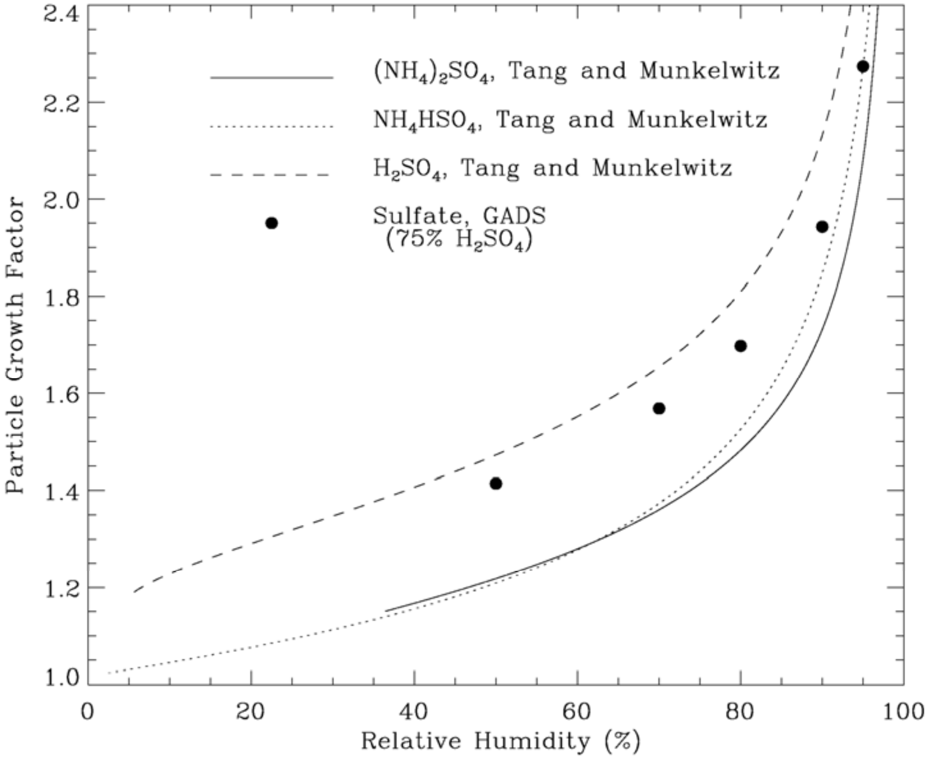
P. S. Bhattacharjee et al., 2008 AGU poster.

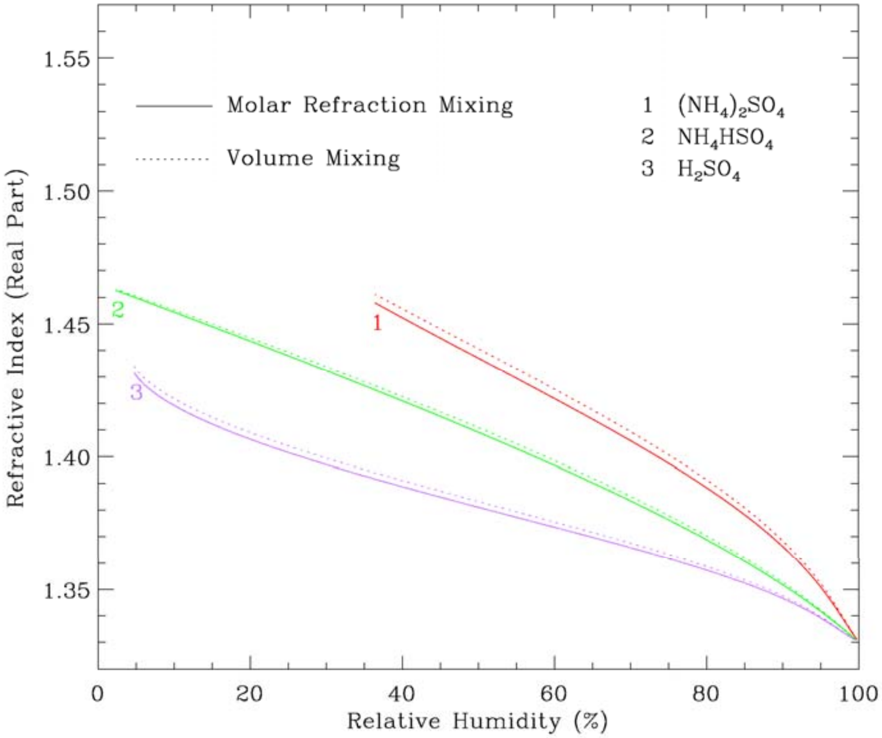
Thank you !

RESULT SENSITIVITY TO RETENTION EFFICIENCY OF NH_3



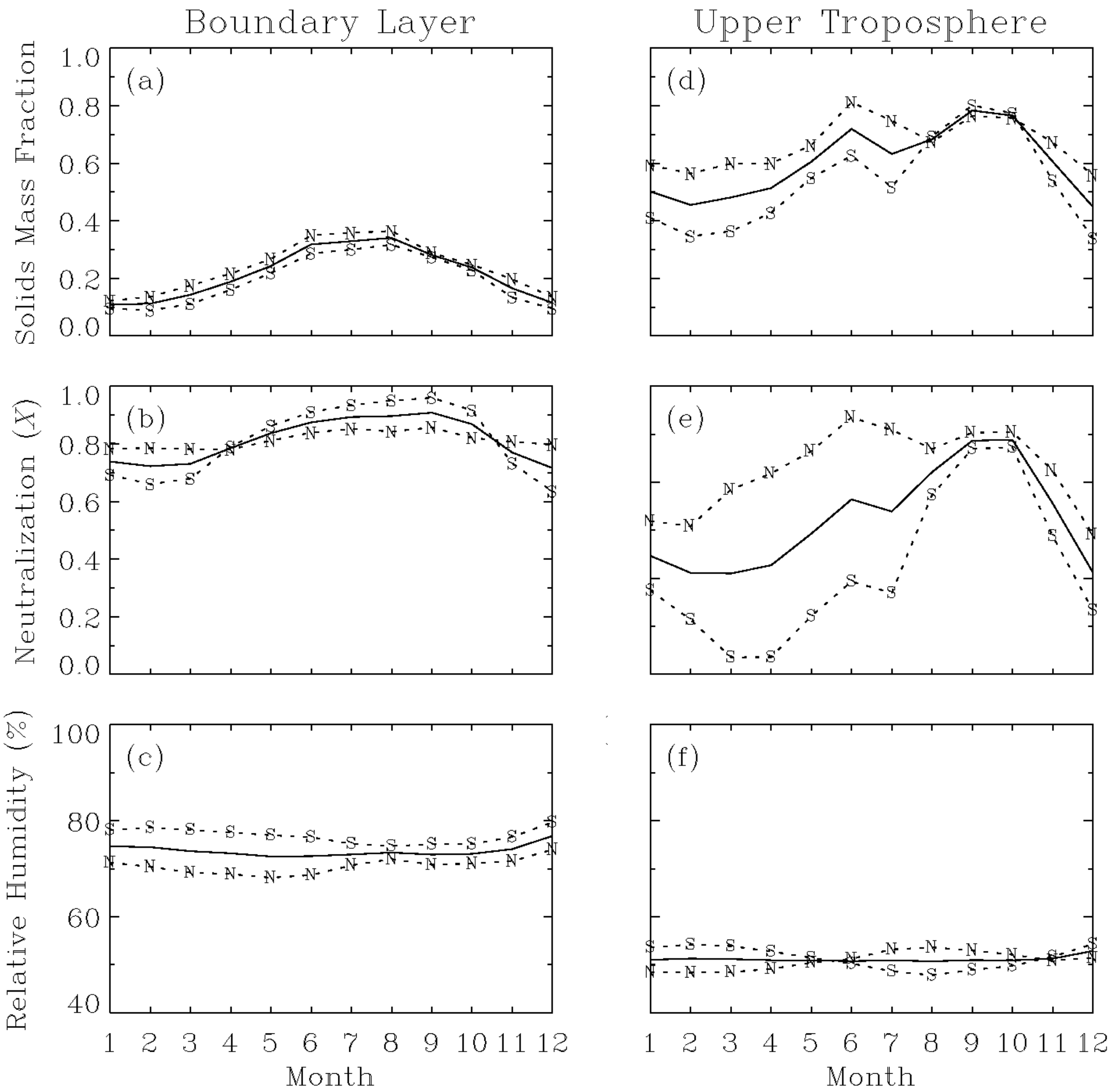
CHANGE OF PARTICLE SIZE AND REFRACTIVE INDEX WITH HYGROSCOPICITY



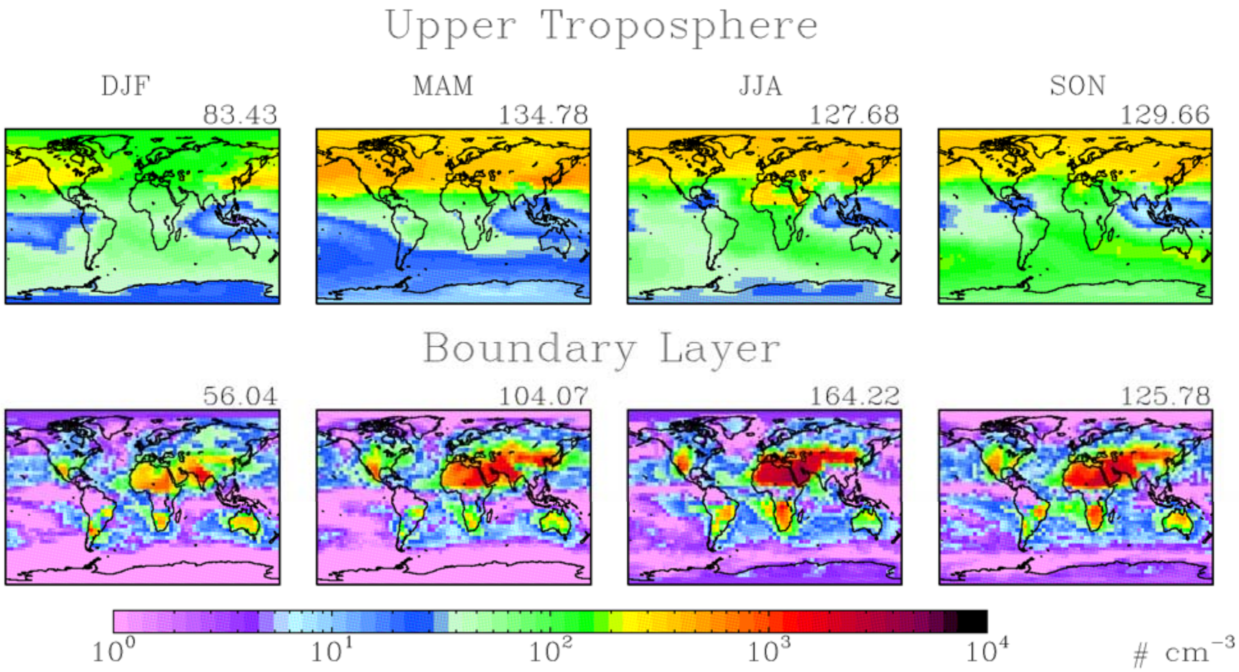


Wang and Martin, 2007, JGR.

SEASONALITY



NEXT STEP: ADDING SULFATE PATHWAY FOR CIRRUS CLOUD FORMATION IN GEOS-5 GCM



NASA GEOS GCM

Fountoukis and Nenes (2005)
For aerosol activation as CCN

Modified Seifert and Beheng (2006)
For autoconversion and accretion

Liu and Penner (2005)
For cloud ice nucleation

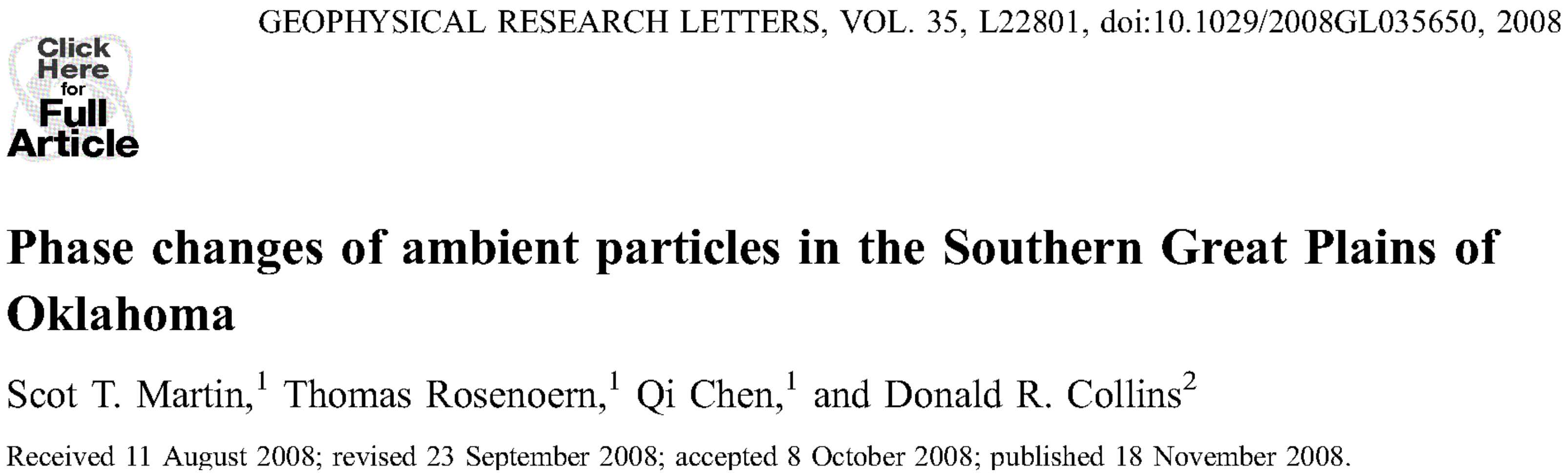
Khvorostyanov and Curry (1999a)
For cloud drop effective radius

+ McRAS

= McRAS - AC

Collaboration with:
Yogesh Sud, Eric Wilcox, Peter Colarco, Julio Bacmeister, Lazaros Orepoulos, Gregory Walker, …

OBSERVATIONAL EVIDENCE OF PHASE TRANSITIONS



GEOPHYSICAL RESEARCH LETTERS, VOL. 35, L22801, doi:10.1029/2008GL035650, 2008

Click Here for Full Article

Phase changes of ambient particles in the Southern Great Plains of Oklahoma

Scot T. Martin,[1] Thomas Rosenoern,[1] Qi Chen,[1] and Donald R. Collins[2]

Received 11 August 2008; revised 23 September 2008; accepted 8 October 2008; published 18 November 2008.

Efflorescence occurred 72% of the time for particles sampled at ambient RH in June.

For other evidences, see reviewed in Martin (2001), *Chem. Rev. 2000, 100, 3403-3453*

Acknowledgement

NASA New Investigator Program and Radiation Sciences Program

GEST Visiting Fellows Program

NOAA Climate and Global Change Postdoctoral Fellowship program under the administration of UCAR visiting scientist program

COMPARISON WITH OTHER MODELS

	$\tau_{an}\times10^4$	SDCF	NSDCF[a]	*NE* [b]	NG_τ	Remarks
Reddy et al. (2005)	300	-0.41	-135	9.90	2.30	For RH < 30%, E_{sd} applies. For RH > 30%, Mie-calculated E_{aq} values apply for increasing RH.
Koch et al. (1999, 2001)	280	-0.68	-206	8.48	1.70	For RH < 60%, E_{sd} applies. For RH > 60%, E_{aq} at 85% RH and E_{sd} are interpolated to obtain E_{aq} at intermediate RH values.
Schulz et al. (2006)						
Mean	190	-0.35	-161	9.10		Statistics from nine CTMs having the same emissions
Standard deviation	±90	±0.15	±41	±2.70		
This Study						
Base Case	103	-0.17	-136	8.26	1.60	E_{sd} and E_{aq} depend on particle composition *X*. The hystereisis loop is fully considered in the base case.

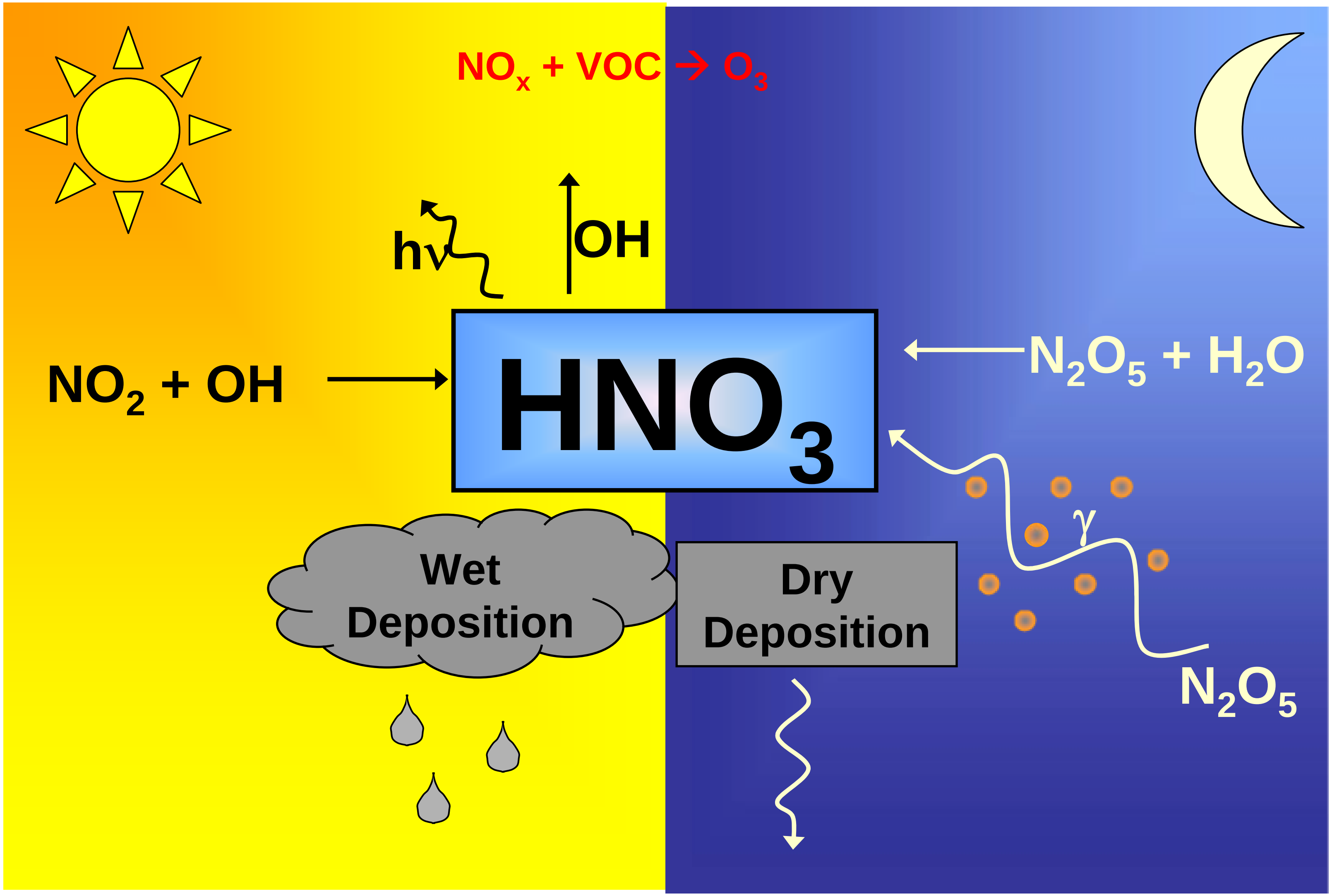
$NSDCF = SDCF/\tau$

$NE = \tau/\text{burden}$

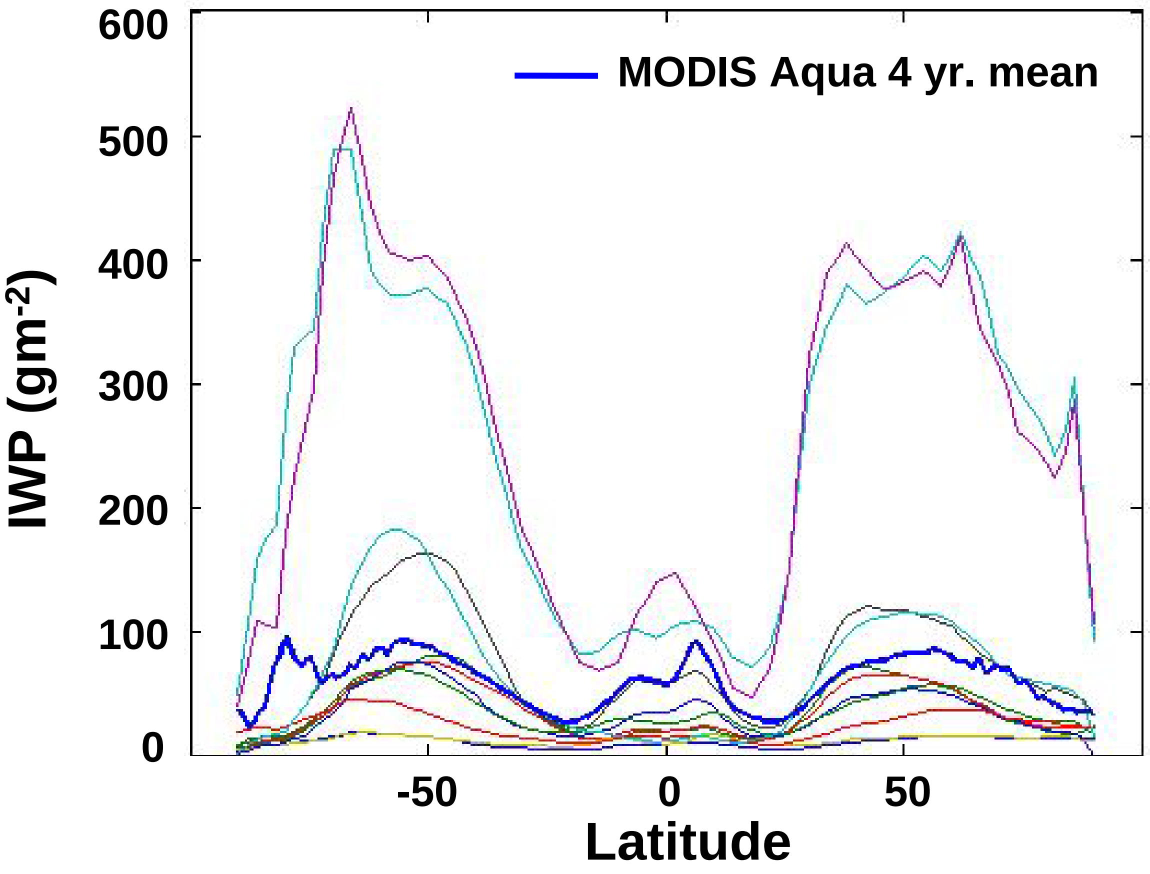
$NG = \tau_{\text{with\_hygroscopicity}} / \tau_{\text{no\_hygroscopicity}}$

Normalized growth factor of optical thickness should be another parameter in comparing CTM results.

Production and loss of HNO_3



Phase effect: increase in daytime + decrease in night time = ?


MODIS Aqua 4 yr. mean
600
500
400
300
200
100
0
IWP (gm-2)
-50
0
50
Latitude

Next Steps (1)

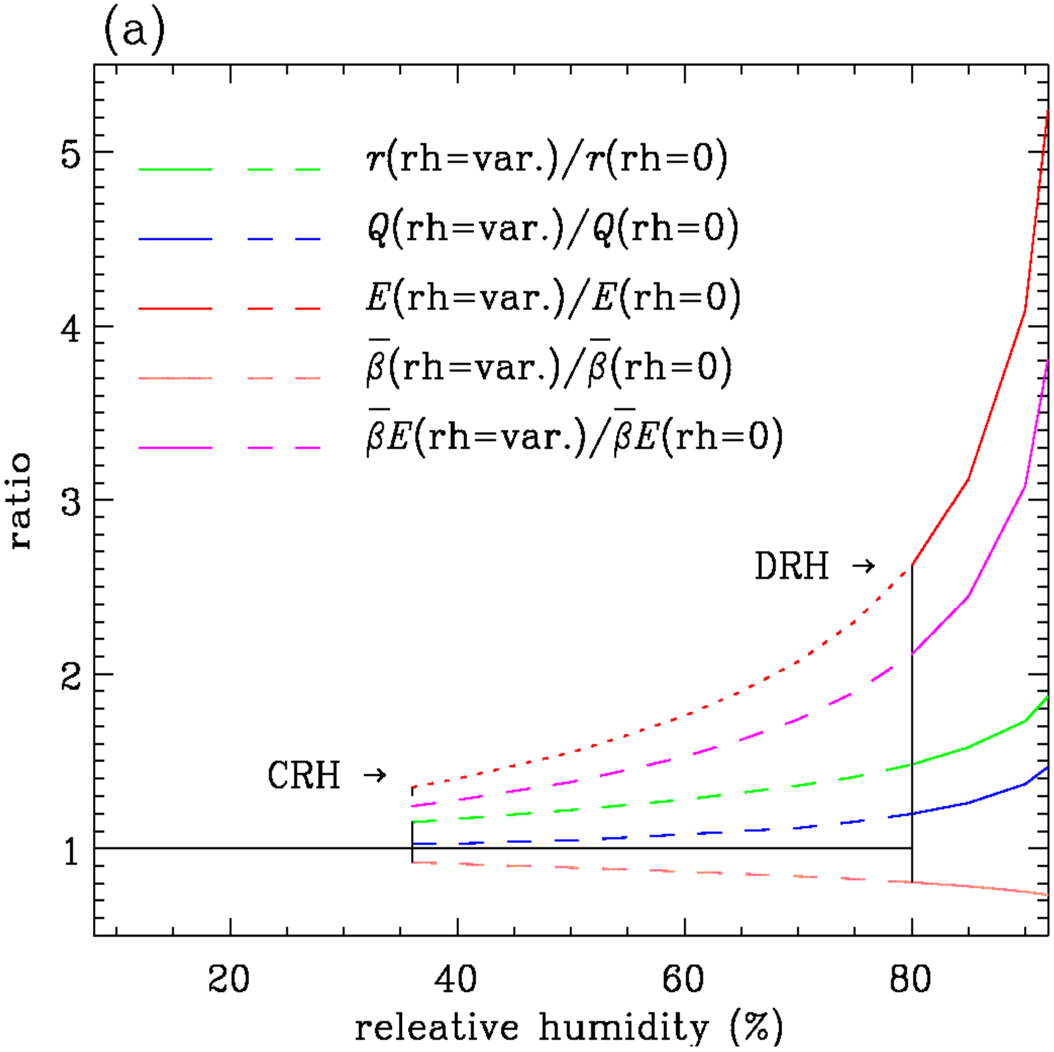
Goal:

Include the sulfate phase into a GCM to study its effect on cirrus cloud formation and radiative forcing.

Approach:

Coupled the sulfate/ammonia cycle including sulfate phase transition in CTM with GCM.

sulfate physical state vs. scattering properties



Between DRH and CRH, sulfate particles can be in either solid or aqueous phase.

For aqueous sulfate particles, as RH increases,

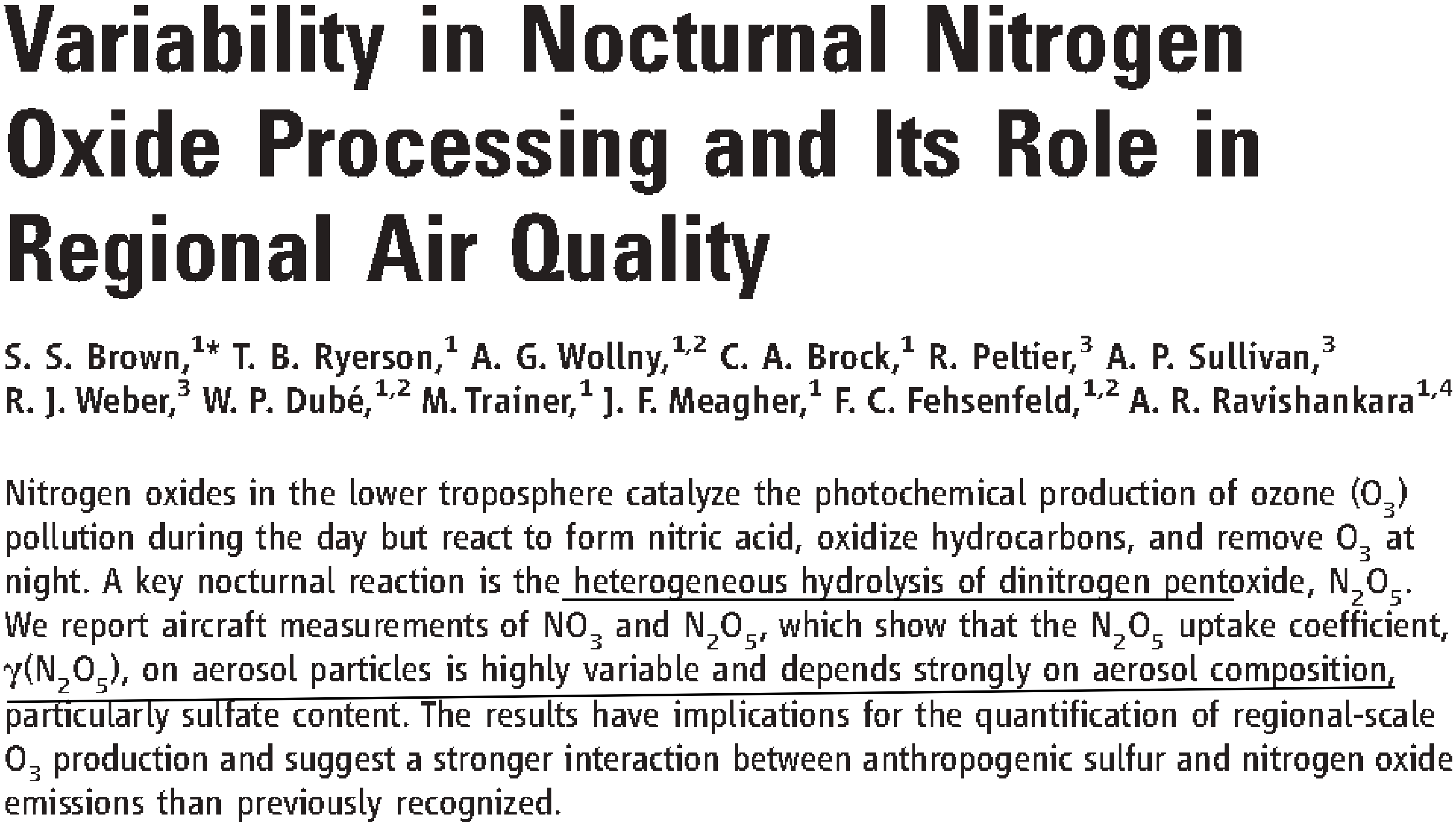
r increases
Q and *E* increase

However,

β decreases

Overall, increase the aerosol forcing.

Next Steps (2)



Variability in Nocturnal Nitrogen Oxide Processing and Its Role in Regional Air Quality

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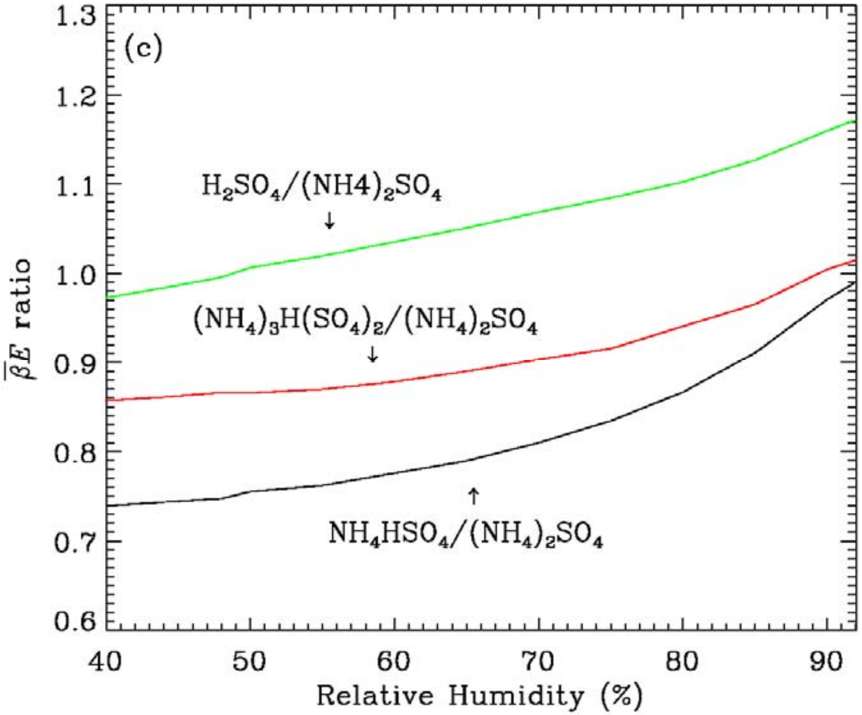
Nitrogen oxides in the lower troposphere catalyze the photochemical production of ozone (O_3) pollution during the day but react to form nitric acid, oxidize hydrocarbons, and remove O_3 at night. A key nocturnal reaction is the heterogeneous hydrolysis of dinitrogen pentoxide, N_2O_5. We report aircraft measurements of NO_3 and N_2O_5, which show that the N_2O_5 uptake coefficient, $\gamma(N_2O_5)$, on aerosol particles is highly variable and depends strongly on aerosol composition, particularly sulfate content. The results have implications for the quantification of regional-scale O_3 production and suggest a stronger interaction between anthropogenic sulfur and nitrogen oxide emissions than previously recognized.


(c)
$\bar{\beta}E$ ratio
Relative Humidity (%)
$H_2SO_4/(NH4)_2SO_4$
$(NH_4)_3H(SO_4)_2/(NH_4)_2SO_4$
$NH_4HSO_4/(NH_4)_2SO_4$
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
40
50
60
70
80
90

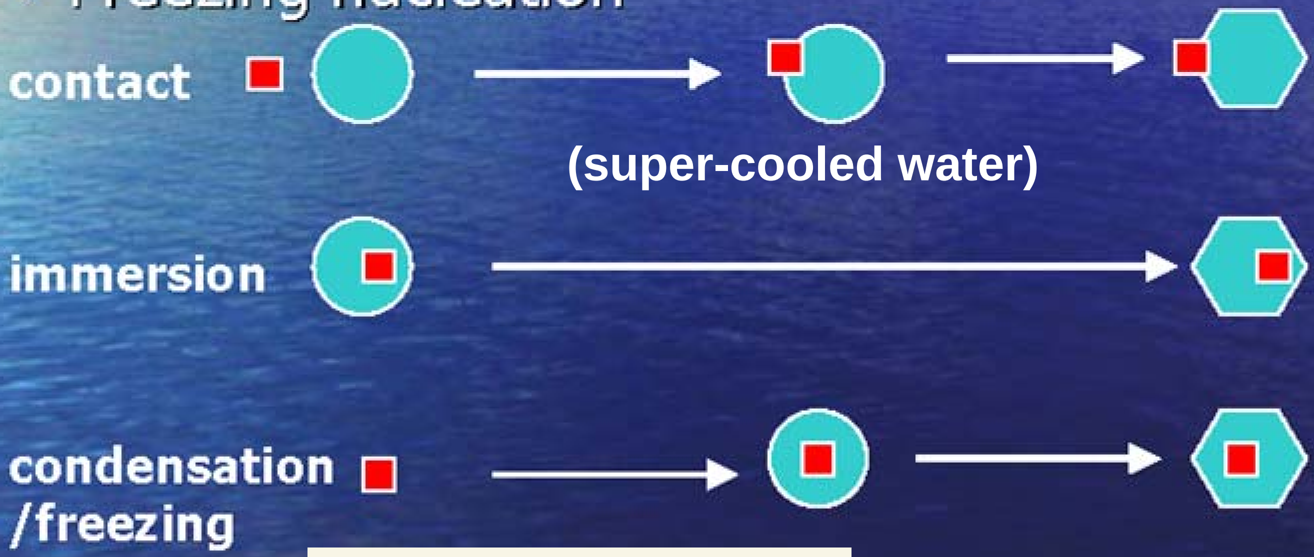
Heterogeneous ice nucleation mechanisms

- Deposition nucleation (deposition nuclei)

H_2O

(solid particle)

- Freezing nucleation

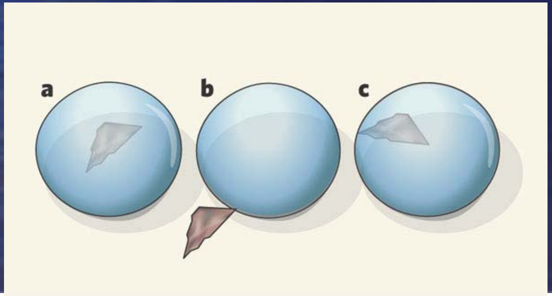


contact

(super-cooled water)

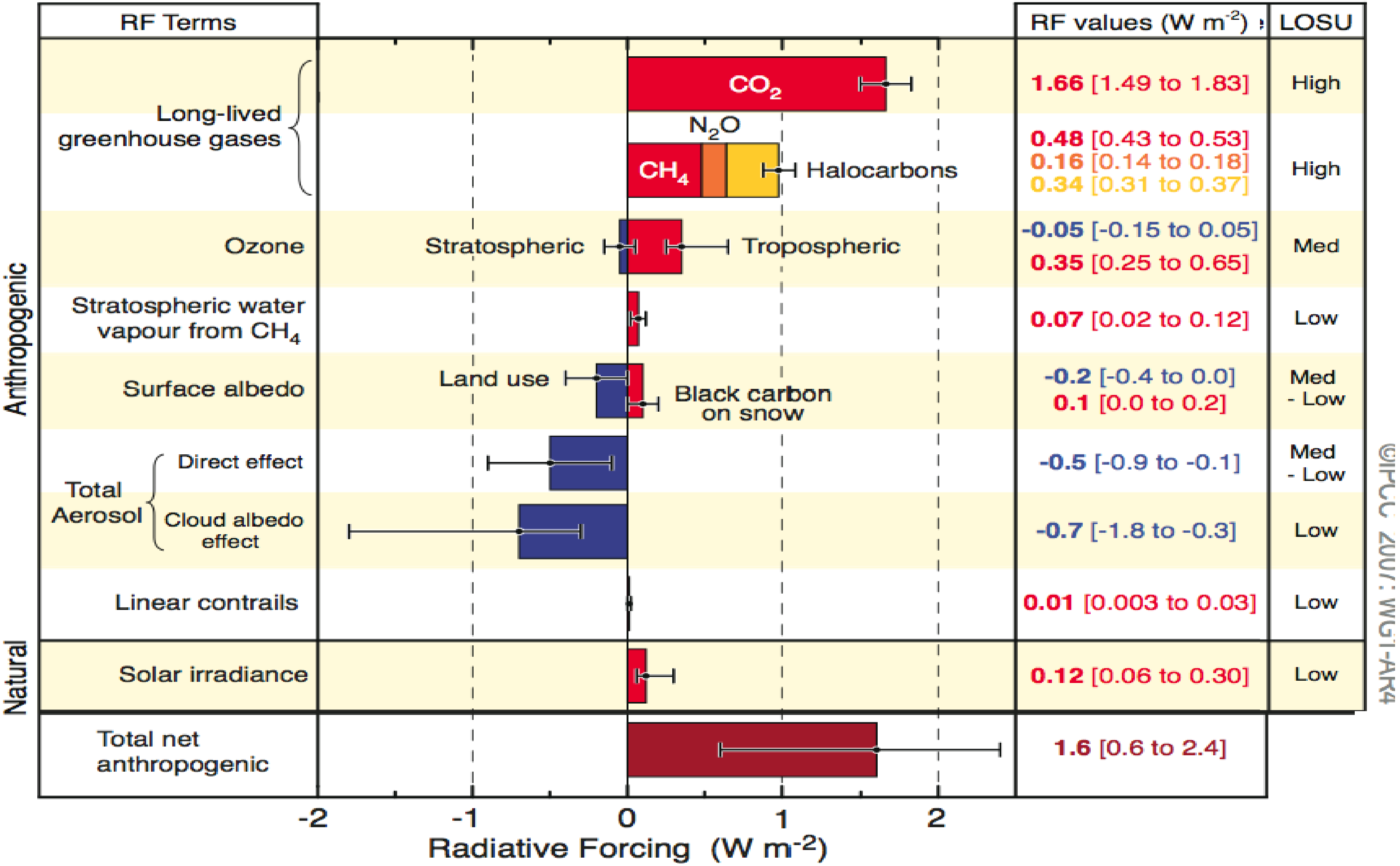
immersion

condensation /freezing



Slide from Xiaohong Liu, PNNL

Radiative Forcing Components



	RF Terms		RF values (W m^{-2})	LOSU
Anthropogenic	Long-lived greenhouse gases	CO$_2$	1.66 [1.49 to 1.83]	High
		CH$_4$ N$_2$O Halocarbons	0.48 [0.43 to 0.53] 0.16 [0.14 to 0.18] 0.34 [0.31 to 0.37]	High
	Ozone	Stratospheric Tropospheric	-0.05 [-0.15 to 0.05] 0.35 [0.25 to 0.65]	Med
	Stratospheric water vapour from CH$_4$		0.07 [0.02 to 0.12]	Low
	Surface albedo	Land use Black carbon on snow	-0.2 [-0.4 to 0.0] 0.1 [0.0 to 0.2]	Med - Low
	Total Aerosol	Direct effect	-0.5 [-0.9 to -0.1]	Med - Low
		Cloud albedo effect	-0.7 [-1.8 to -0.3]	Low
	Linear contrails		0.01 [0.003 to 0.03]	Low
Natural	Solar irradiance		0.12 [0.06 to 0.30]	Low
	Total net anthropogenic		1.6 [0.6 to 2.4]	