2nd Workshop on Eulerian vs. Lagrangian methods for cloud microphysics

Kraków, April 2019

Aqueous chemical reactions in atmospheric clouds

Anna Jaruga

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Example: sulfur oxidation

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- **chemistry 101 and sulfur budget**
- **example results from a high resolution model**
- **example results from a global model**

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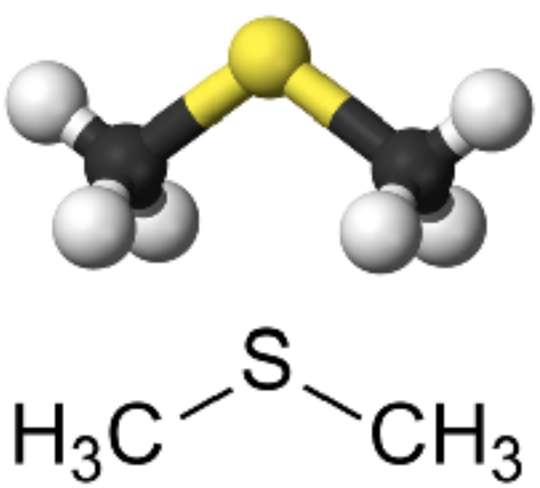
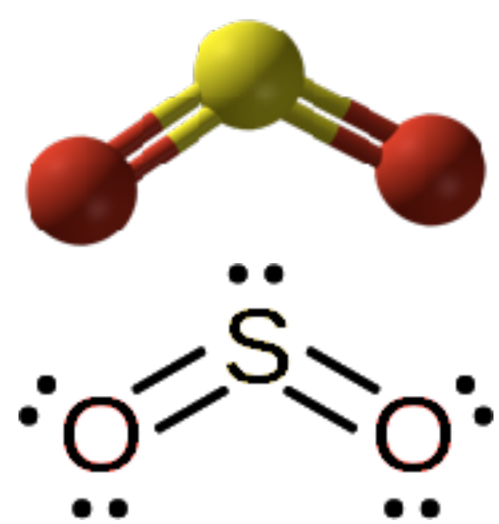
Sulfur chemistry 101: sulfur oxidation

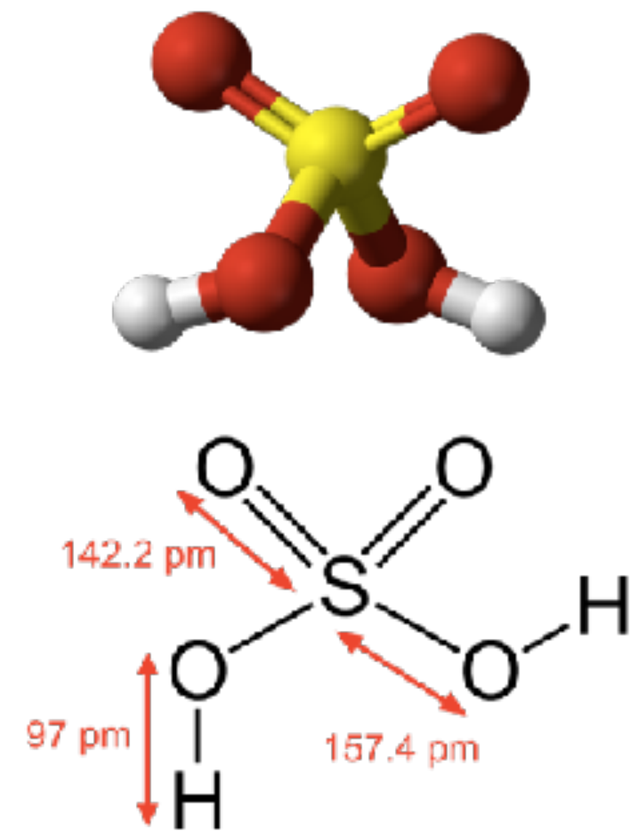
DMS - dimethyl sulfide



SO_2 - sulfur dioxide



H_2SO_4 - sulfuric acid



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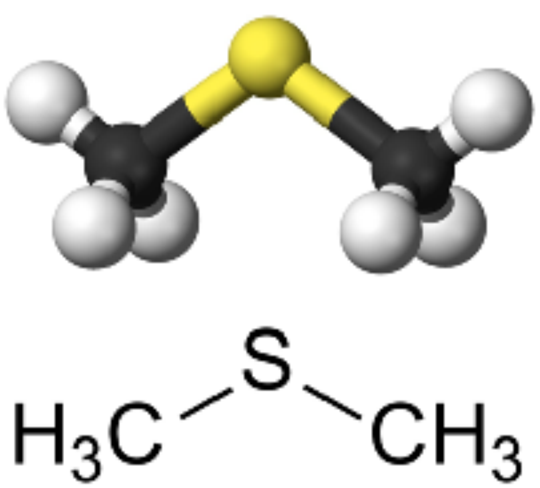

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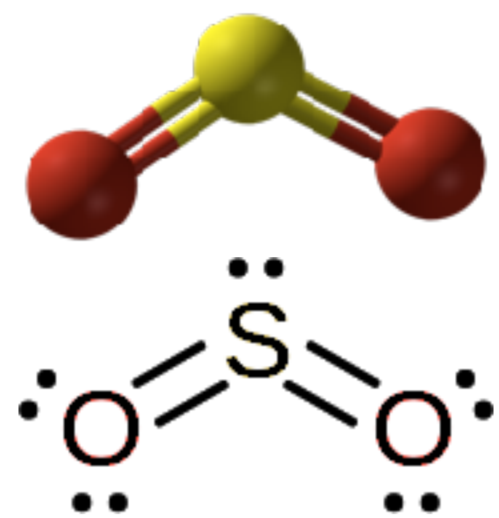

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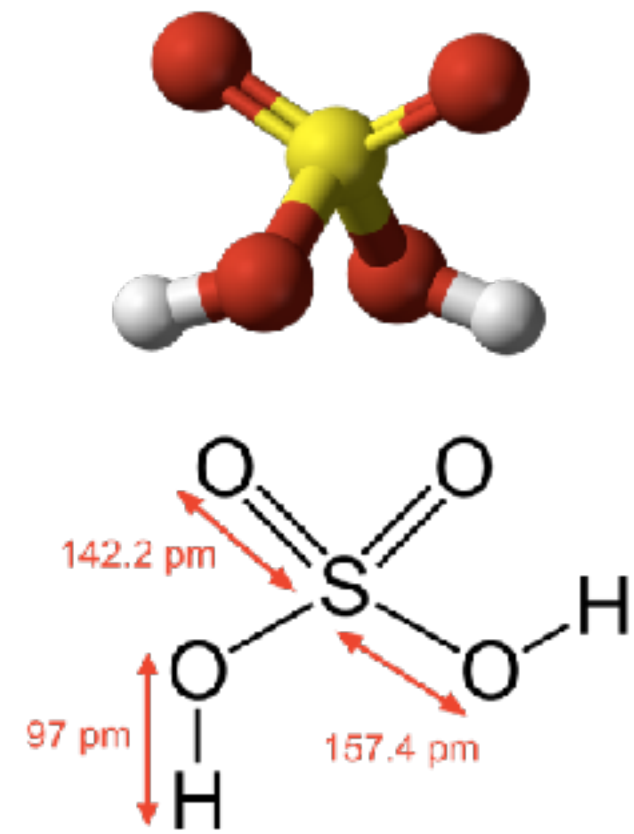

-II

-IV

-VI

oxidation reaction

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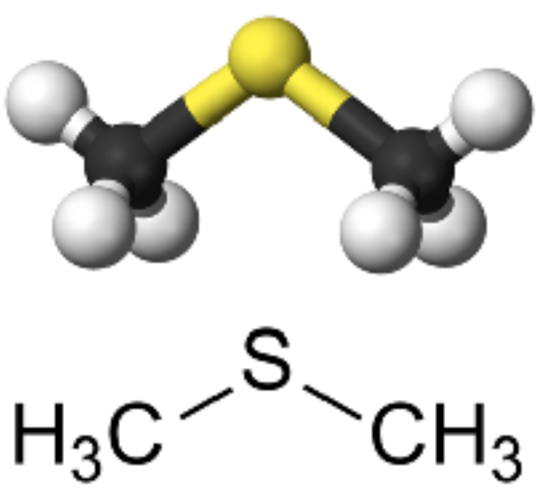

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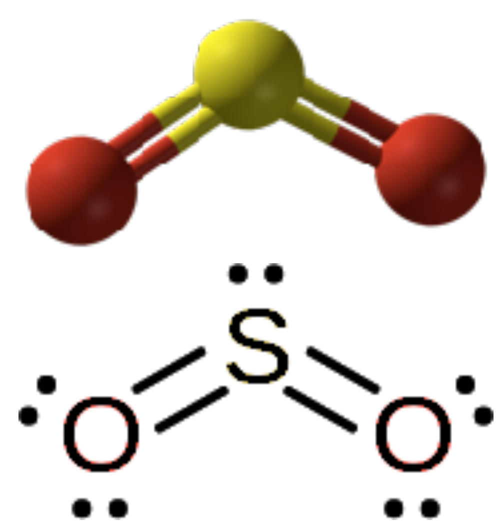

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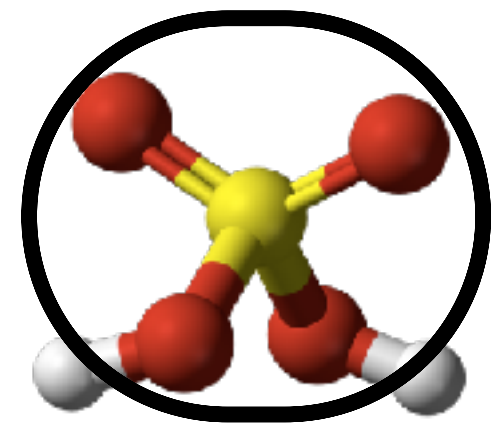


sulfate

- sulfate is a major aerosol component
    - 10-67% of sub-micron particle mass
    - 32% on average

-II

-IV

-VI

oxidation reaction

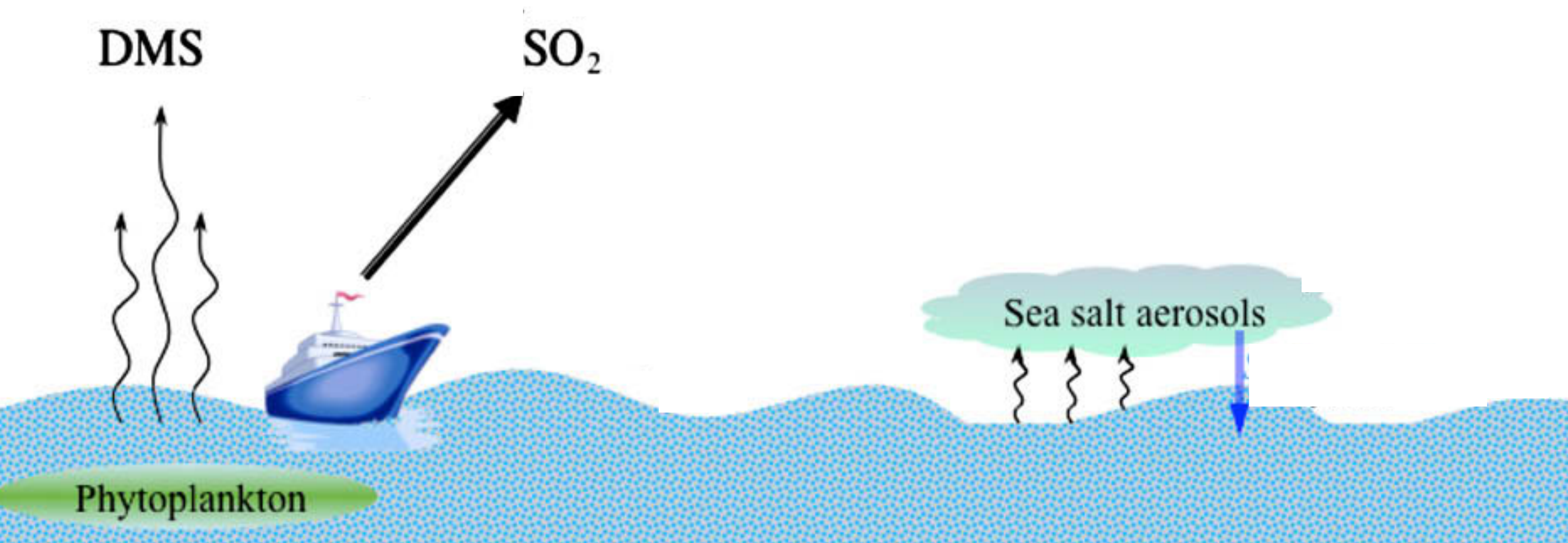
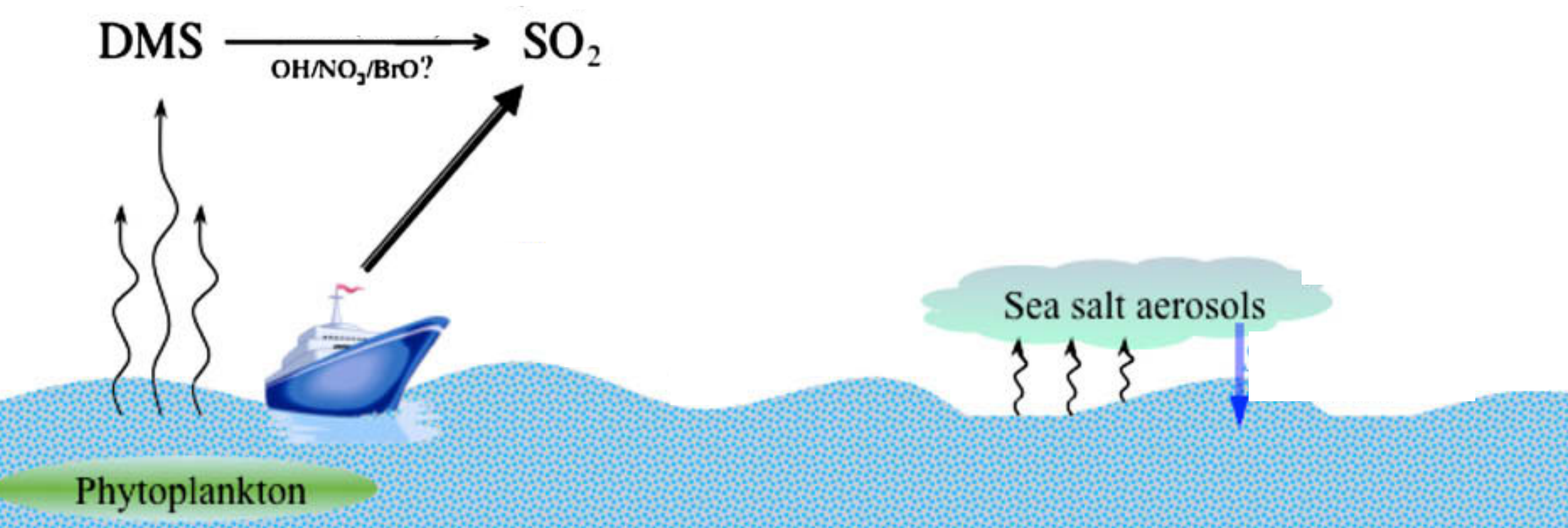


Fig 1 from Faloona 2009: important processes in the marine BL affecting the sulfur cycle



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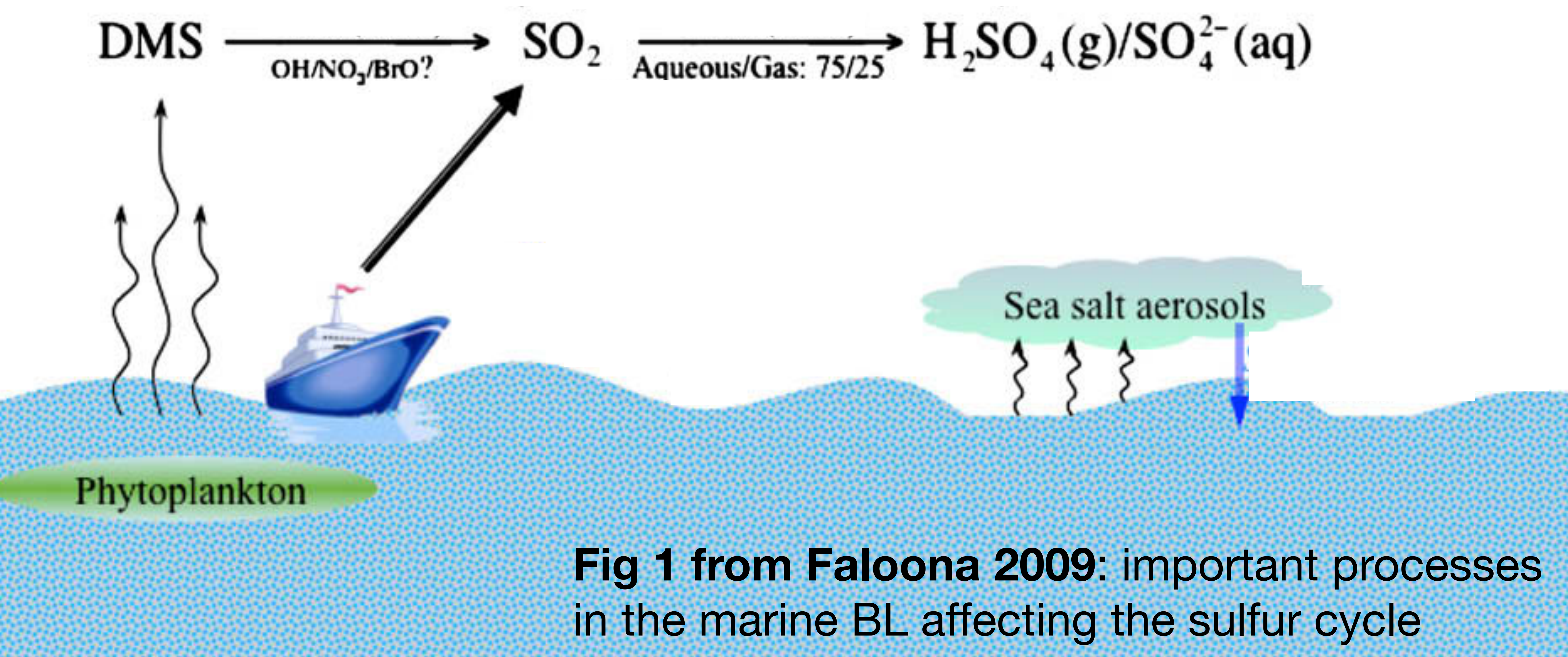

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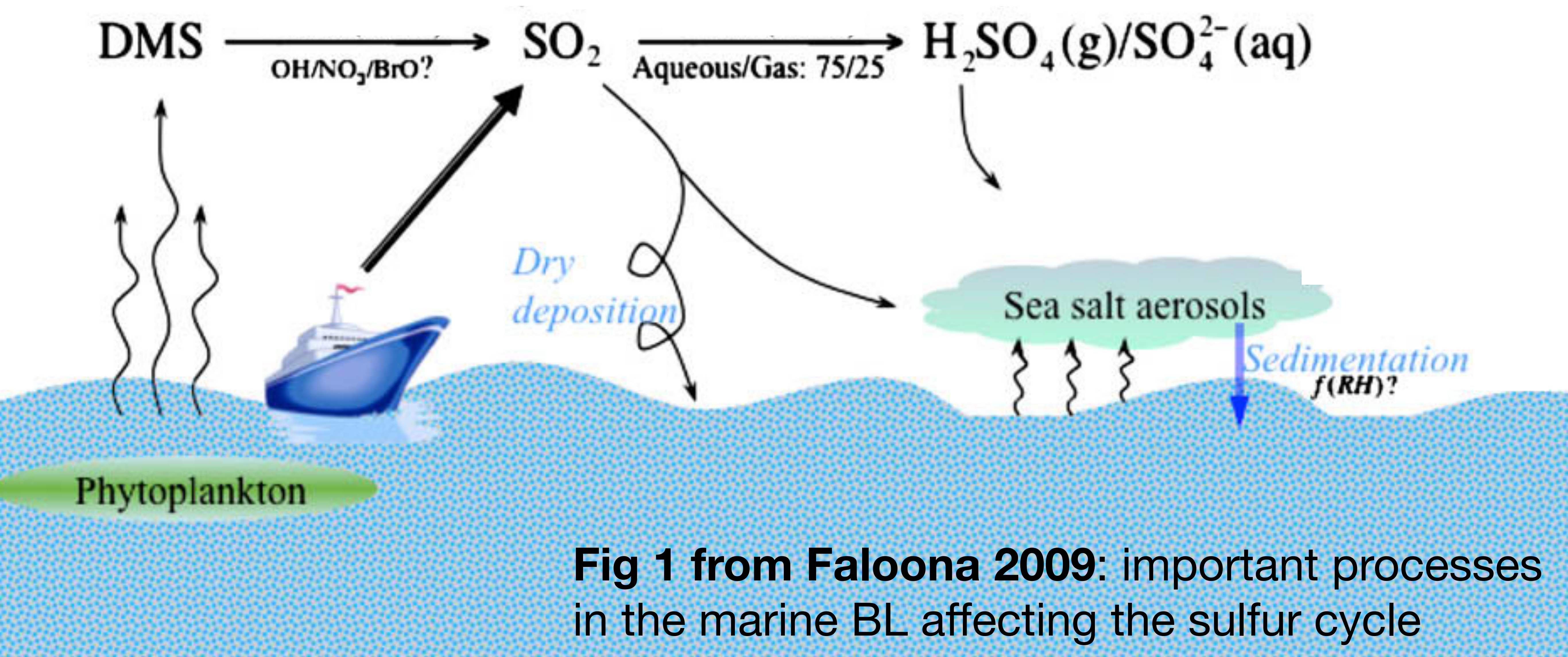

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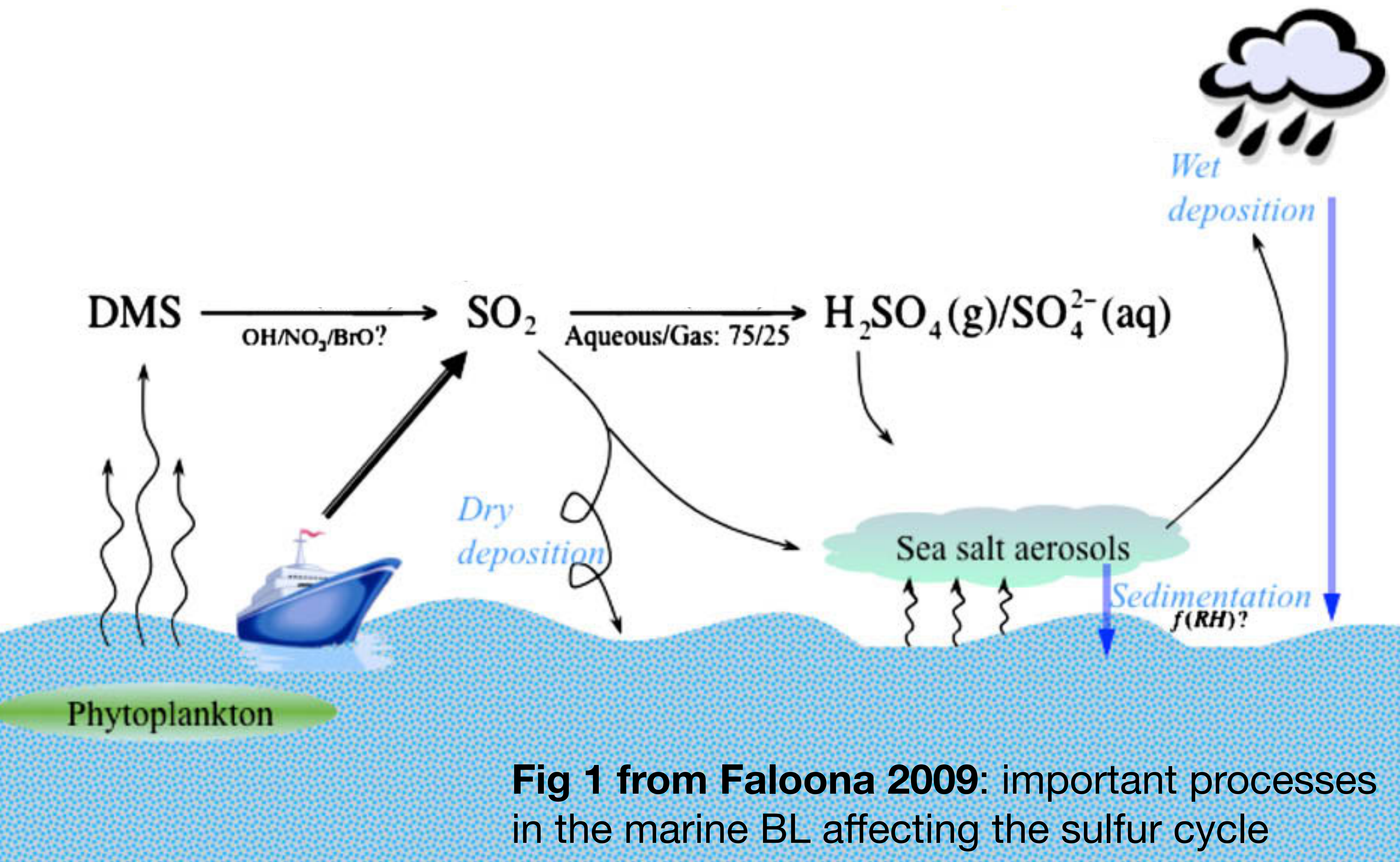

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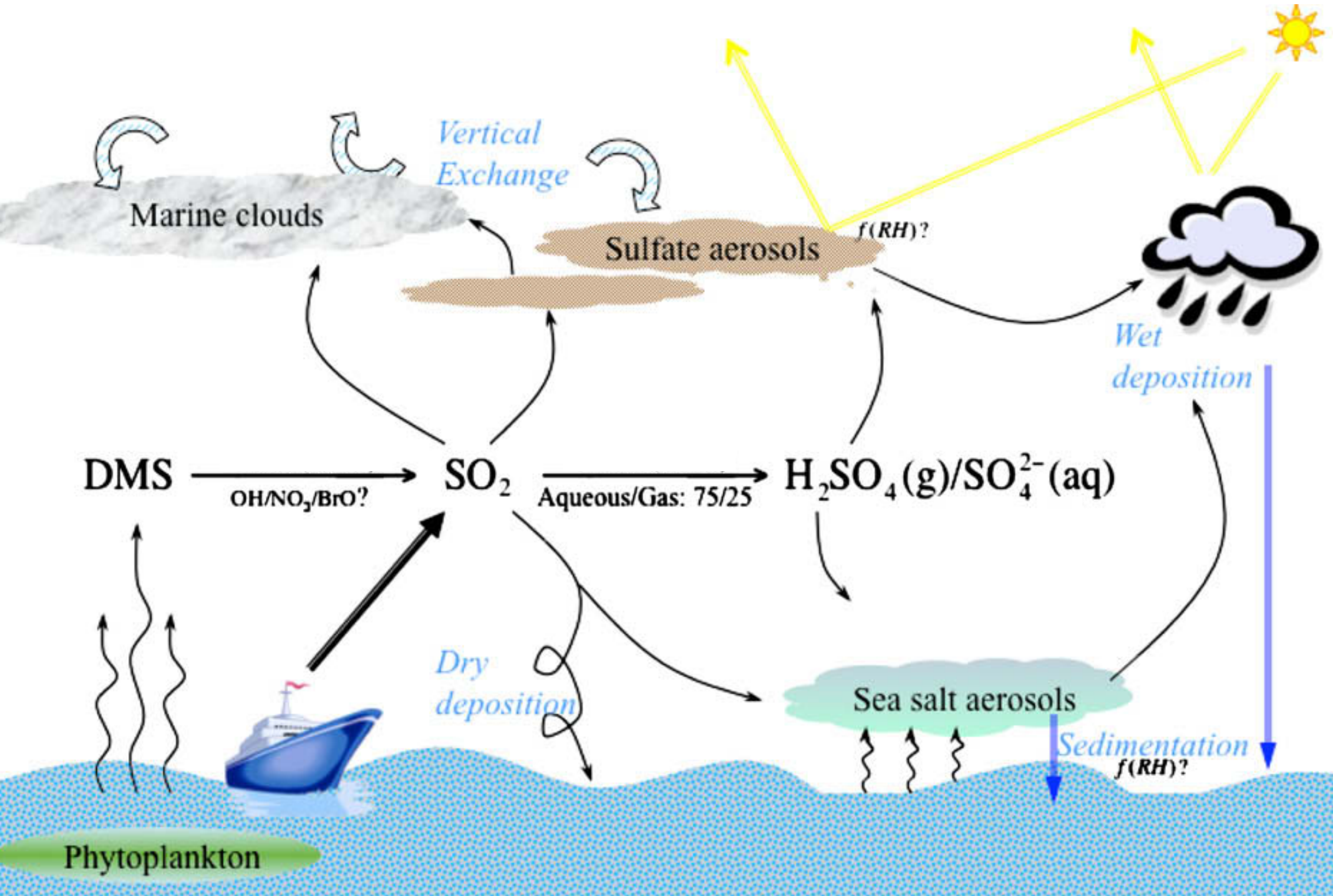

Fig 1 from Faloona 2009: important processes in the marine BL affecting the sulfur cycle

Global budget of the main sulfur species [Tg S/ year]

		Sources	Sinks	lifetime [days]
DMS		19.4		
SO_2	anthropogenic	67.2		
	volcanic	7.8		
	DMS oxidation	18.5		
sulfate	direct emissions	2		
	homogeneous ox.	11		
	heterogeneous ox.	42		

Faloona 2009: median based on 20 atmospheric modelling studies

Global budget of the main sulfur species [Tg S/ year]

	Sources		Sinks		lifetime [days]
DMS		19.4			
SO_2	anthropogenic	67.2	dry deposition	34.6	
	volcanic	7.8	wet deposition	7.3	
	DMS oxidation	18.5	oxidation	51.6	
sulfate	direct emissions	2	dry deposition	6.4	
	homogeneous ox.	11	wet deposition	44.6	
	heterogeneous ox.	42			

Faloona 2009: median based on 20 atmospheric modelling studies

Global budget of the main sulfur species [Tg S/ year]

	Sources		Sinks		lifetime [days]
DMS		19.4			1.95
SO_2	anthropogenic	67.2	dry deposition	34.6	1.8
	volcanic	7.8	wet deposition	7.3	
	DMS oxidation	18.5	oxidation	51.6	
sulfate	direct emissions	2	dry deposition	6.4	4.6
	homogeneous ox.	11	wet deposition	44.6	
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fast redox: small amounts in the atmosphere but big fluxes

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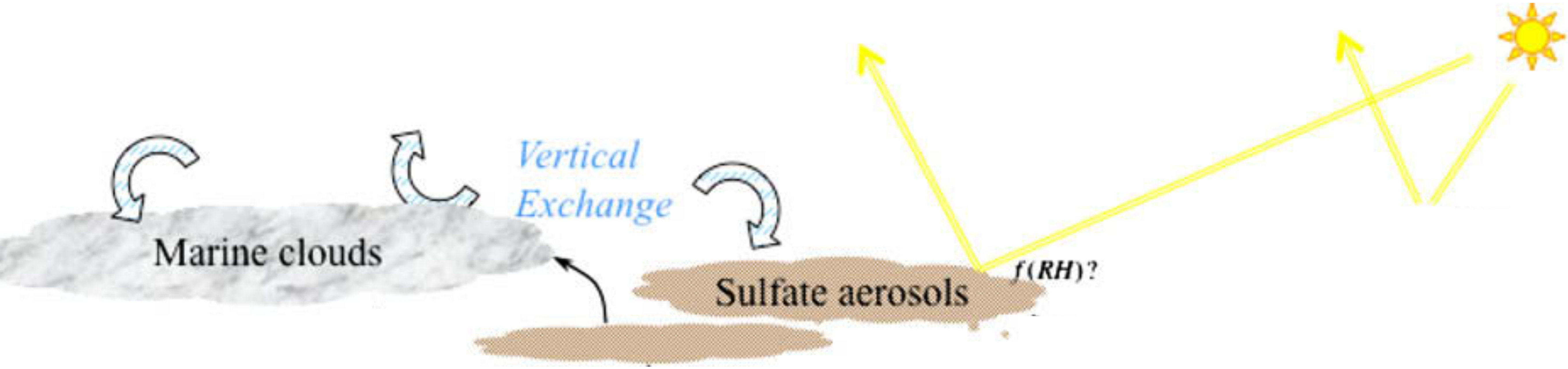
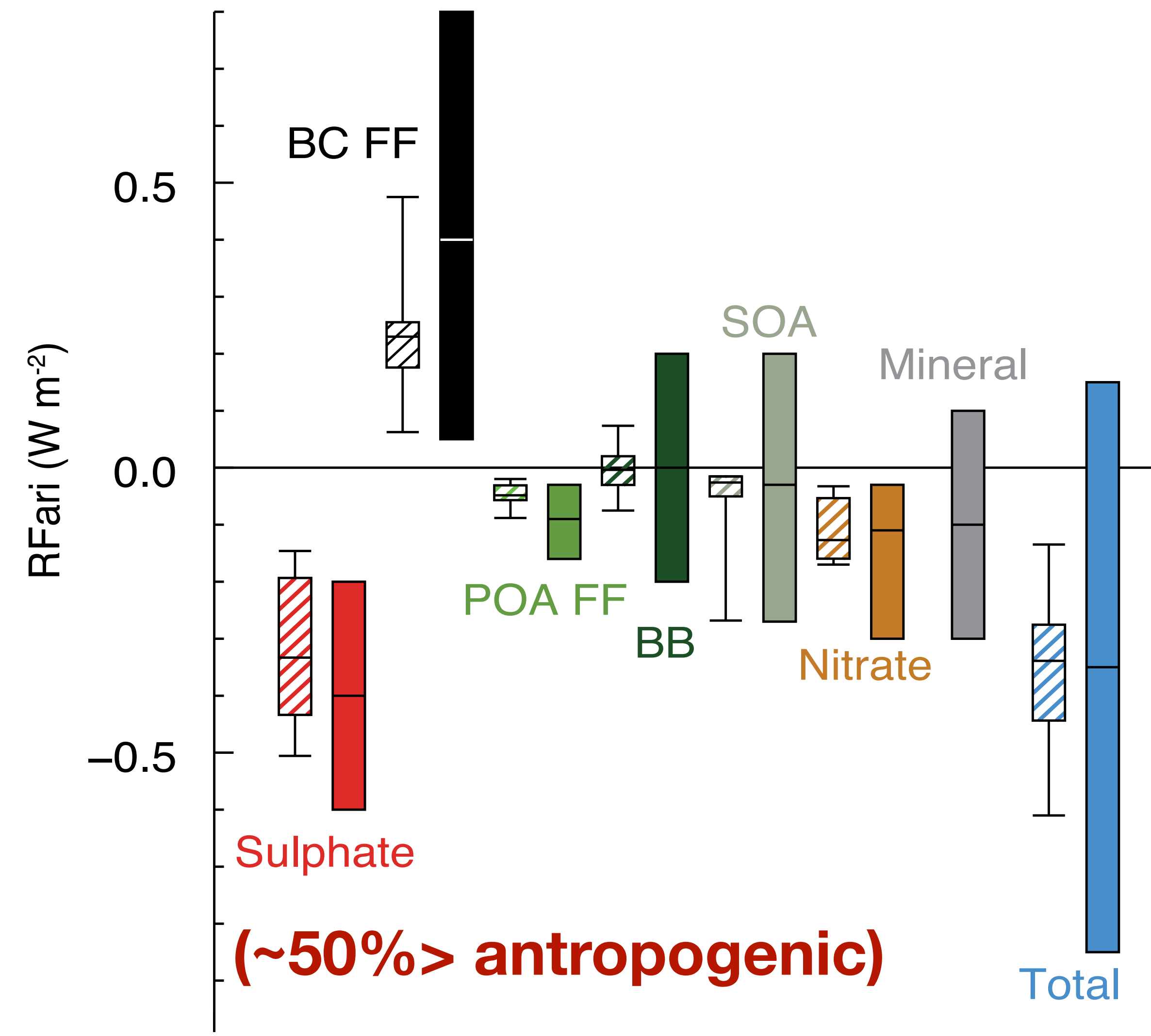
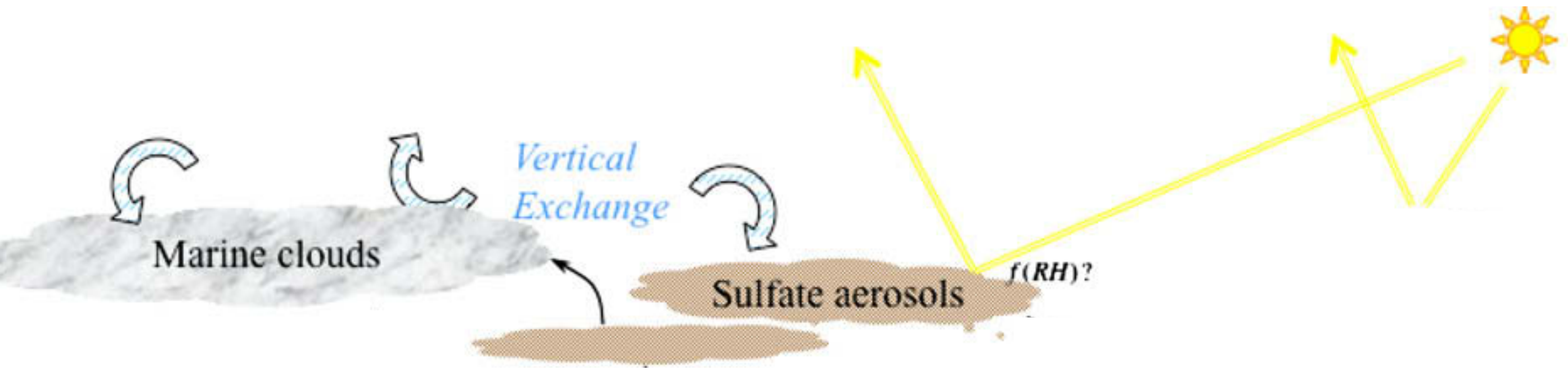


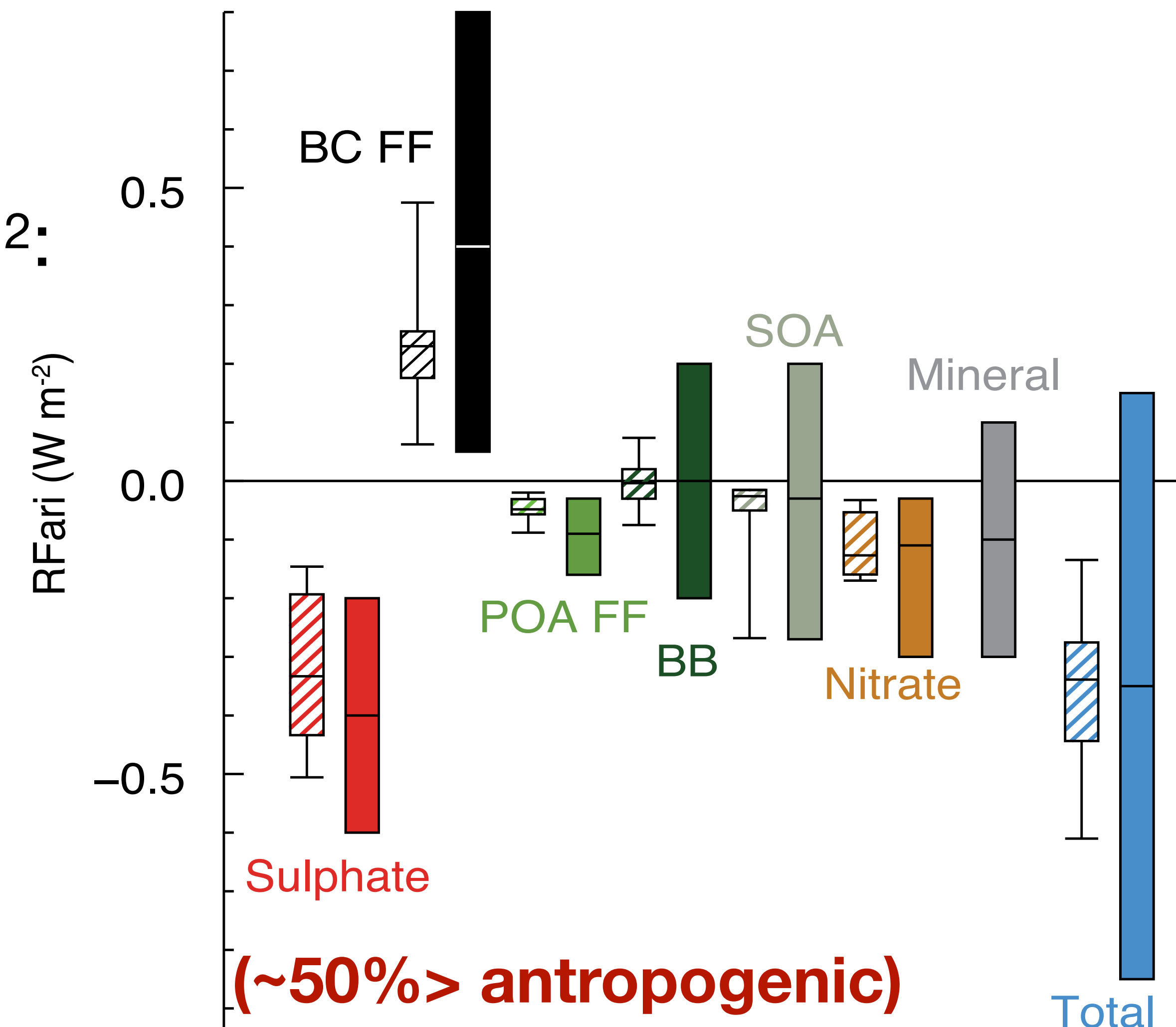


IPCC 5AR Myhre et al 2013



Effective Radiative Forcing (**ERFari+aci**) W/m^2:
- —0.9 (—1.9, —0.1) our best knowledge

CMIP ACCMIP multi model mean W/m^2:
- —1.08 from anthropogenic aerosols
- —0.89 from sulfate aerosols only



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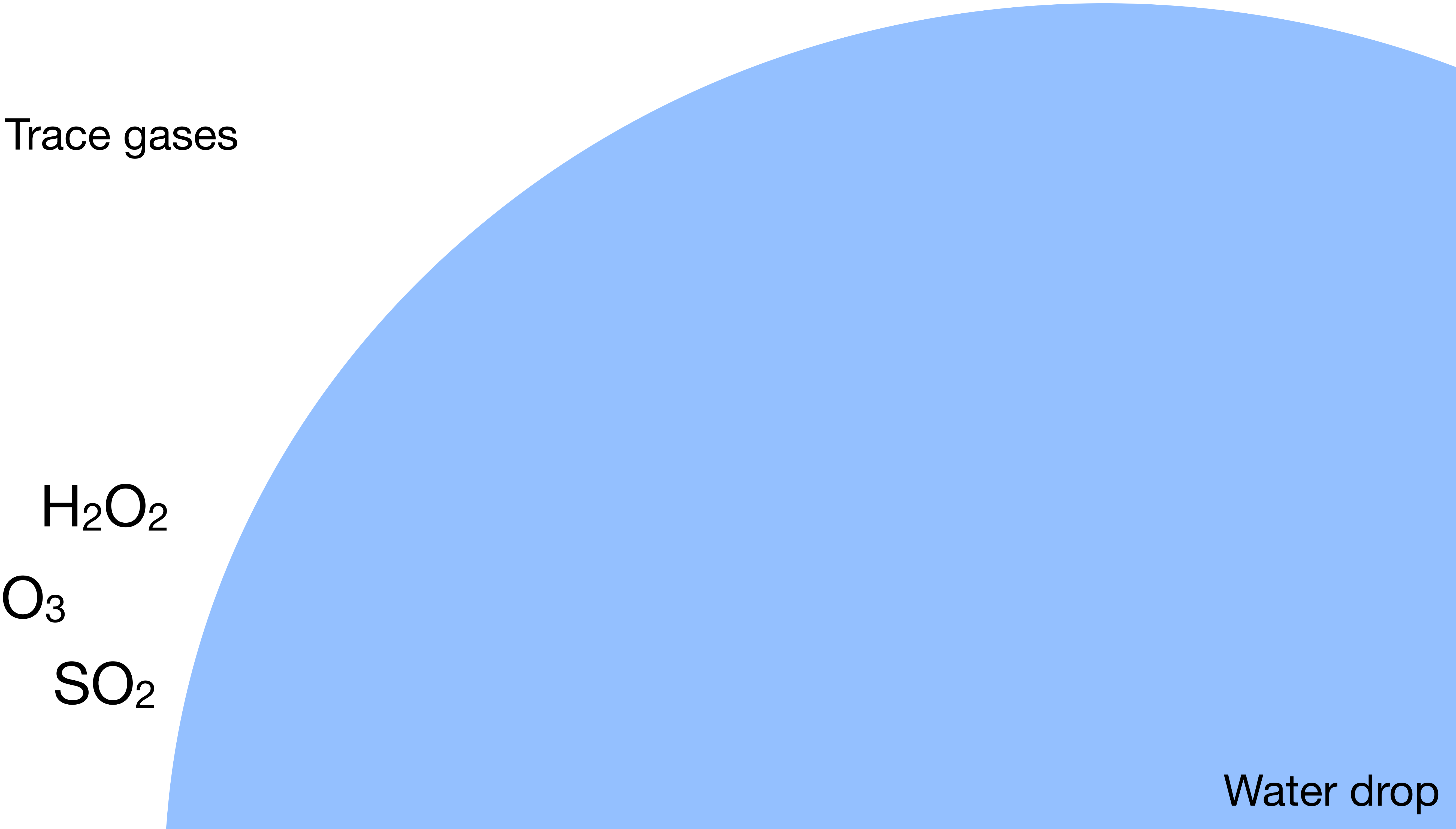
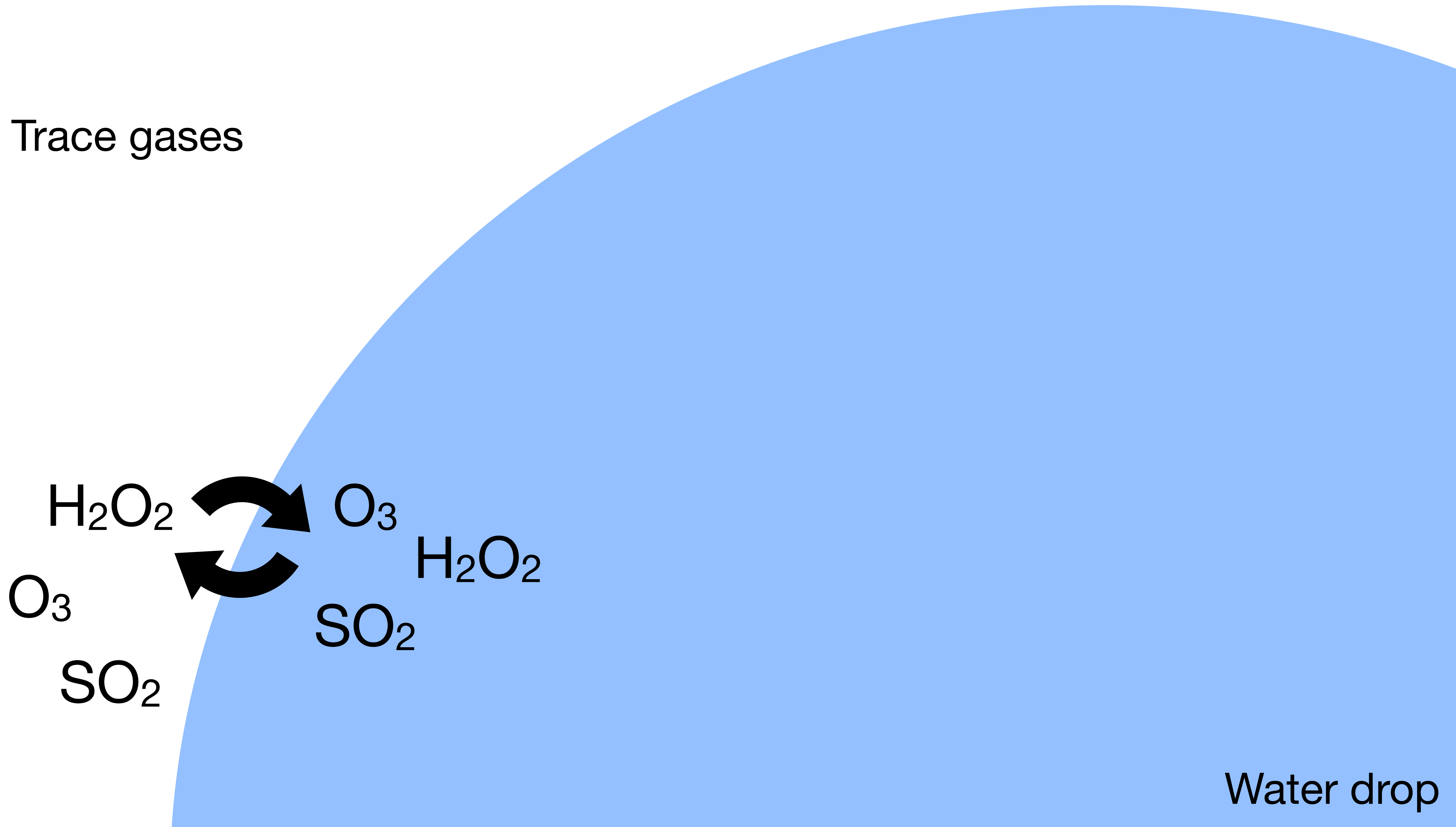
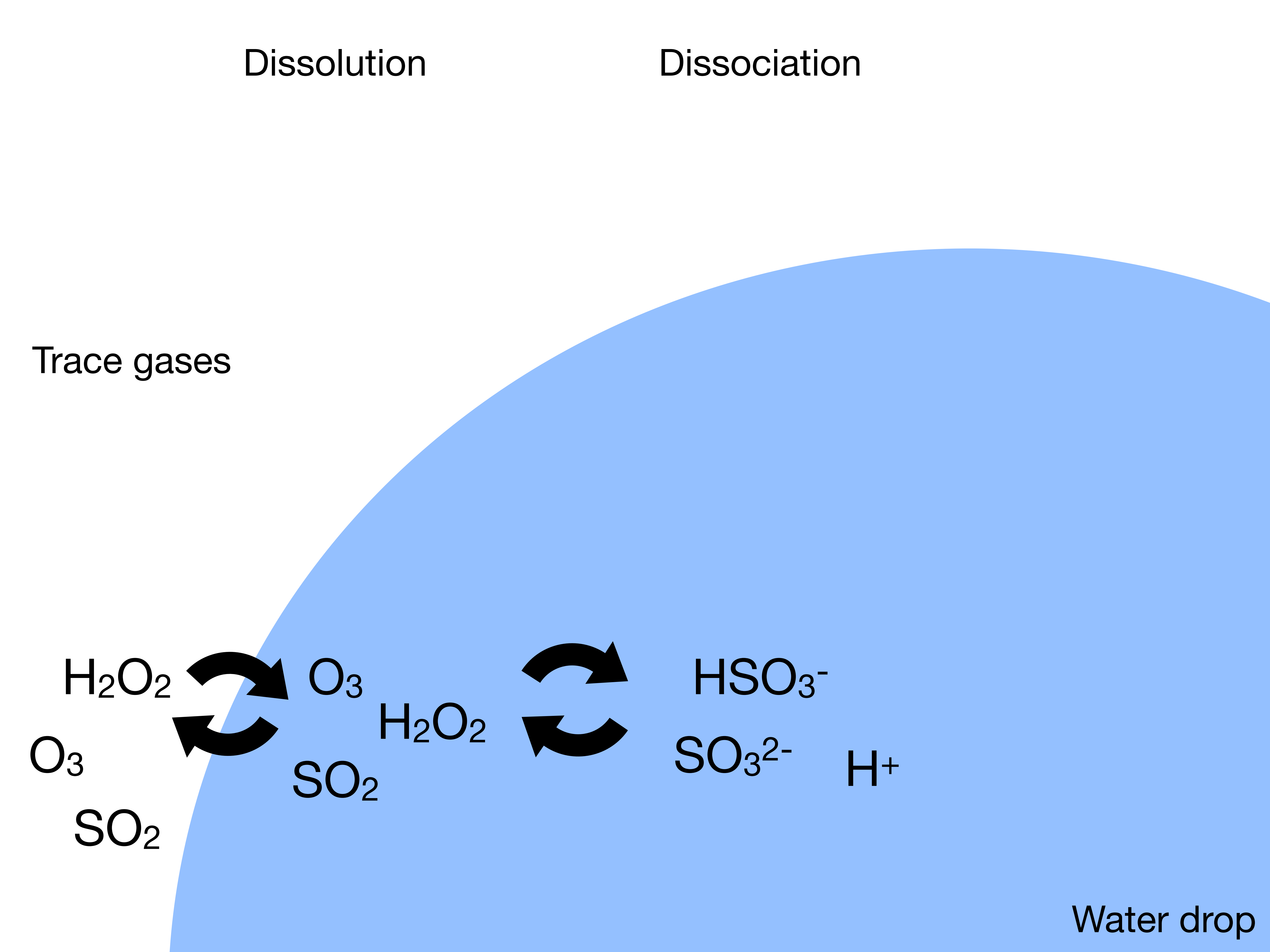
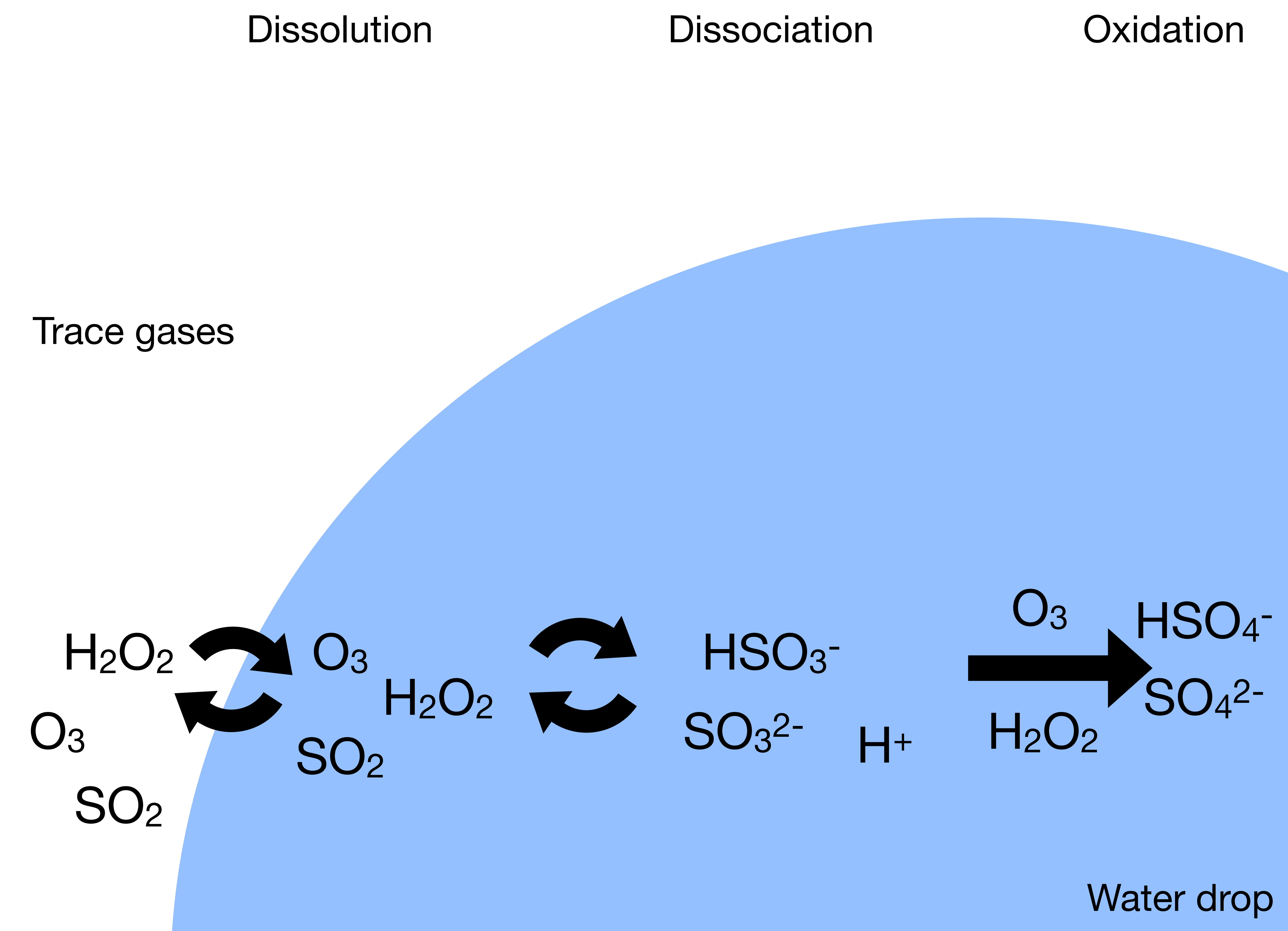
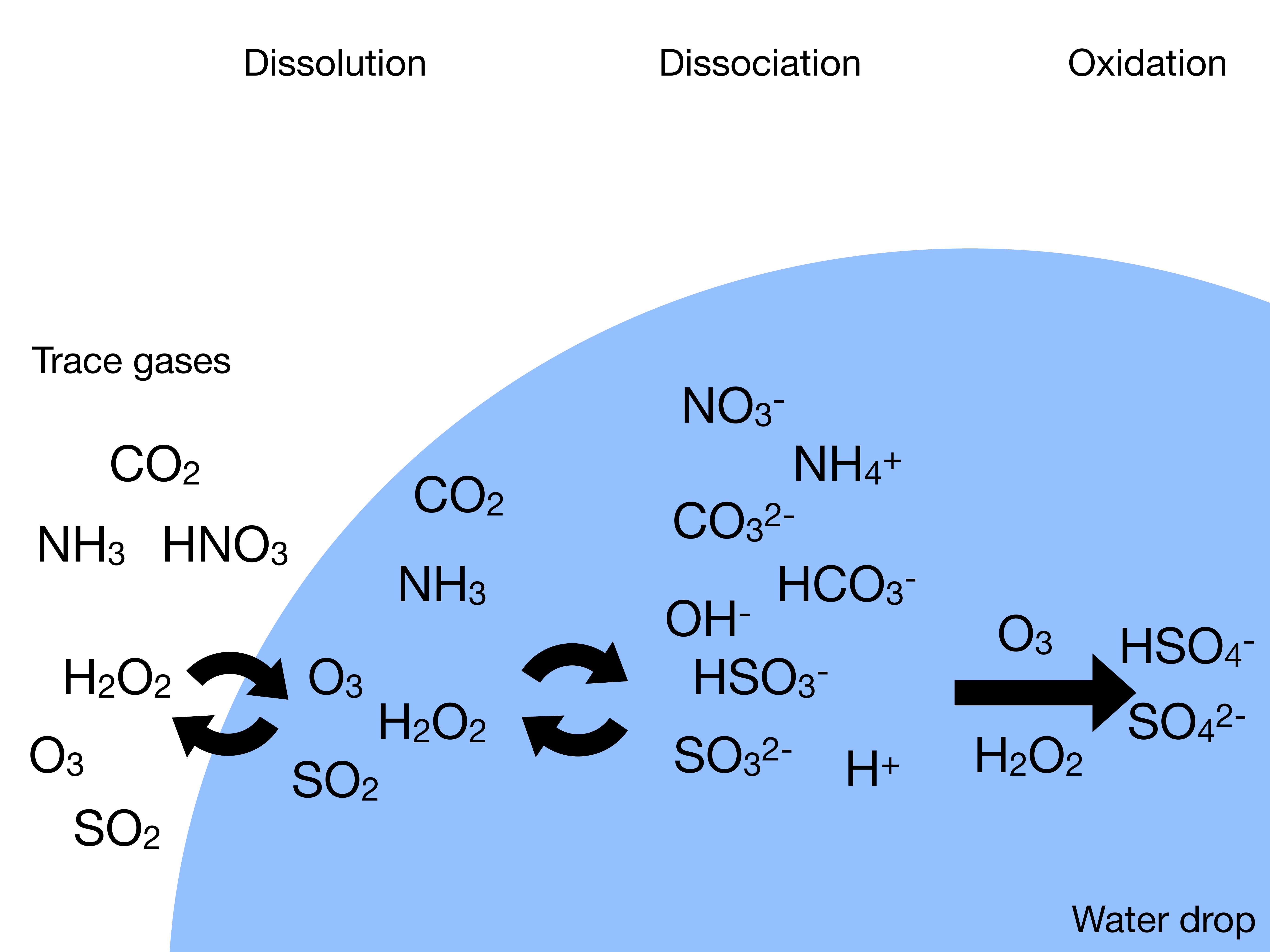

Trace gases
H_2O_2
O_3
SO_2
Water drop

Dissolution

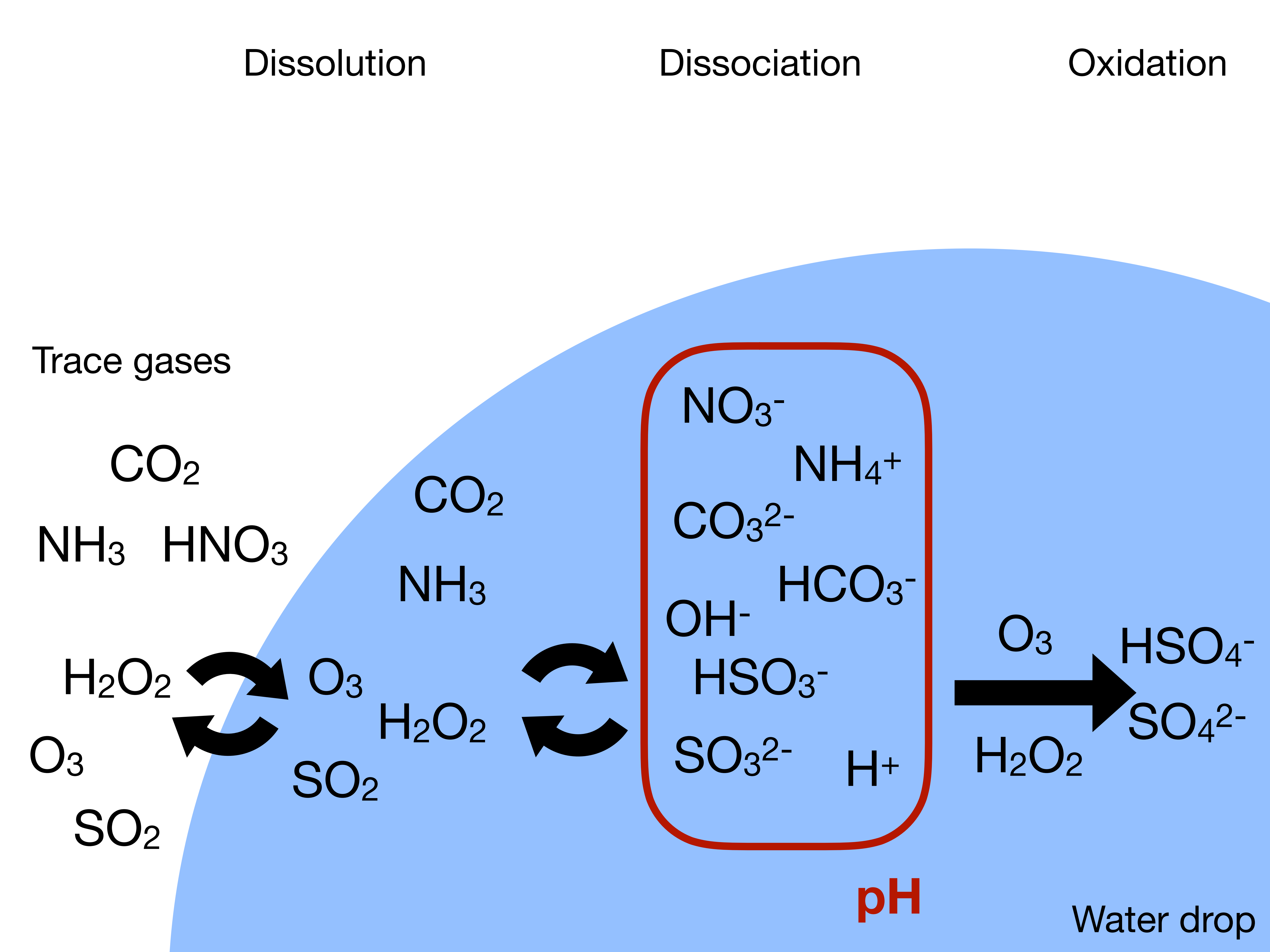


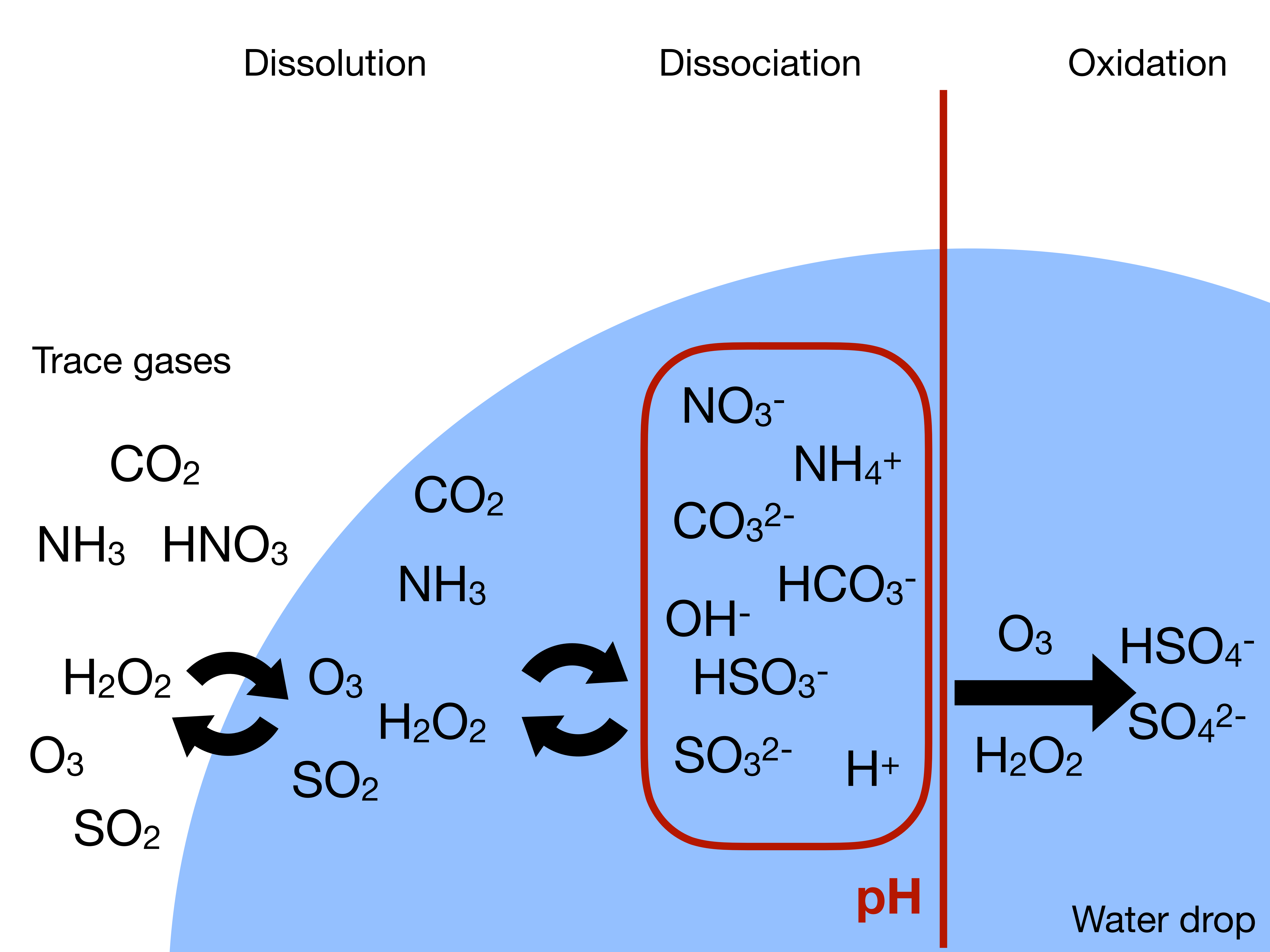

Dissolution
Dissociation
Trace gases
H2O2
O3
SO2
O3
H2O2
SO2
HSO3-
SO32-
H+
Water drop


Dissolution
Dissociation
Oxidation
Trace gases
H_2O_2
O_3
SO_2
O_3
H_2O_2
SO_2
HSO_3^-
SO_3^{2-}
H^+
O_3
H_2O_2
HSO_4^-
SO_4^{2-}
Water drop

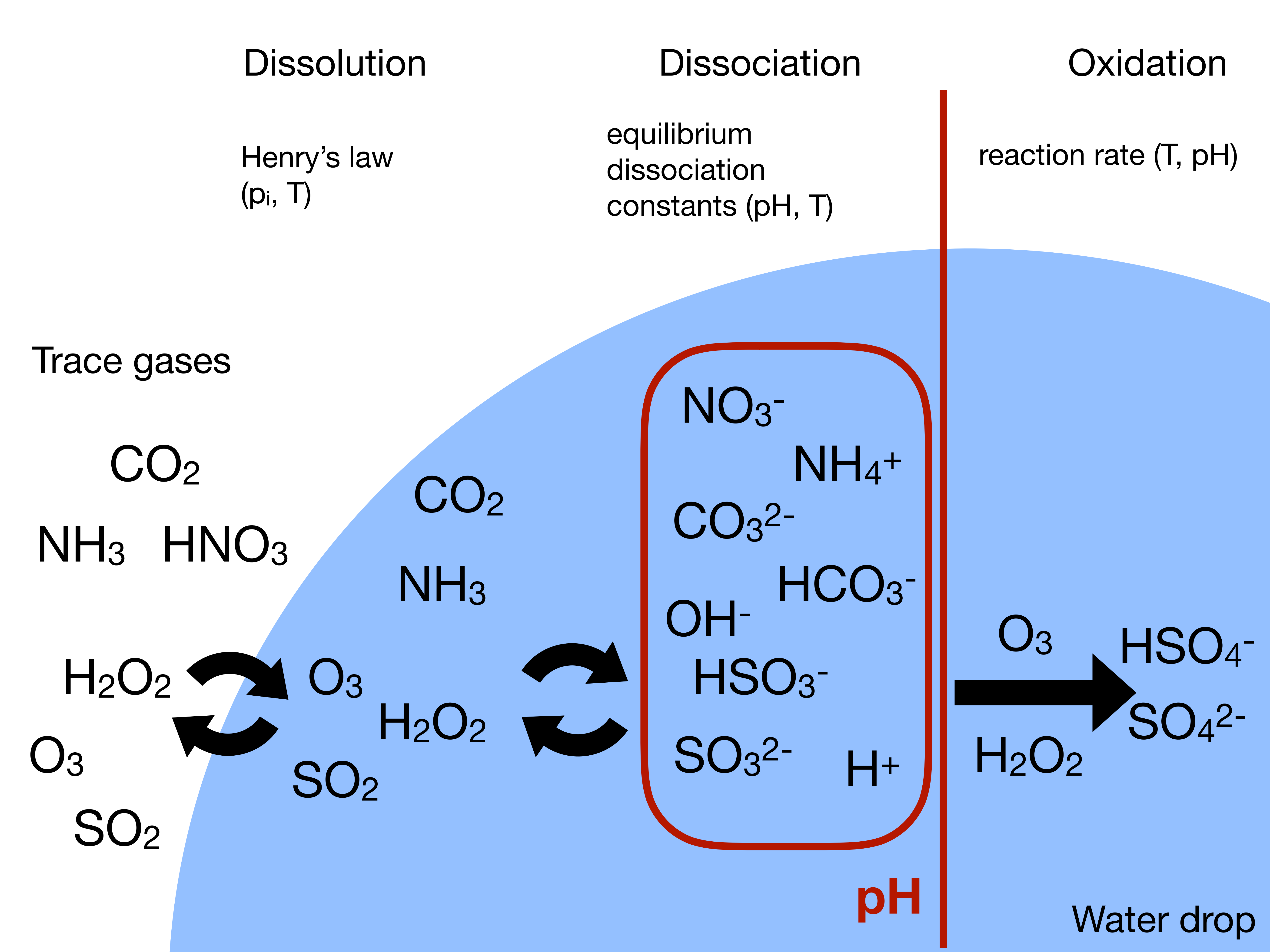


Dissolution
Dissociation
Oxidation
Trace gases
CO_2
NH_3
HNO_3
H_2O_2
O_3
SO_2
CO_2
NH_3
O_3
H_2O_2
SO_2
NO_3^-
NH_4^+
CO_3^{2-}
HCO_3^-
OH^-
HSO_3^-
SO_3^{2-}
H^+
O_3
H_2O_2
HSO_4^-
SO_4^{2-}
Water drop


Dissolution
Dissociation
Oxidation
Trace gases
CO_2
NH_3 HNO_3
H_2O_2
O_3
SO_2
CO_2
NH_3
O_3
H_2O_2
SO_2
NO_3^-
NH_4^+
CO_3^{2-}
HCO_3^-
OH^-
HSO_3^-
SO_3^{2-}
H^+
pH
O_3
H_2O_2
HSO_4^-
SO_4^{2-}
Water drop



Dissolution
Dissociation
Oxidation
Trace gases
CO_2
NH_3 HNO_3
H_2O_2
O_3
SO_2
CO_2
NH_3
O_3
H_2O_2
SO_2
NO_3^-
NH_4^+
CO_3^{2-}
HCO_3^-
OH^-
HSO_3^-
SO_3^{2-}
H^+
pH
O_3
H_2O_2
HSO_4^-
SO_4^{2-}
Water drop


Dissolution
Dissociation
Oxidation
Henry's law
(pi, T)
equilibrium
dissociation
constants (pH, T)
reaction rate (T, pH)
Trace gases
CO2
NH3 HNO3
H2O2
O3
SO2
CO2
NH3
O3
H2O2
SO2
NO3-
NH4+
CO32-
HCO3-
OH-
HSO3-
SO32-
H+
pH
O3
H2O2
HSO4-
SO42-
Water drop

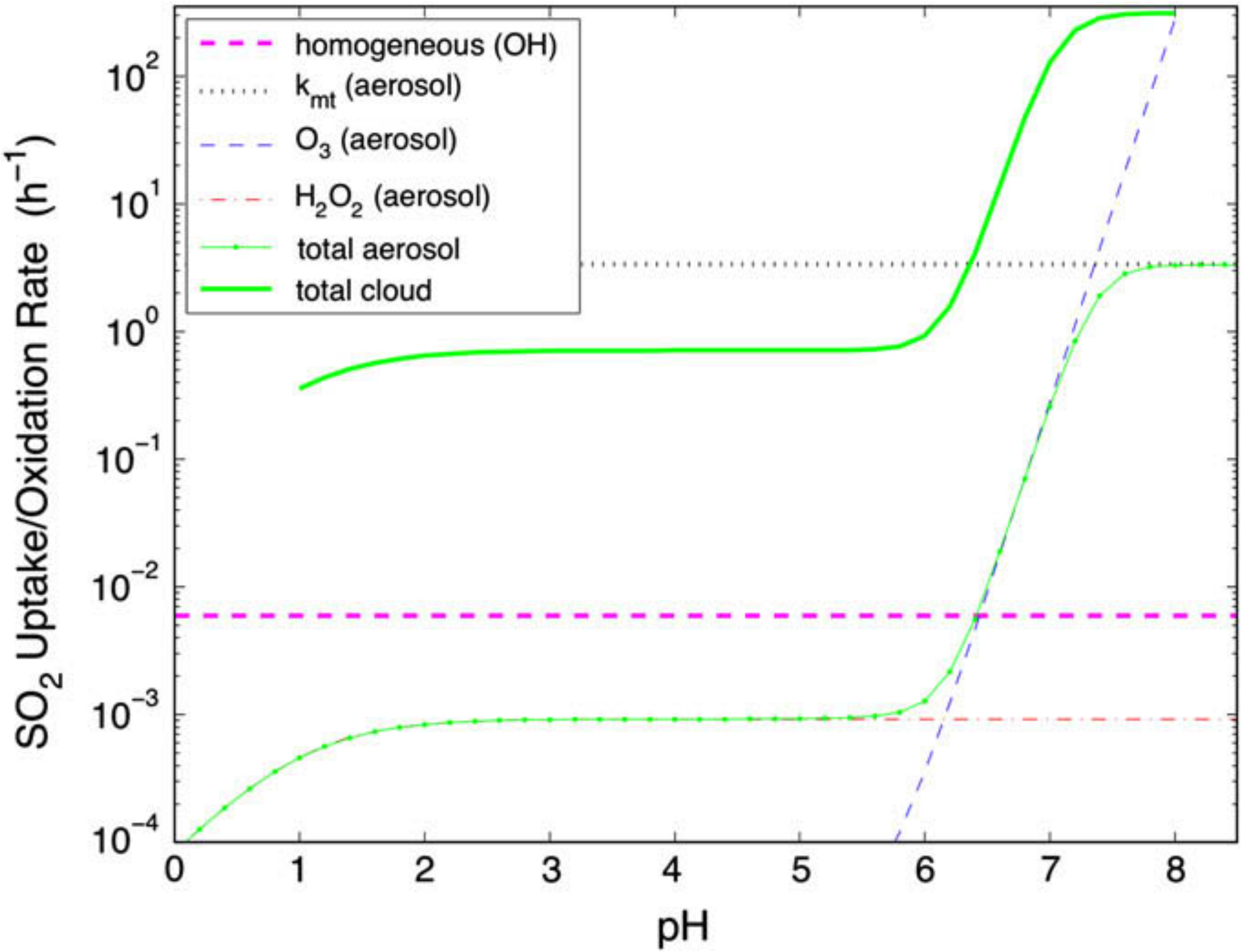
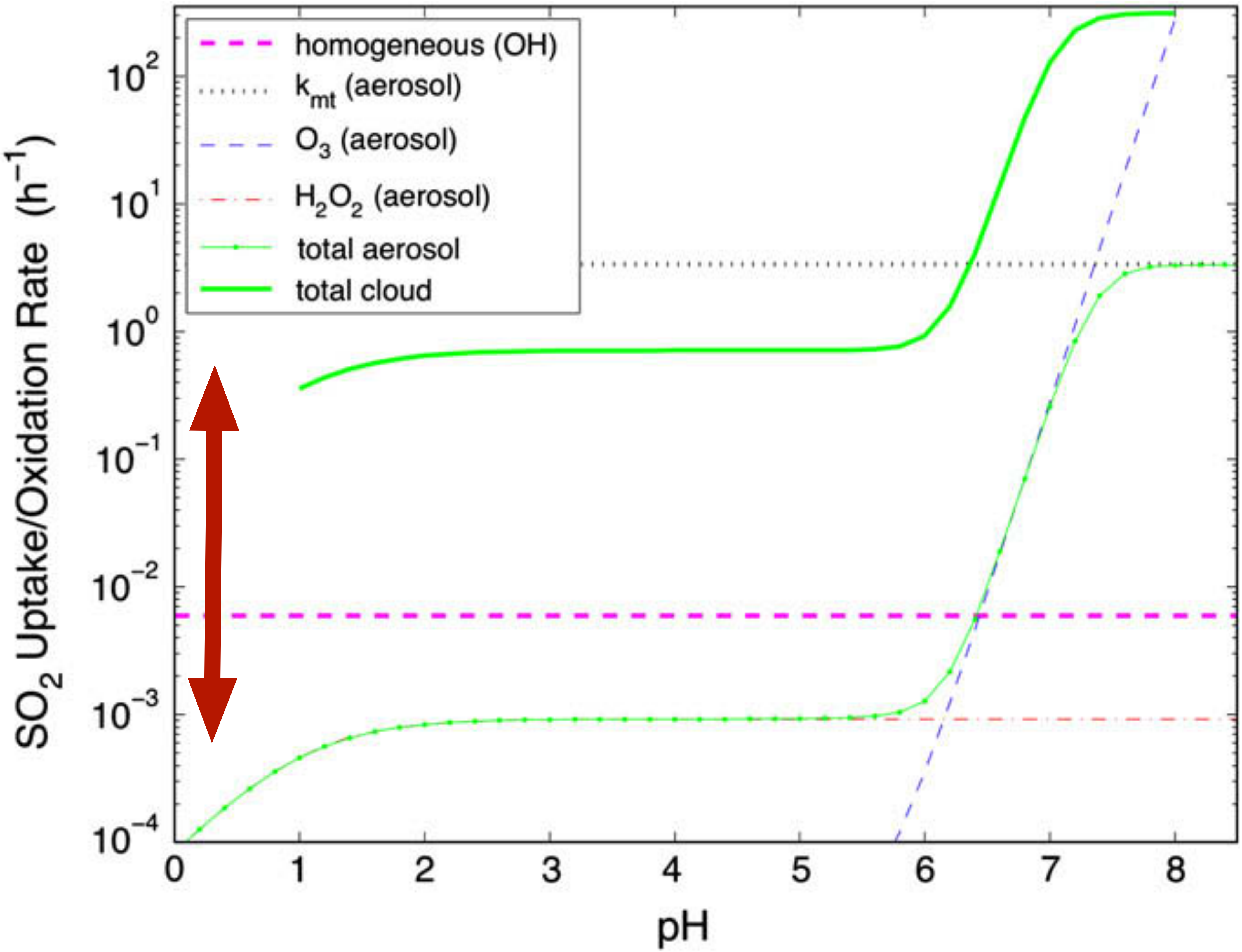


Fig 5 from Faloona 2009



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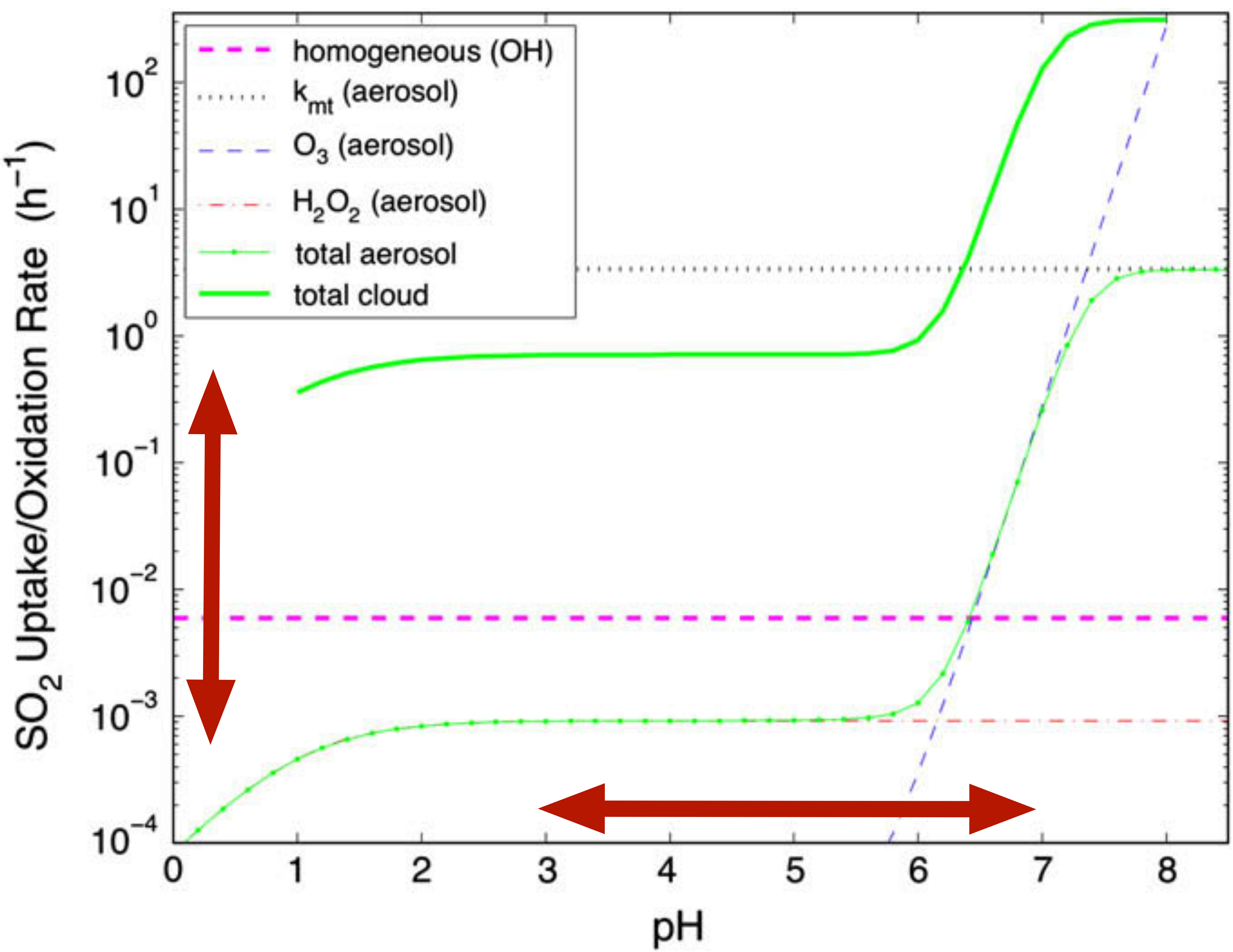

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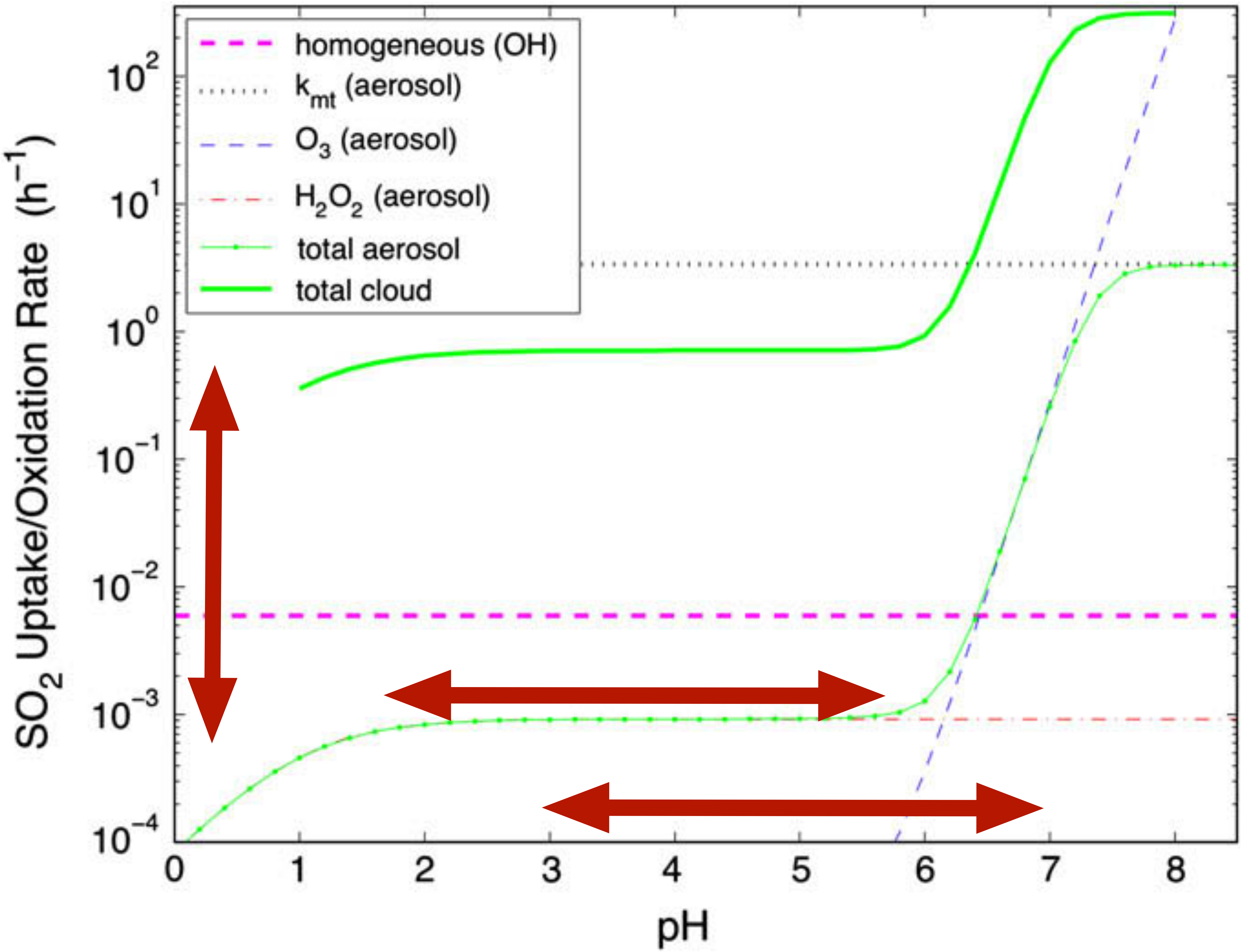

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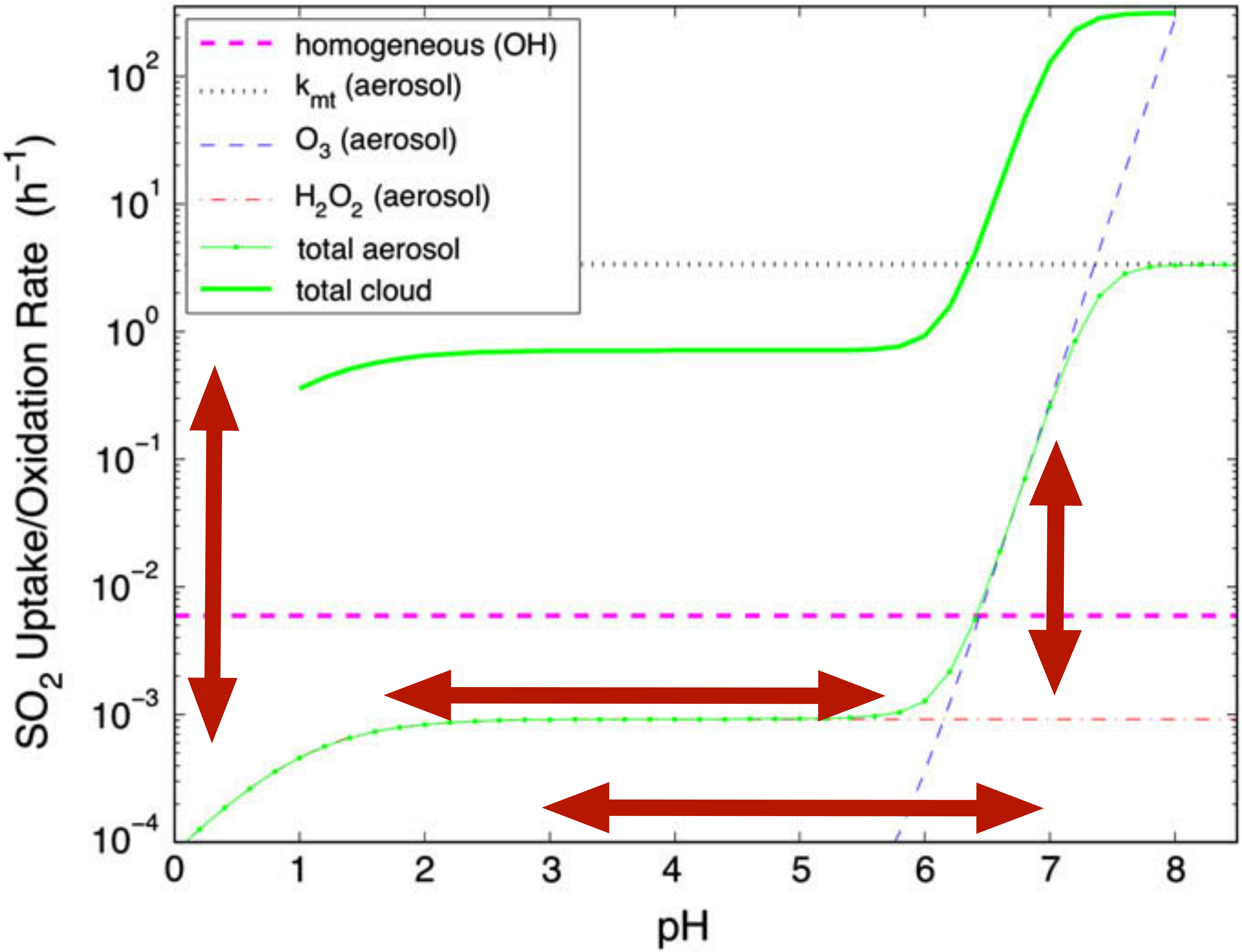

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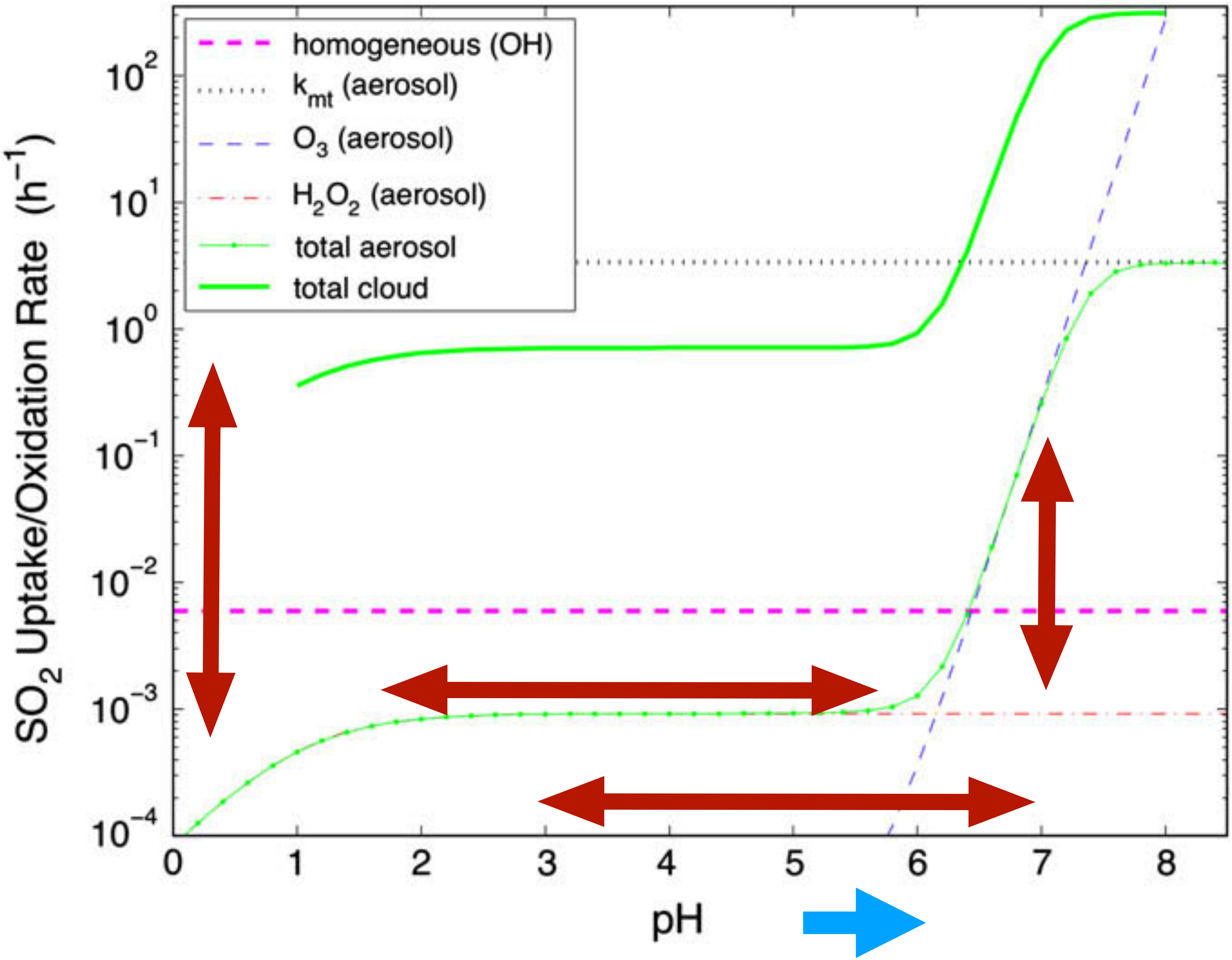
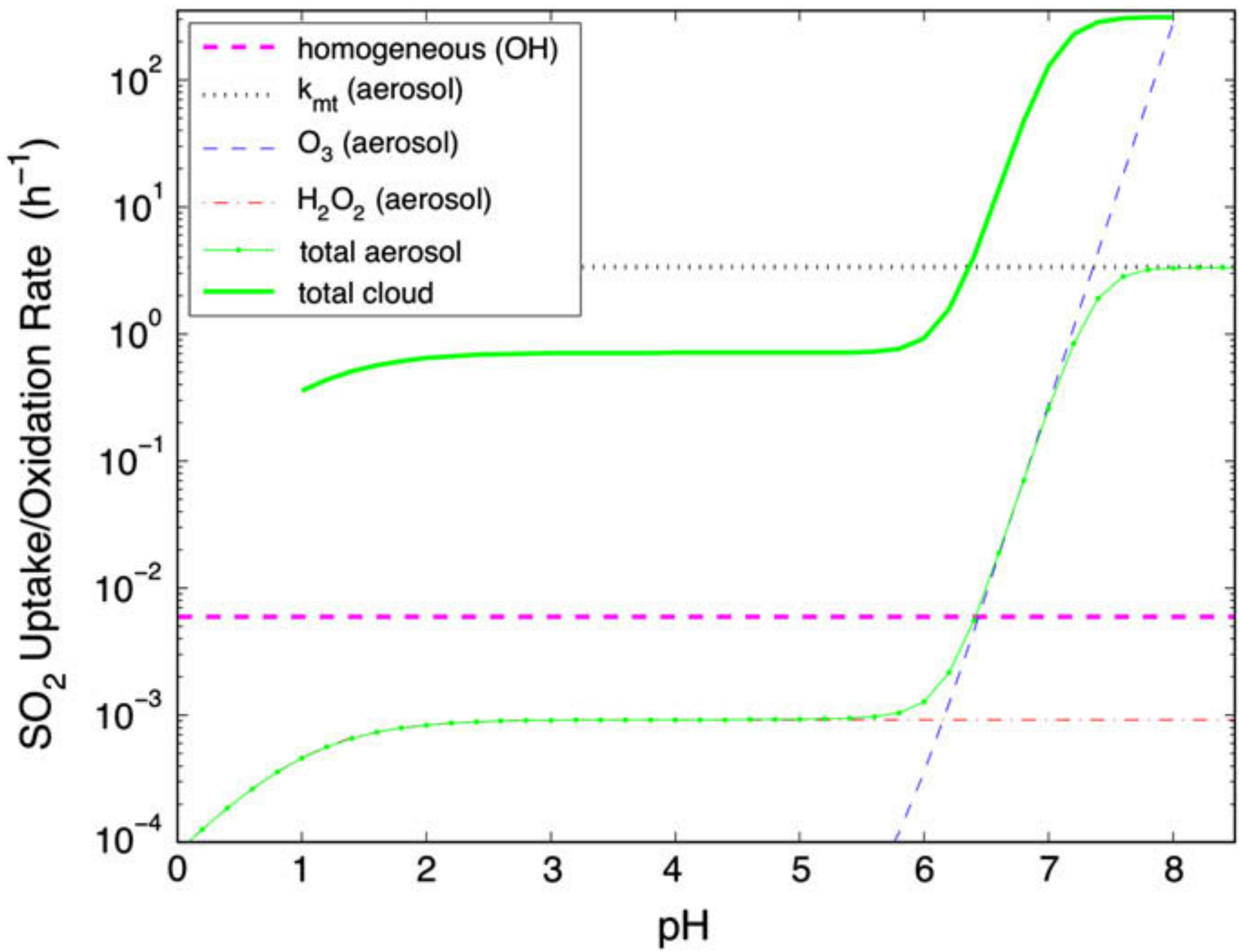


Fig 5 from Faloona 2009

pH is the biggest source of uncertainty:

- what is the chemical composition of droplets
- what is the droplet size distribution



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- example results from a high resolution model
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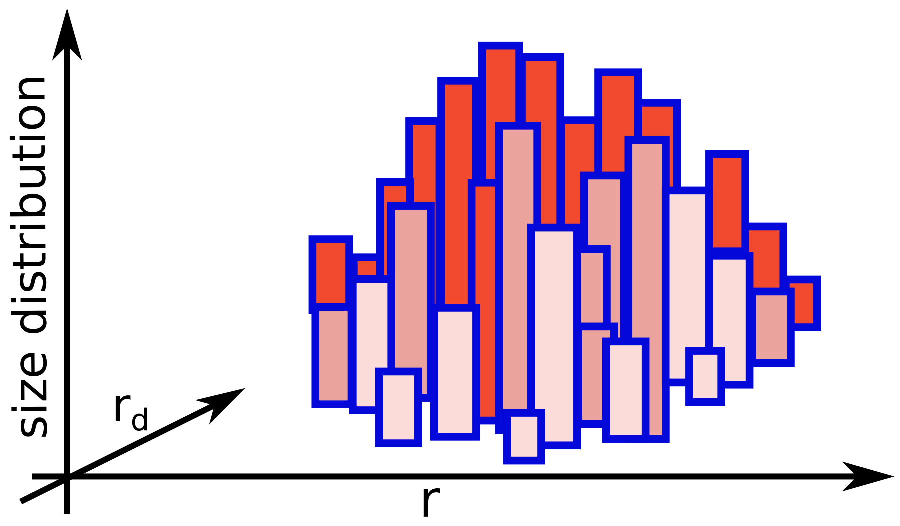
High resolution microphysics + aqueous phase chemistry model

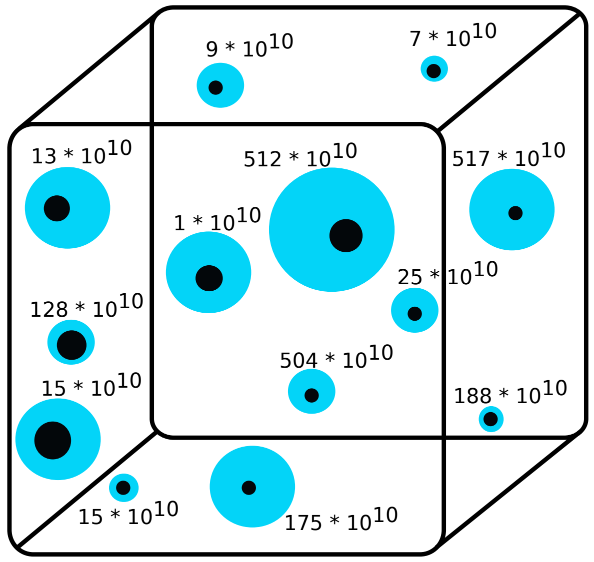
multi-dimensional bin scheme



Ovchinnikov and Easter 2010

vs

Lagrangian scheme



Jaruga and Pawlowska 2018

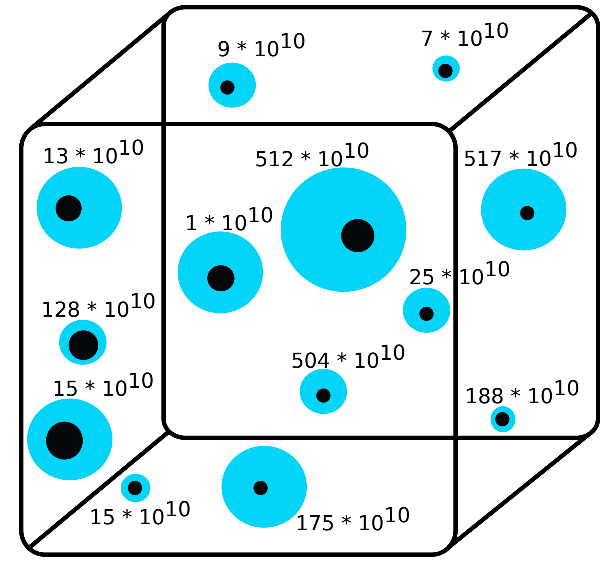
High resolution microphysics + aqueous phase chemistry model

Super-droplet microphysics:

- location (x,y,z)
- wet radius
- dry radius
- hygroscopicity
- multiplicity

= 7

Lagrangian scheme



Jaruga and Pawlowska 2018

Shima et al. 2009

Arabas et al. 2015

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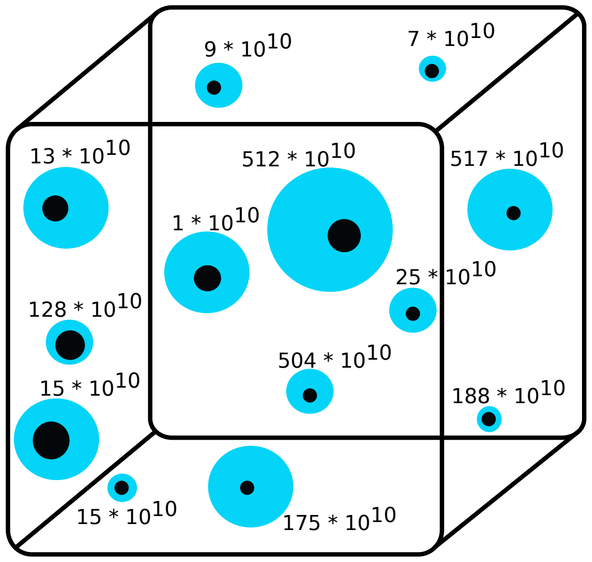
Lagrangian scheme

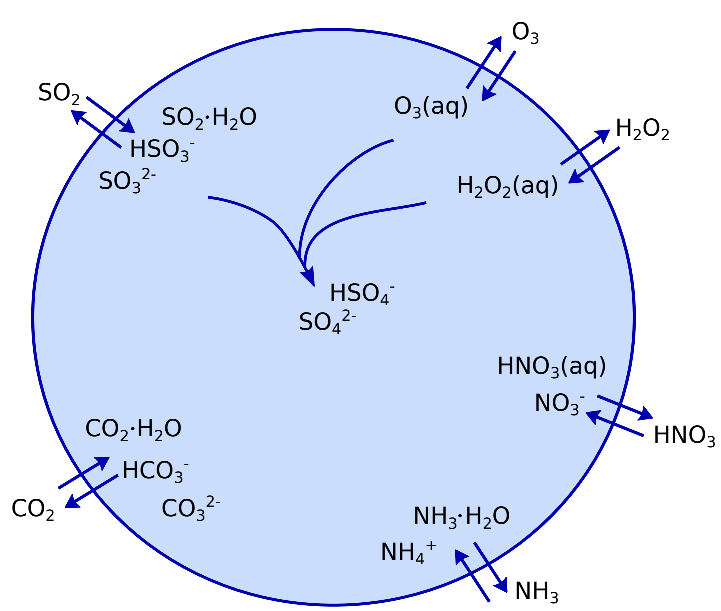


Jaruga and Pawlowska 2018

Super-droplet aq. chemistry:

- mass of each chemical compound

= 8



Adiabatic parcel simulations - Kreidenweis 2003 setup

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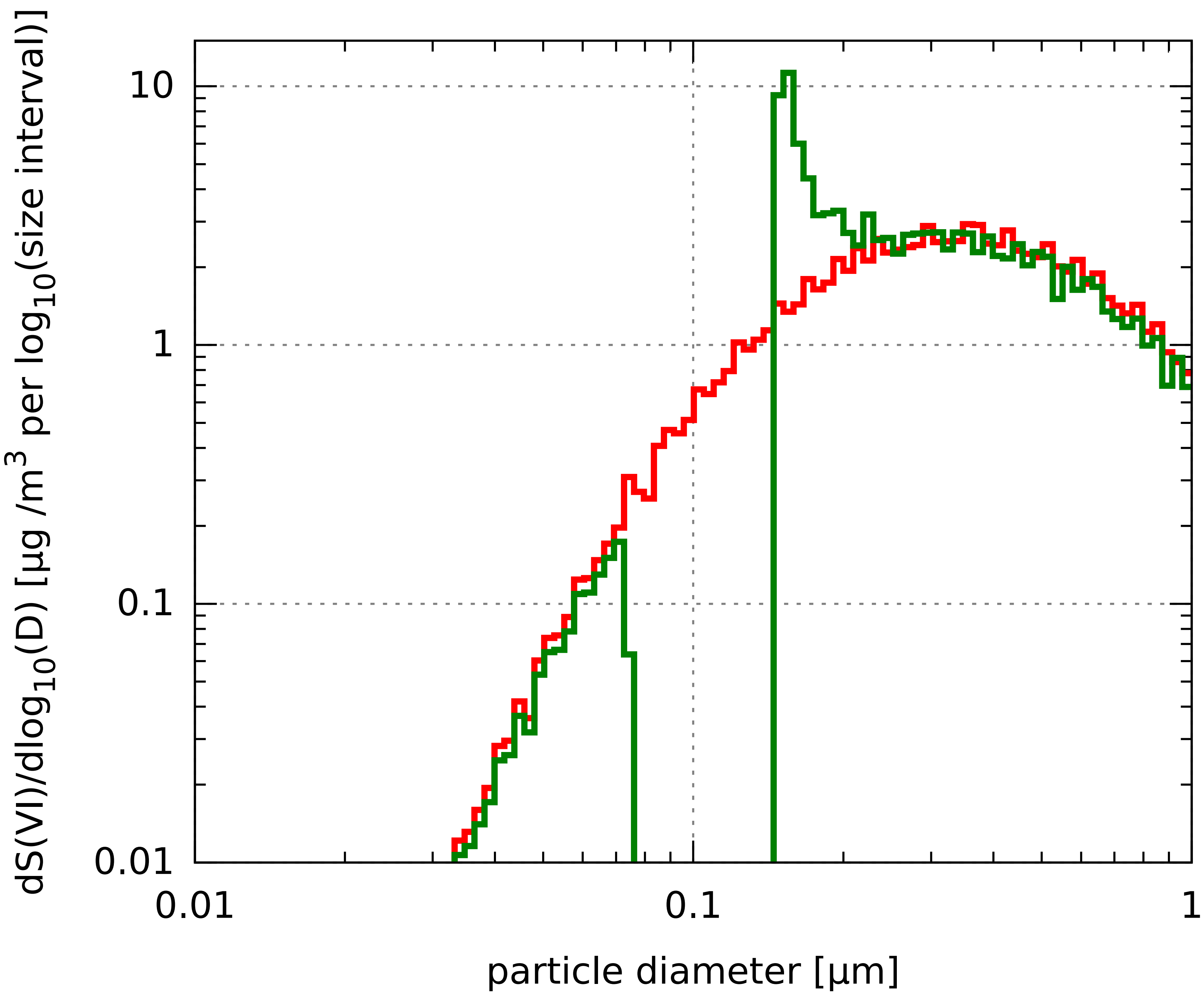

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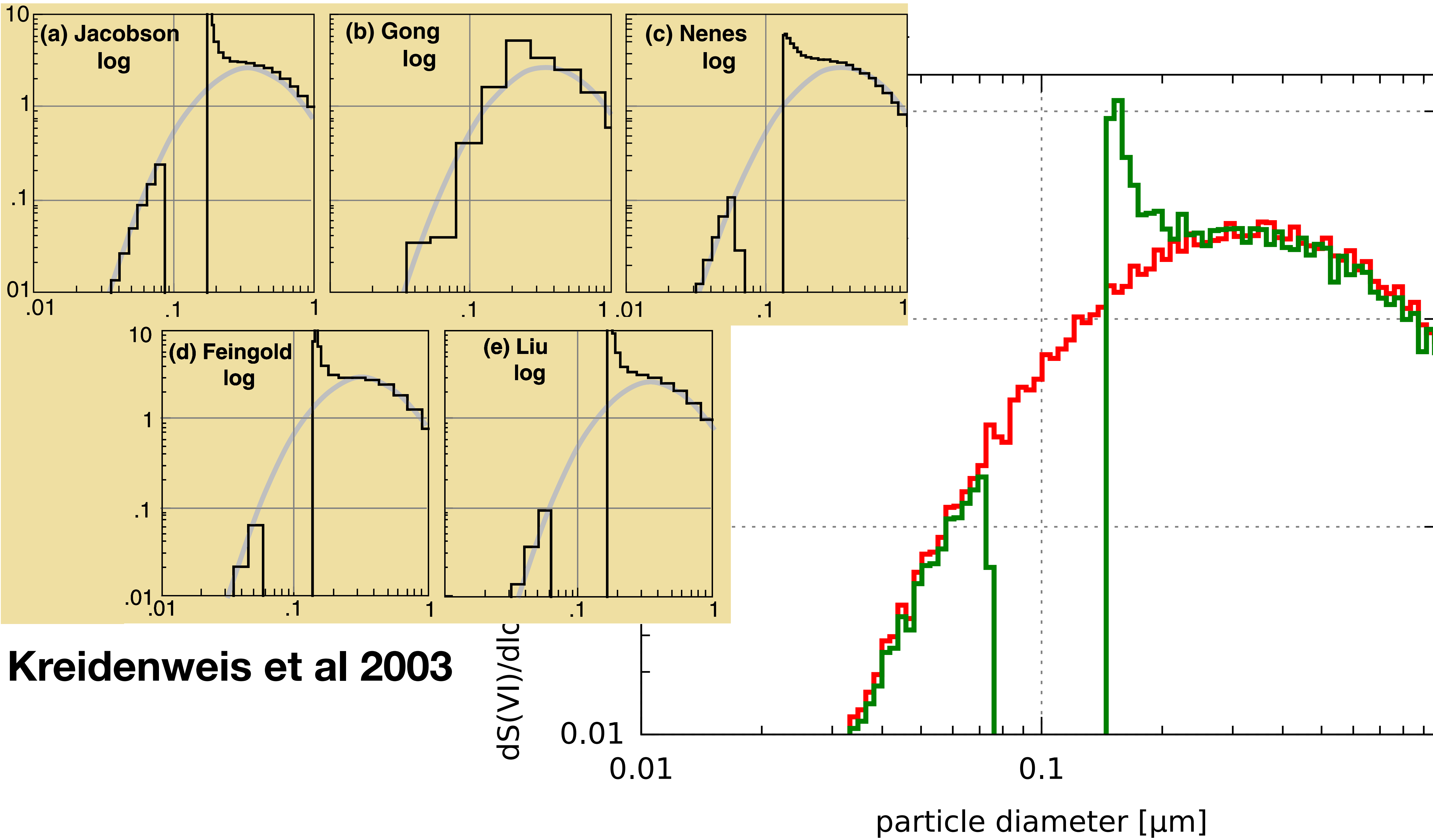
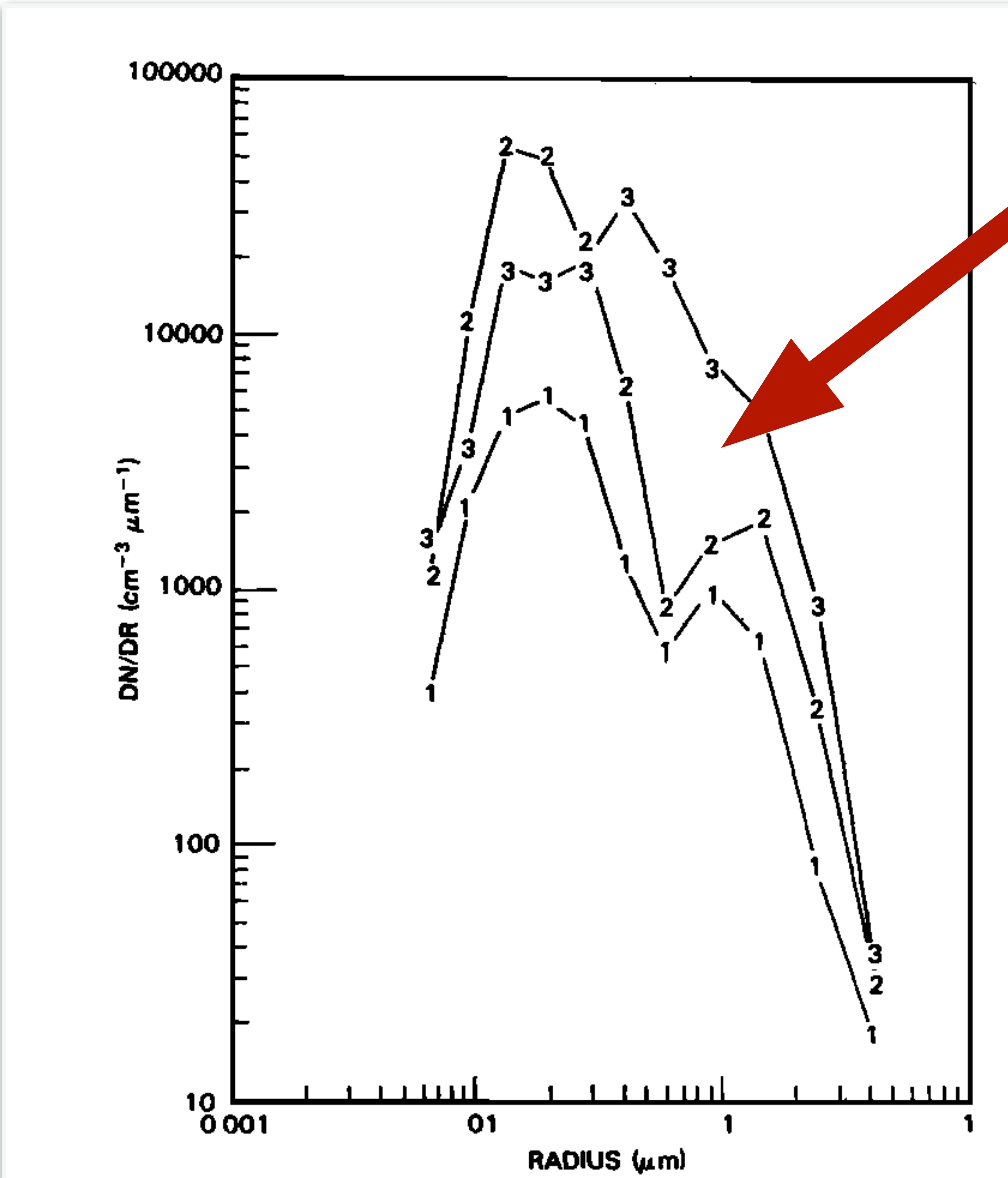
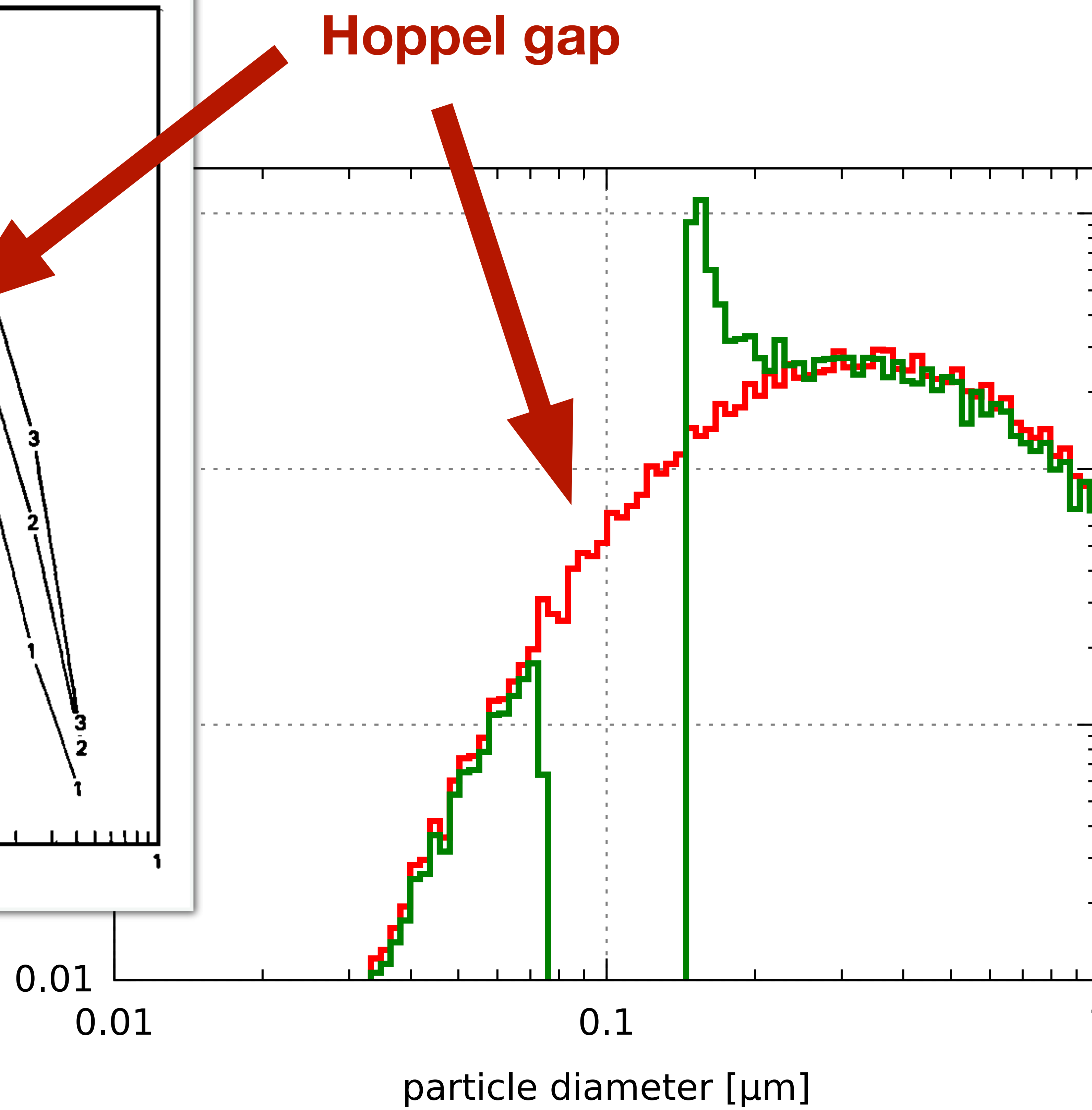


Kreidenweis et al 2003

Adiabatic parcel simulations - Kreidenweis 2003 setup

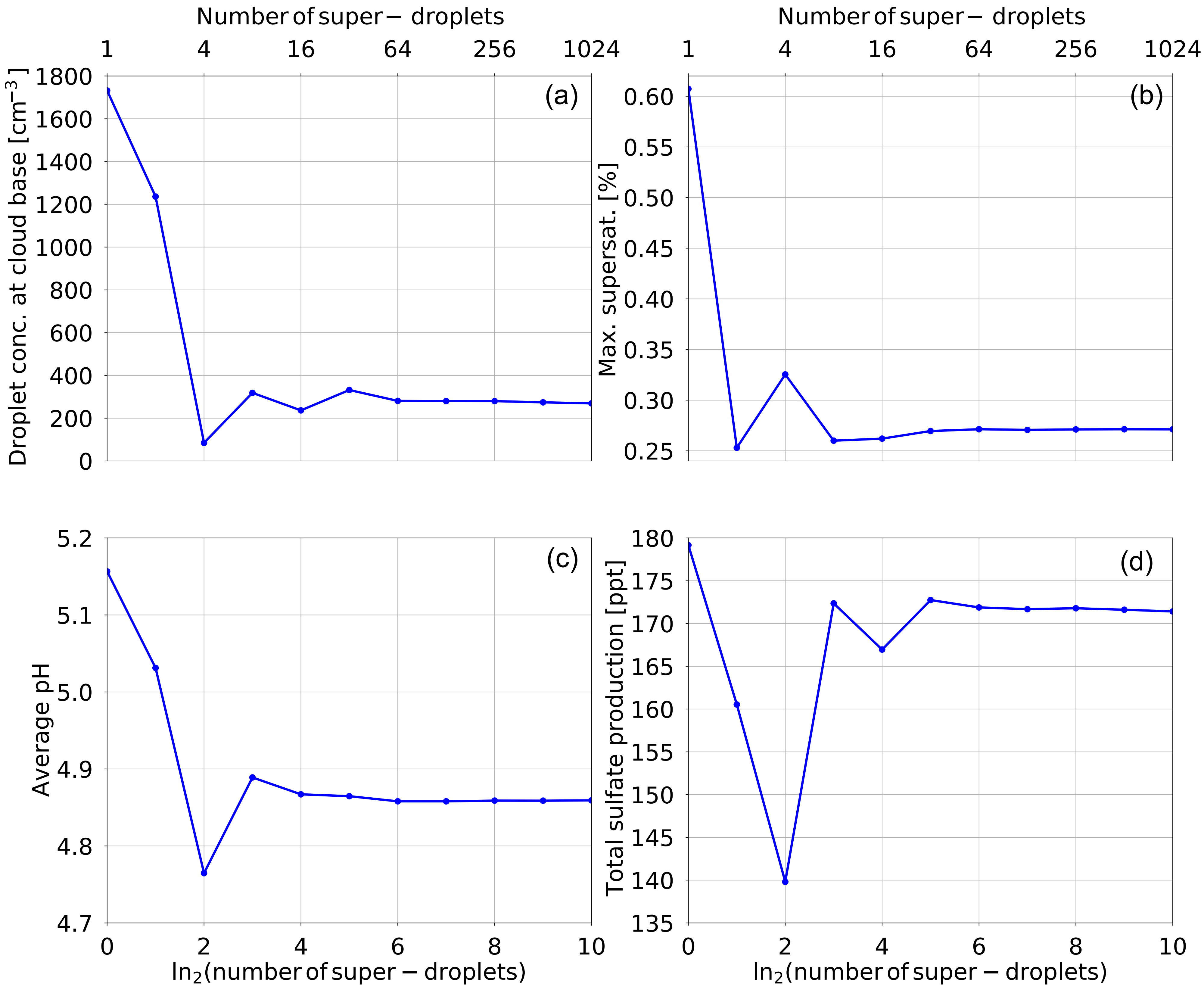


Hoppel et al 1986



Adiabatic parcel simulations - Kreidenweis 2003 setup

275 – 358 cm $^{-3}$



2D prescribed flow simulations - 8th ICMW case 1; Muhlbauer et al 2013

collisions + aqueous phase chemistry

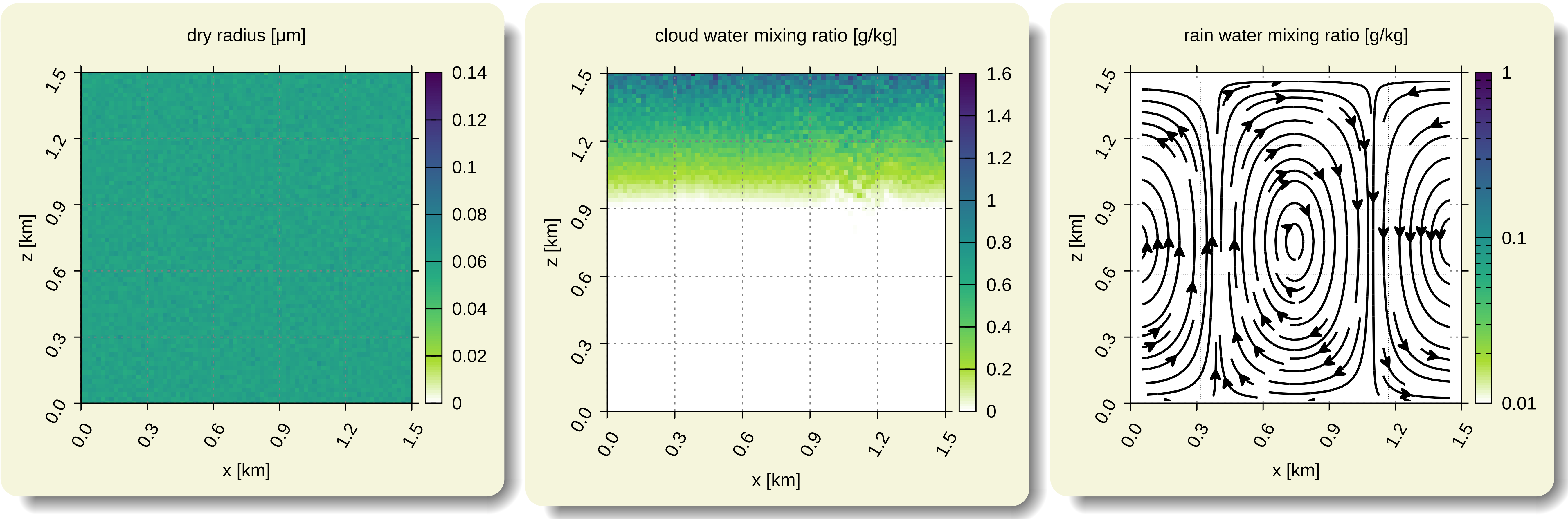
Factor	Value	Units
Number of super-droplets	256	no. per grid cell
Model time step	1	s
Particle-based scheme time step	0.1	s
Dry air potential temperature at $t = 0$	289	K
Water vapour mixing ratio at $t = 0$	7.5	$g\,kg^{-1}$
Pressure at $z = 0$	1015	hPa
Median radius	0.05	µm
Geometric standard deviation	1.8	–
Total aerosol number concentration	50	cm^{-3}
Dry particle density	1.8	$g\,cm^{3}$
Hygroscopicity	0.61	–
Concentration of SO_2 at $t = 0$	0.2	ppbv
Concentration of O_3 at $t = 0$	25	ppbv
Concentration of H_2O_2 at $t = 0$	0.4	ppbv
Concentration of CO_2 at $t = 0$	360	ppmv
Concentration of HNO_3 at $t = 0$	0.1	ppbv
Concentration of NH_3 at $t = 0$	0.1	ppbv

convergence

“clean”

maritime

2D prescribed flow simulations - 8thICMW case 1; Muhlbauer et al 2013



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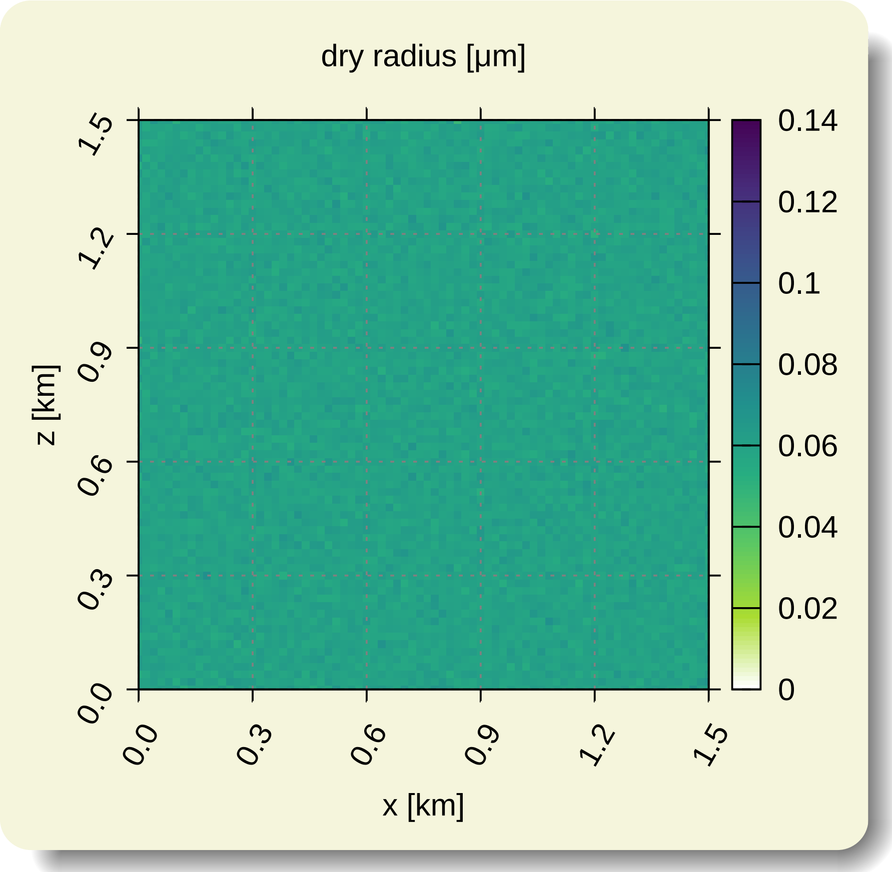
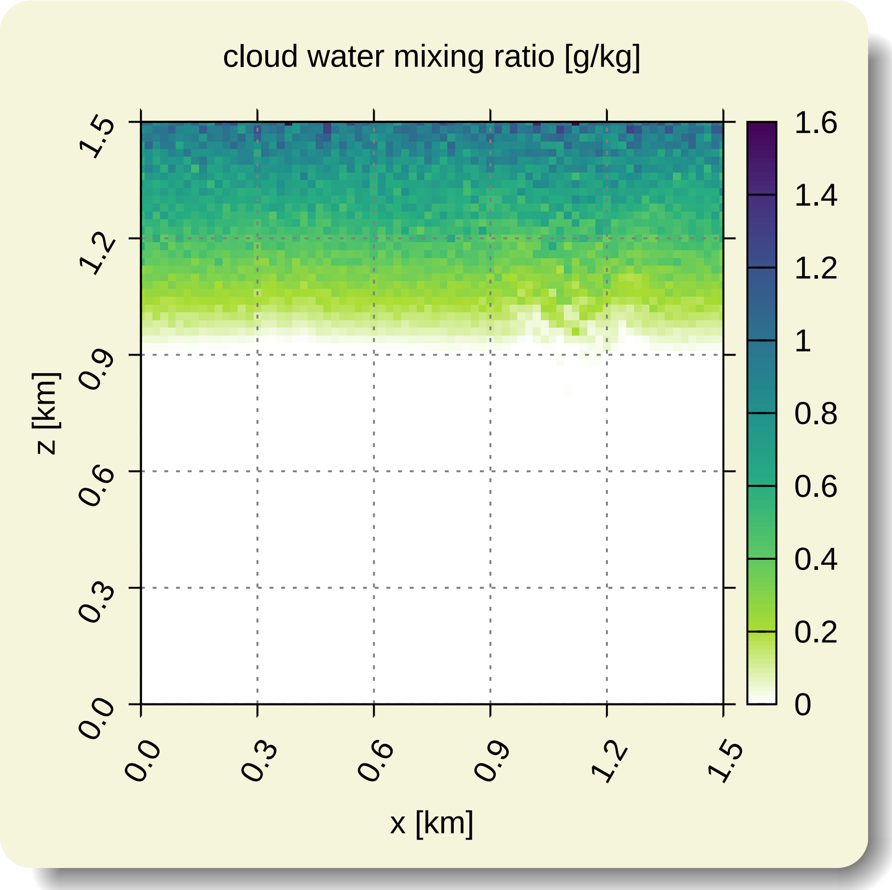
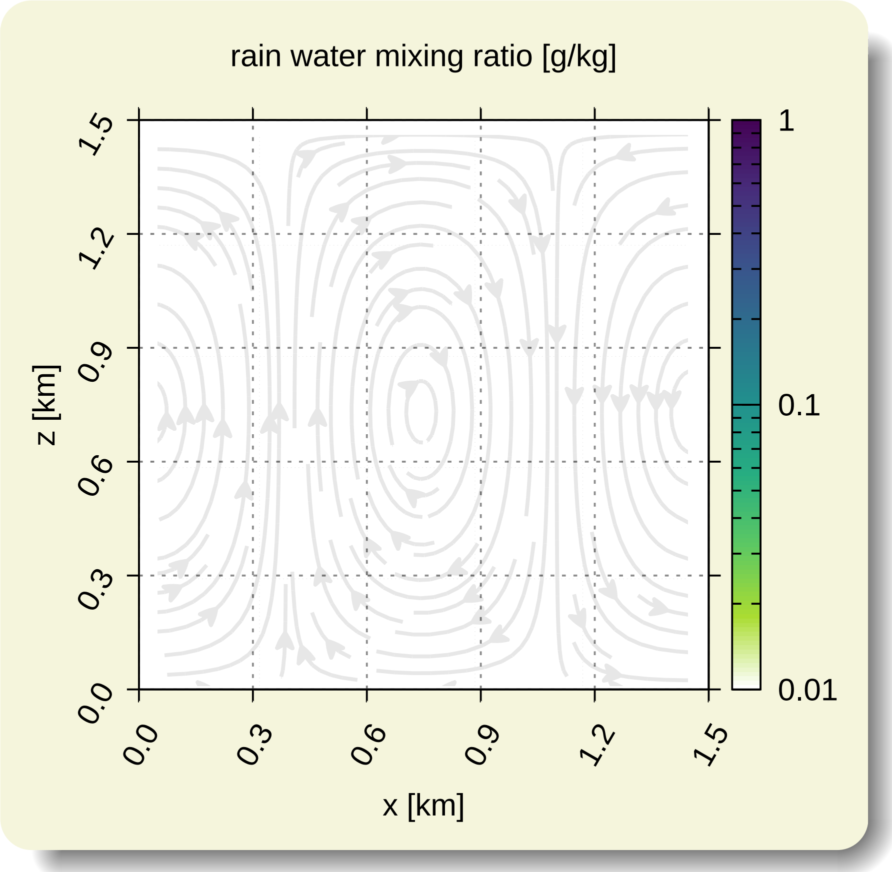
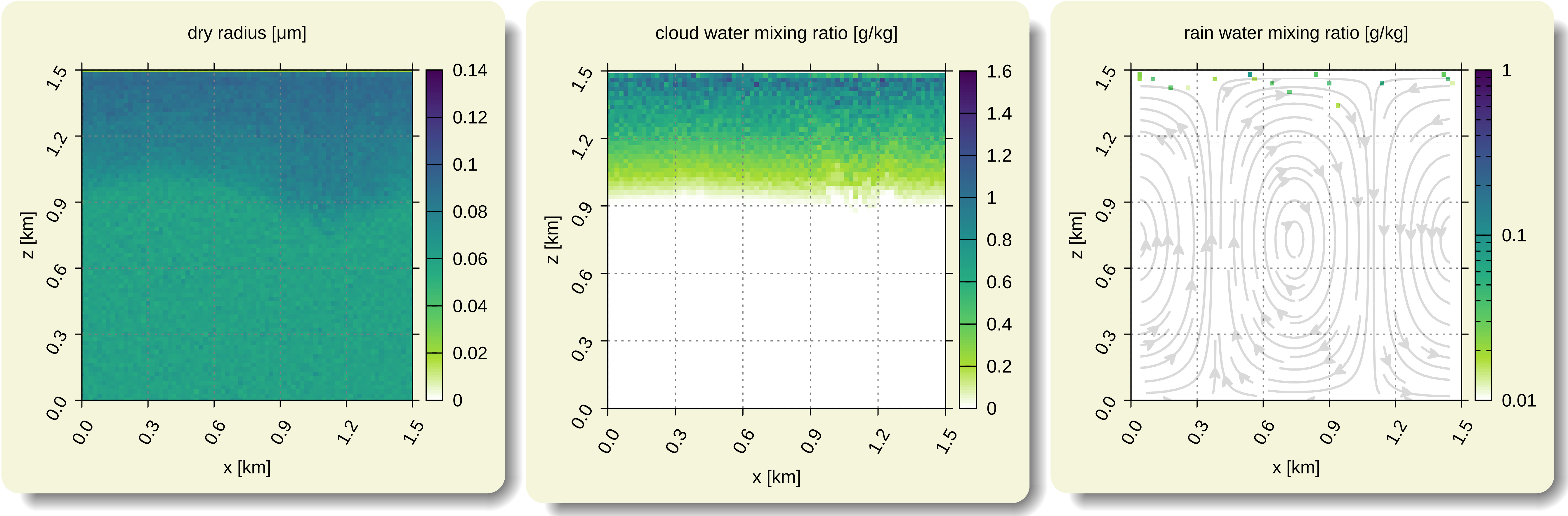






2D prescribed flow simulations - 8thICMW case 1; Muhlbauer et al 2013



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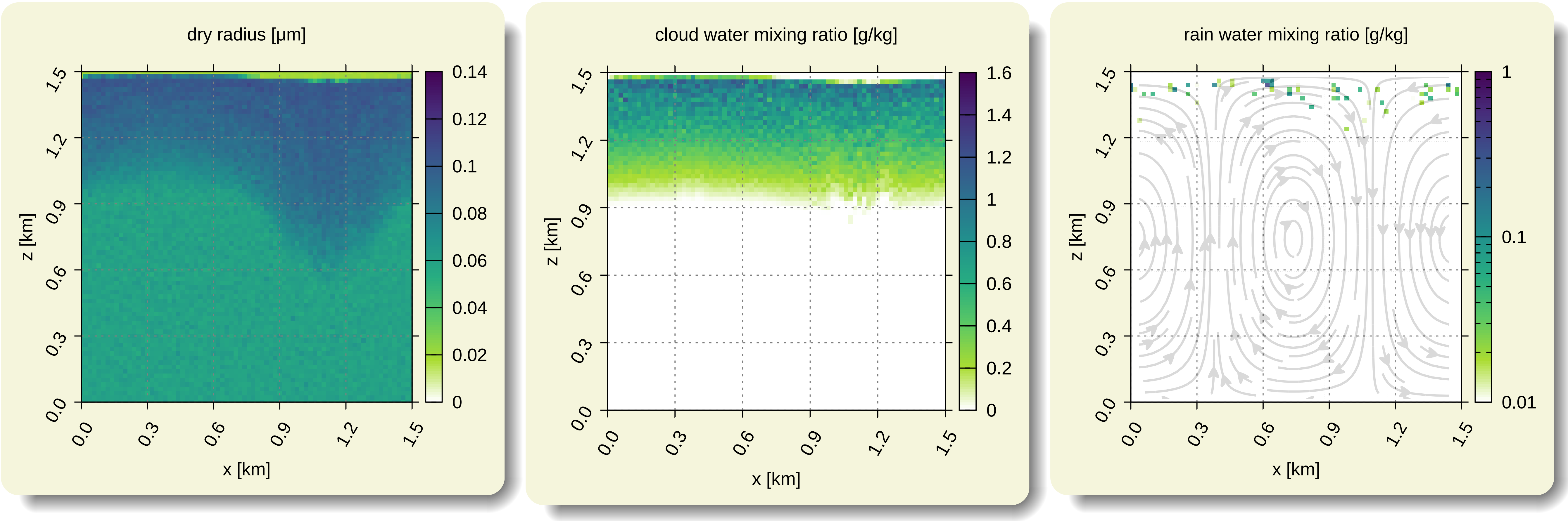

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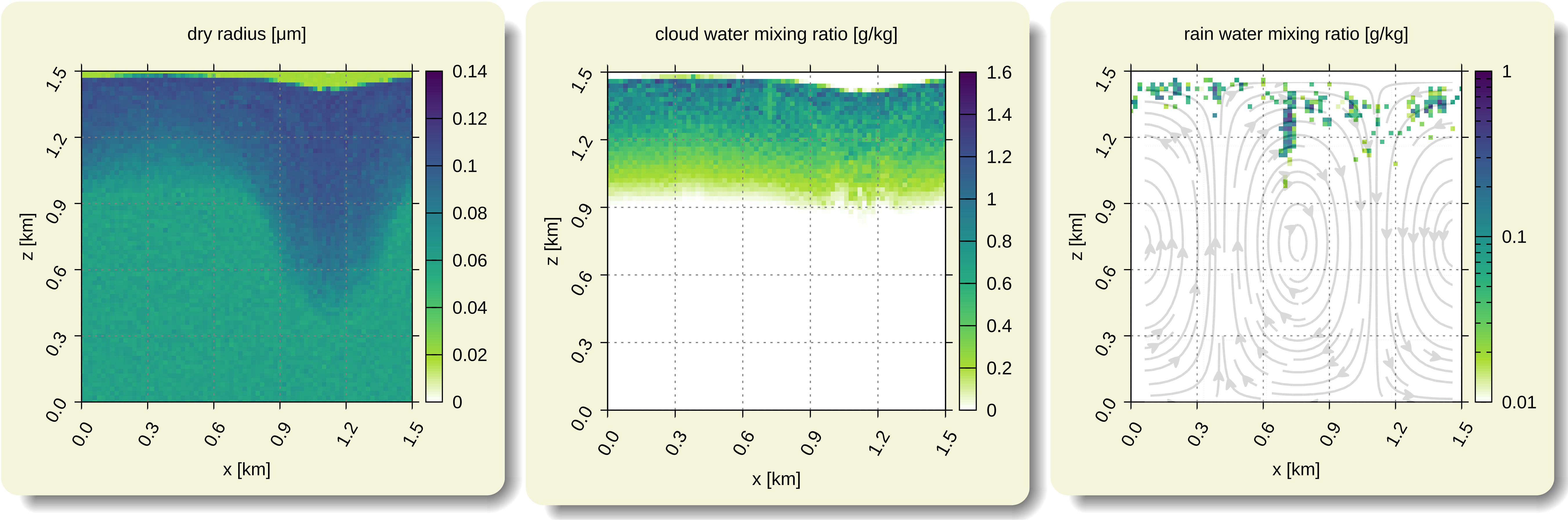

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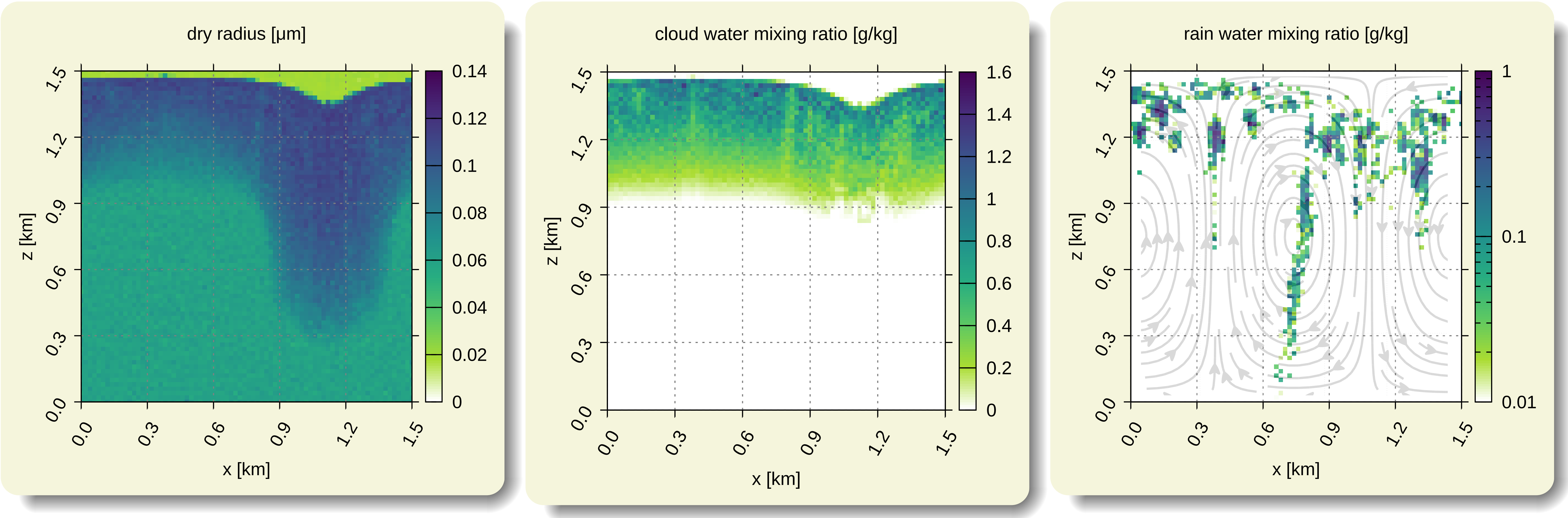

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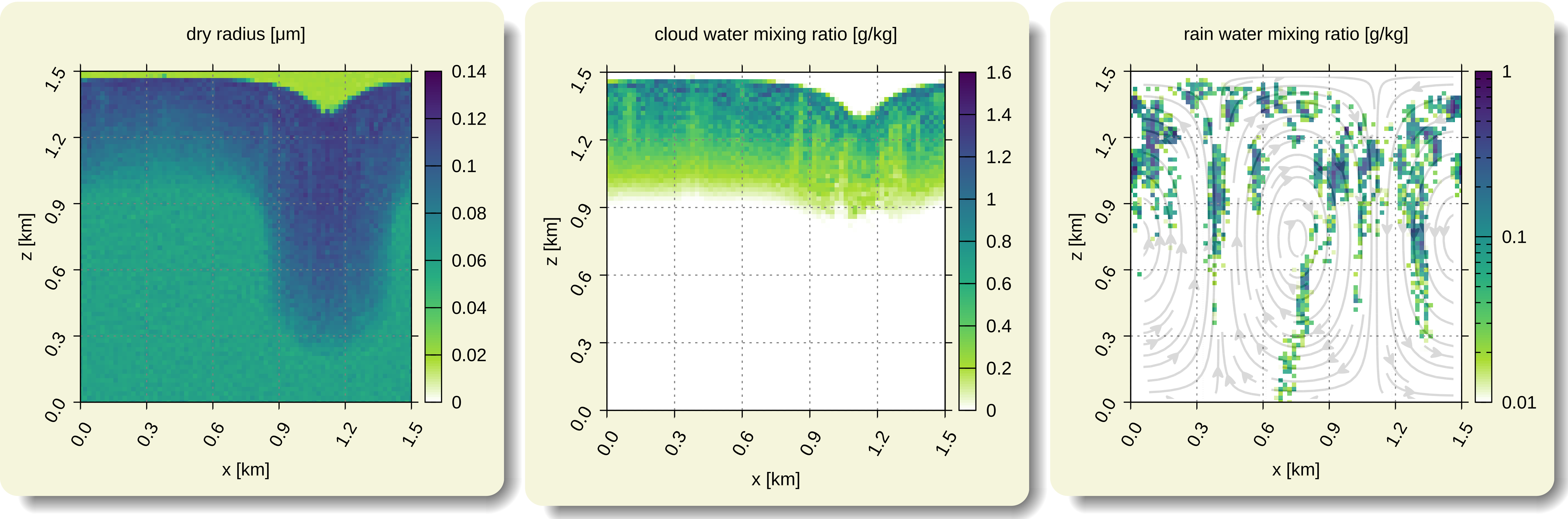
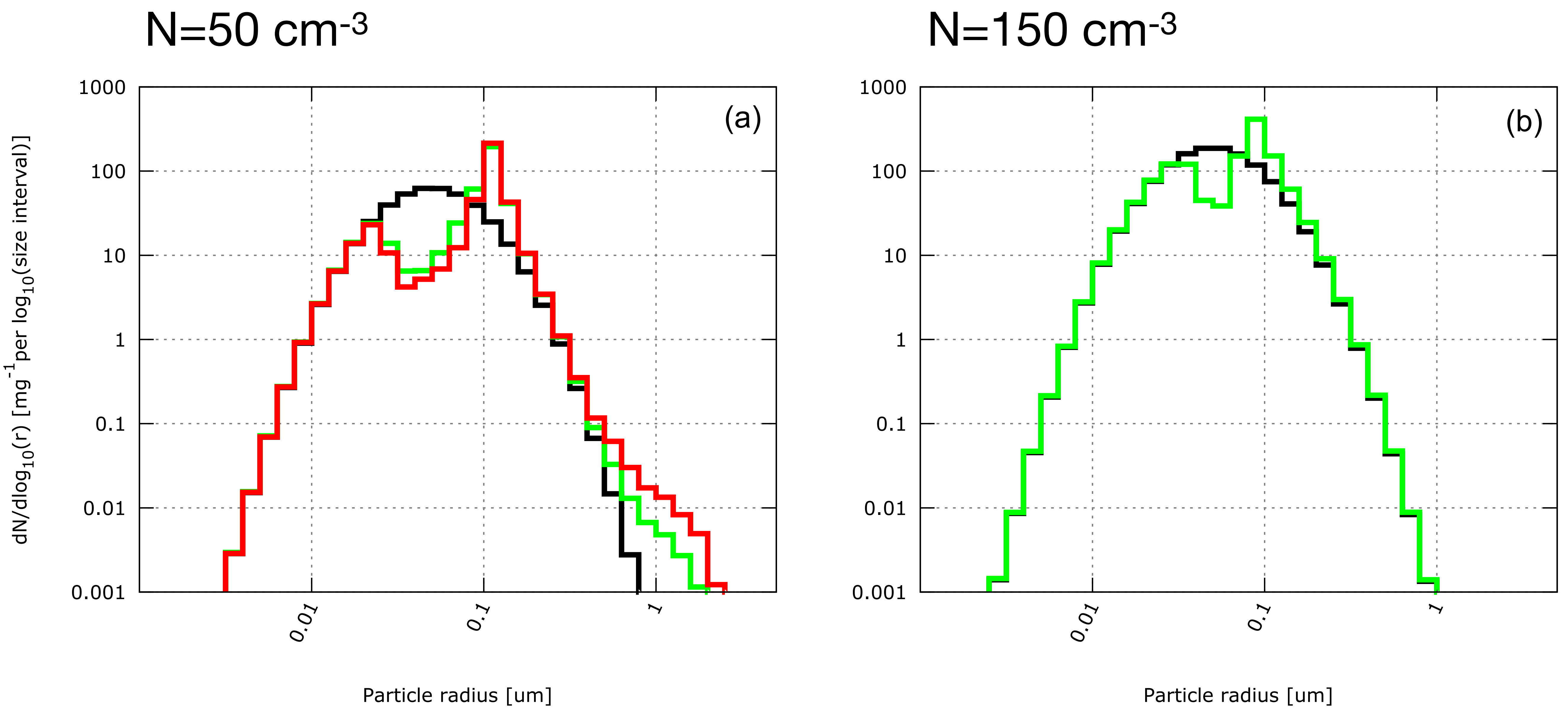
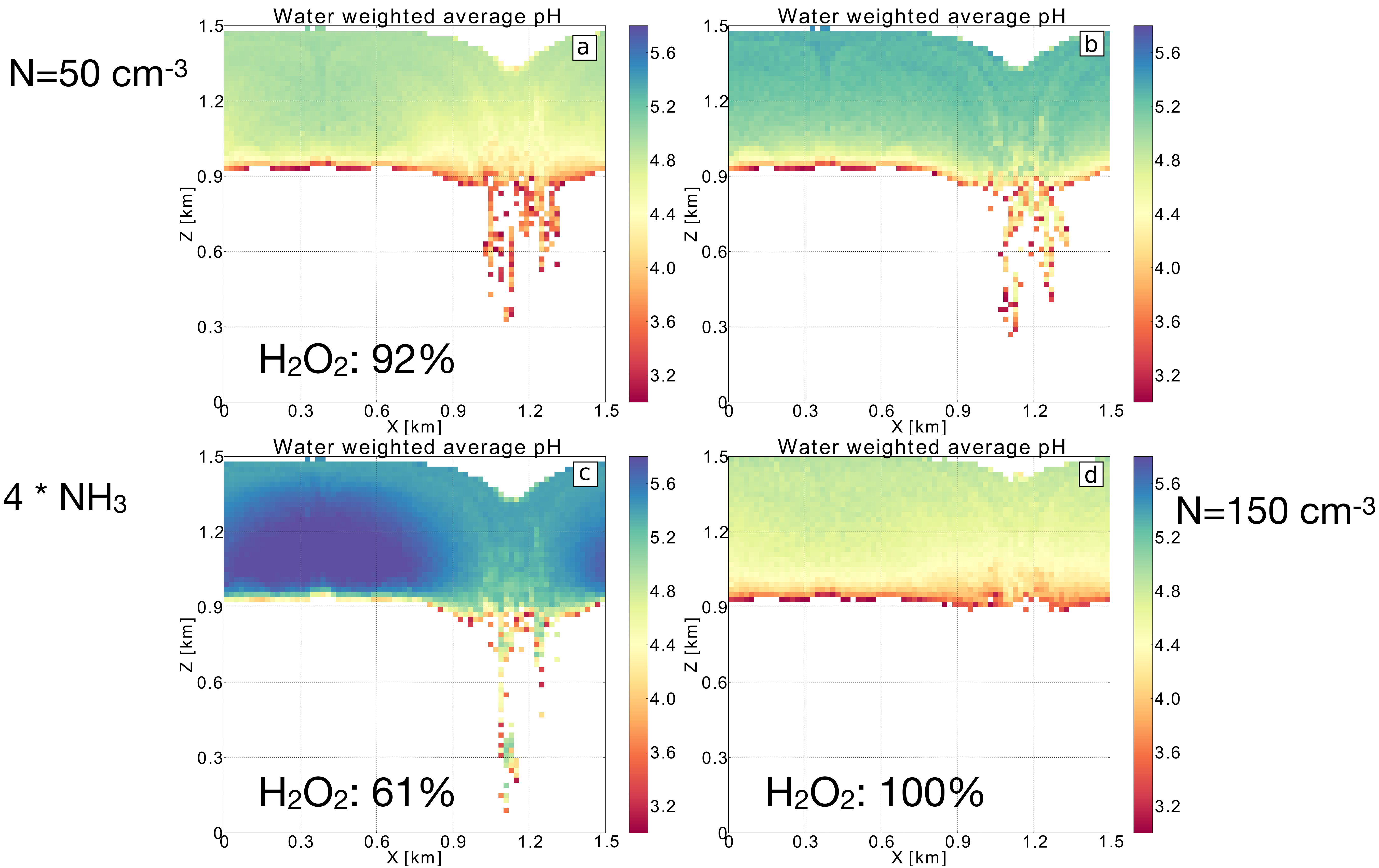


Changes in aerosol size distribution



Changes in pH



- chemistry 101 and sulfur budget
- **example results from a high resolution model**
- example results from a global model

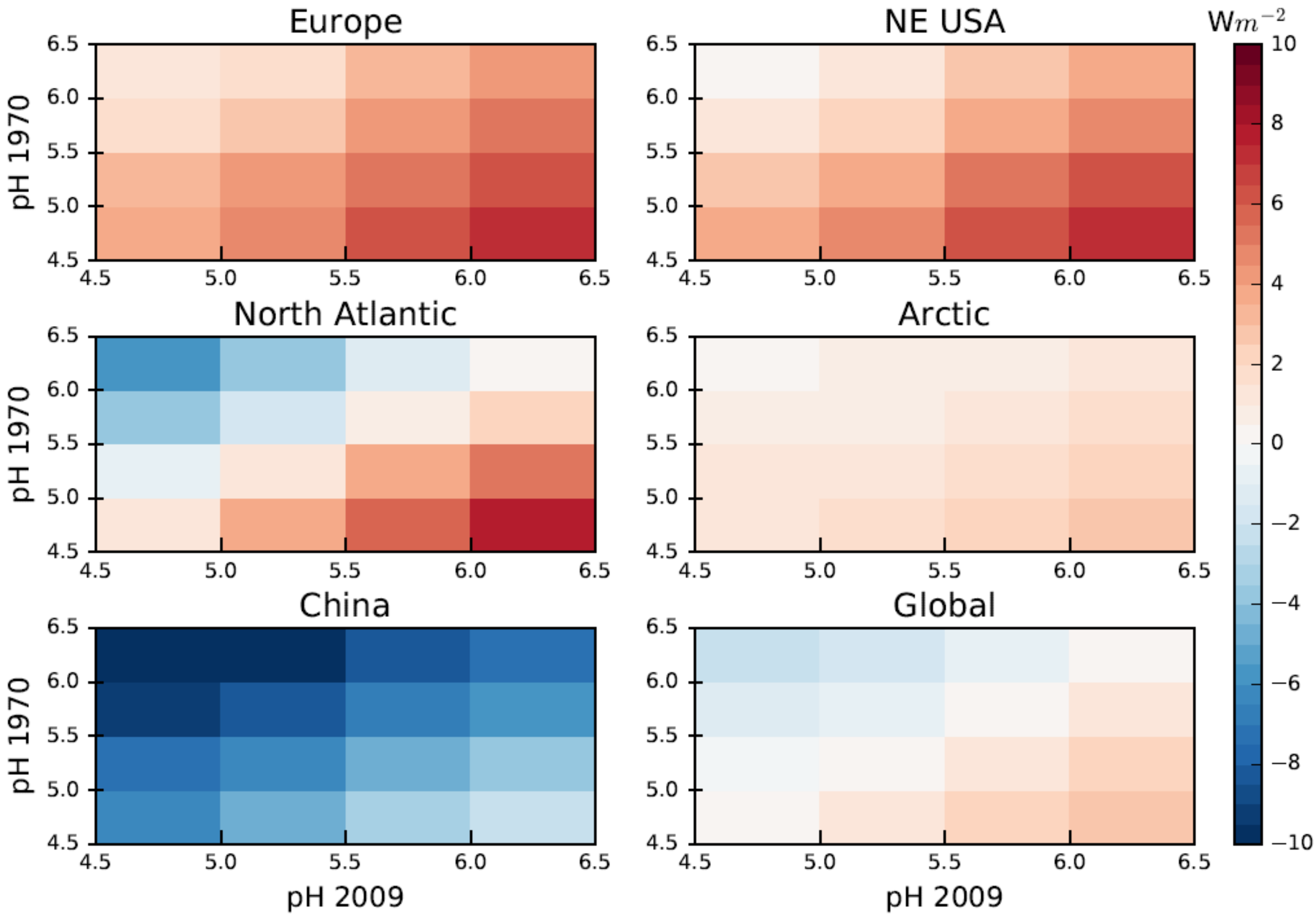
- chemistry 101 and sulfur budget
- example results from a high resolution model
- **example results from a global model**

Turnock et al 2019 (just accepted to GRL)

- Reductions in Europe/USA sulfur emissions have contributed to higher cloud-water pH, thereby altering sulfate formation rates.

- How changes in cloud-water pH affect:
  - aerosol formation
  - aerosol size distributions
  - aerosol radiative effects.

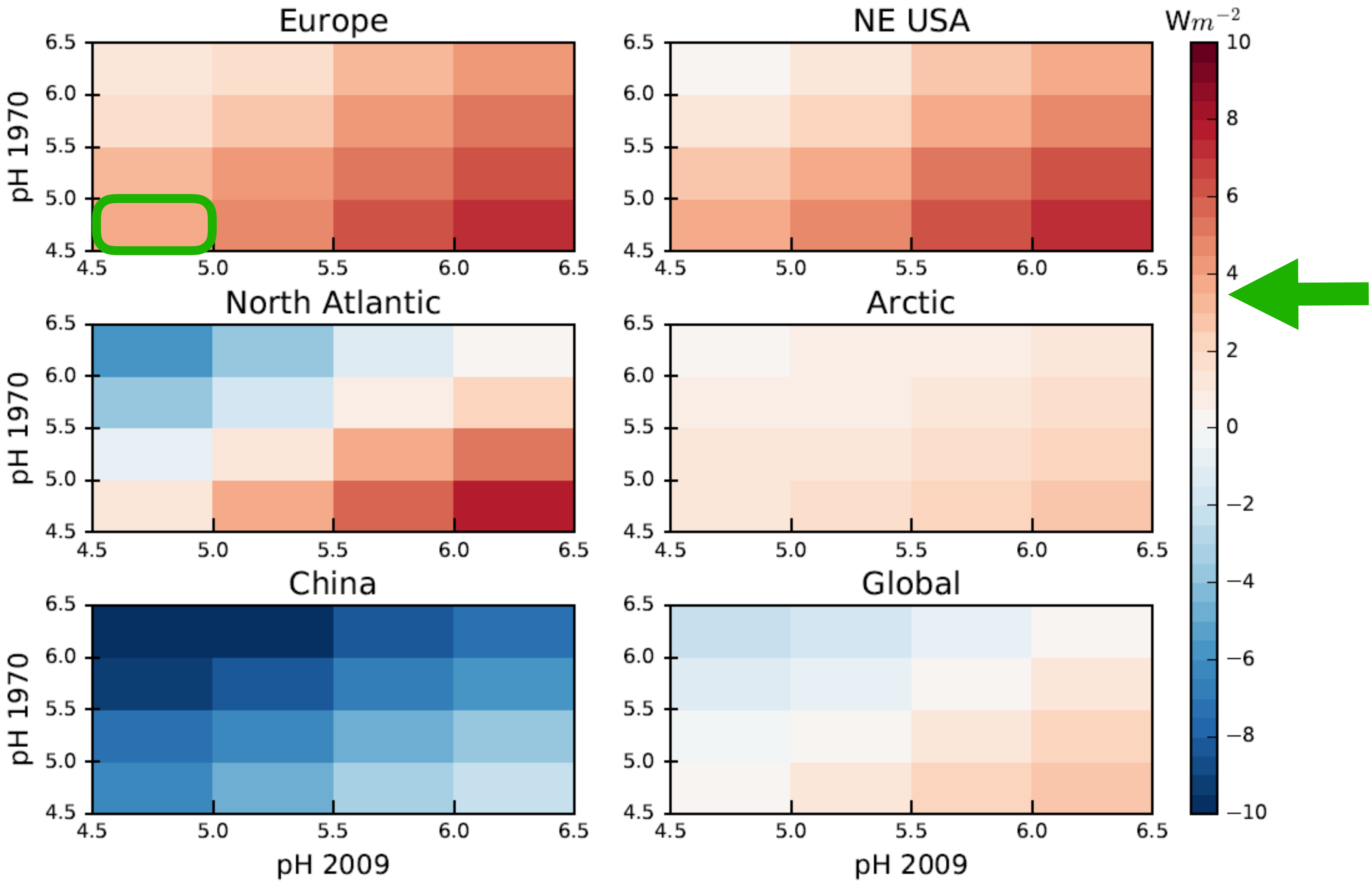
- The models shouldn’t assume constant in-cloud pH



all-sky shortwave TOA aerosol radiative forcing

Turnock et al 2019 (just accepted to GRL)

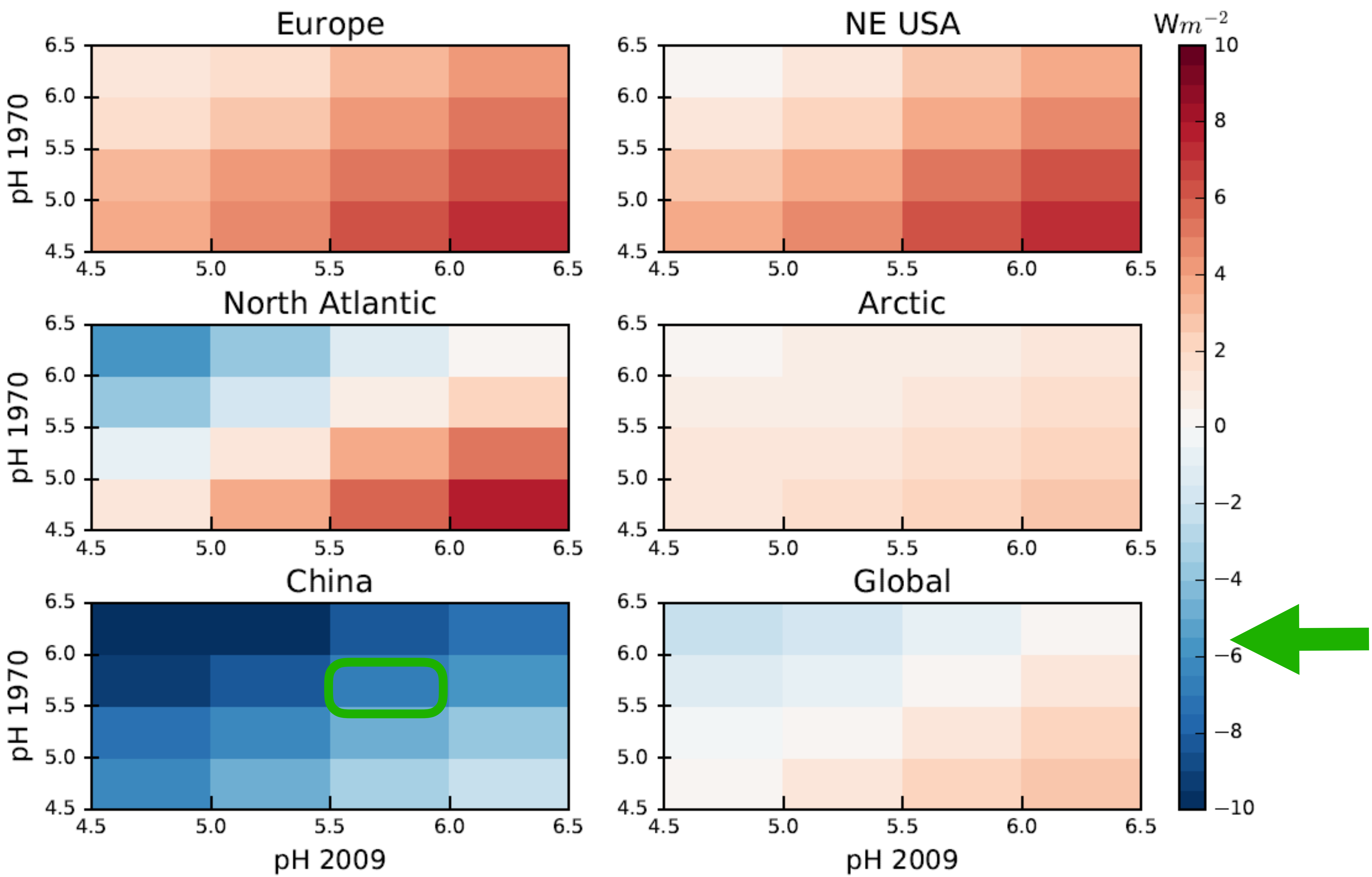
Decrease in sulfur emissions in Europe



all-sky shortwave TOA aerosol radiative forcing

Turnock et al 2019 (just accepted to GRL)

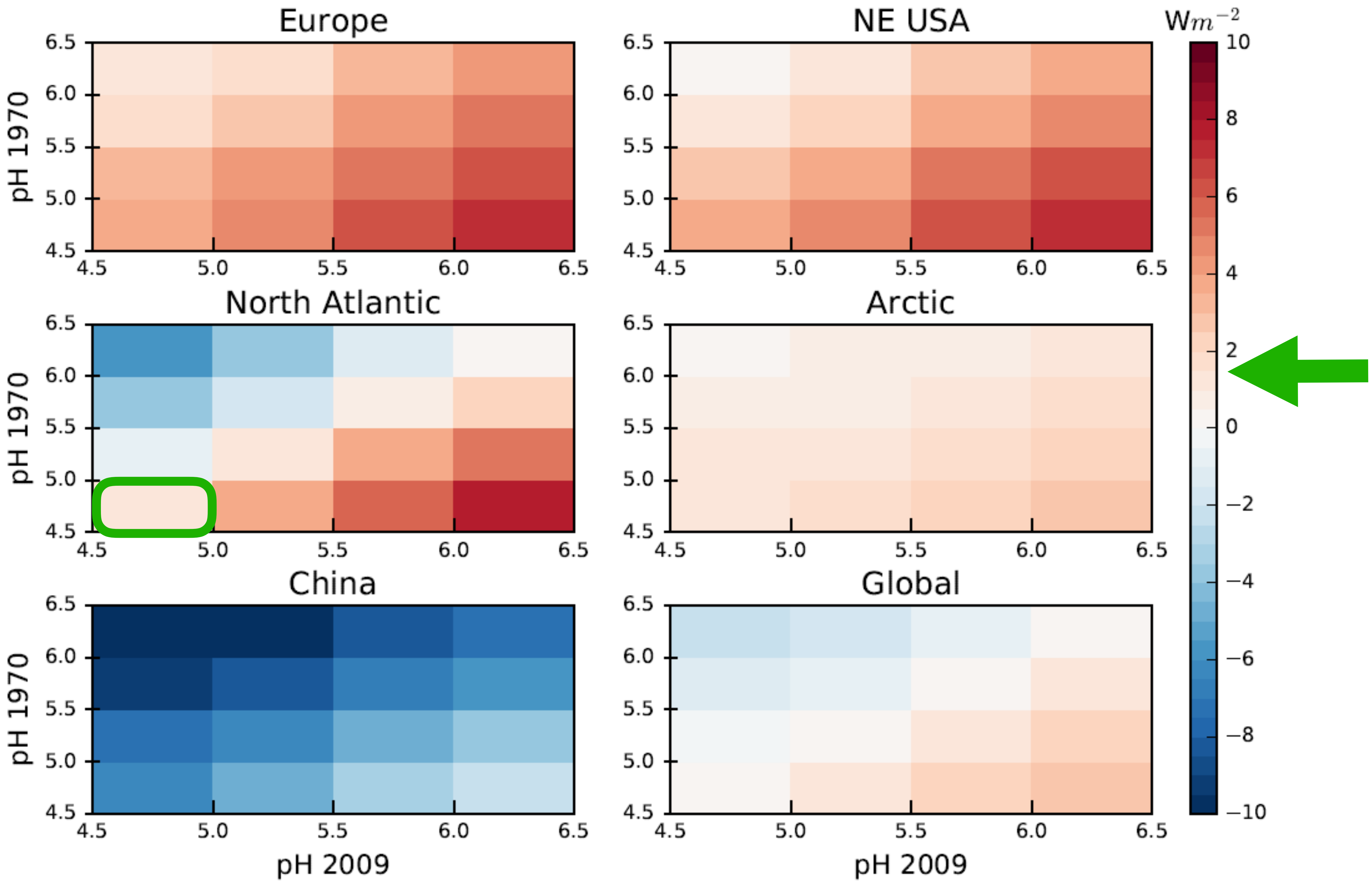
Increase in sulfur emissions in China



all-sky shortwave TOA aerosol radiative forcing

Turnock et al 2019 (just accepted to GRL)

Impact of the assumed in-cloud pH



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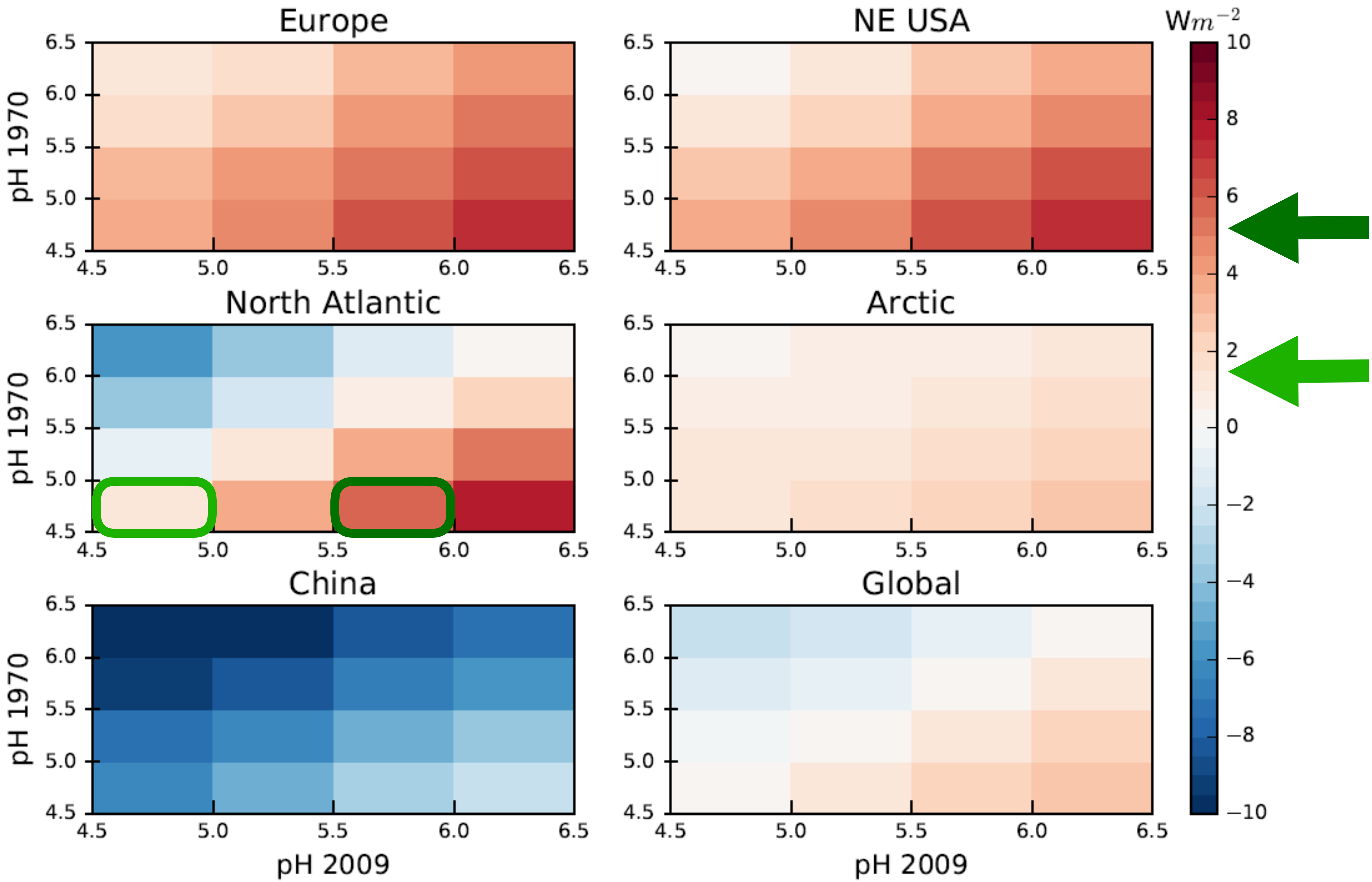

all-sky shortwave TOA aerosol radiative forcing

Turnock et al 2019 (just accepted to GRL)

- chemistry 101 and sulfur budget
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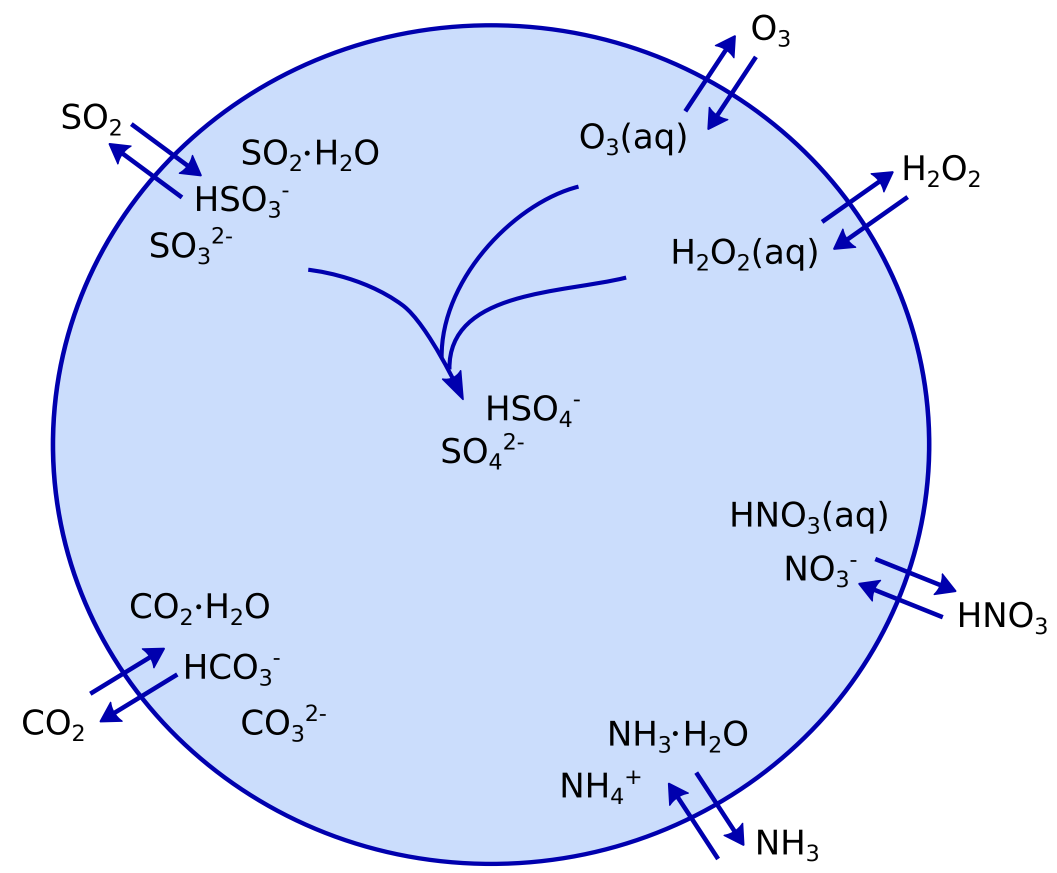
Summary 1/3

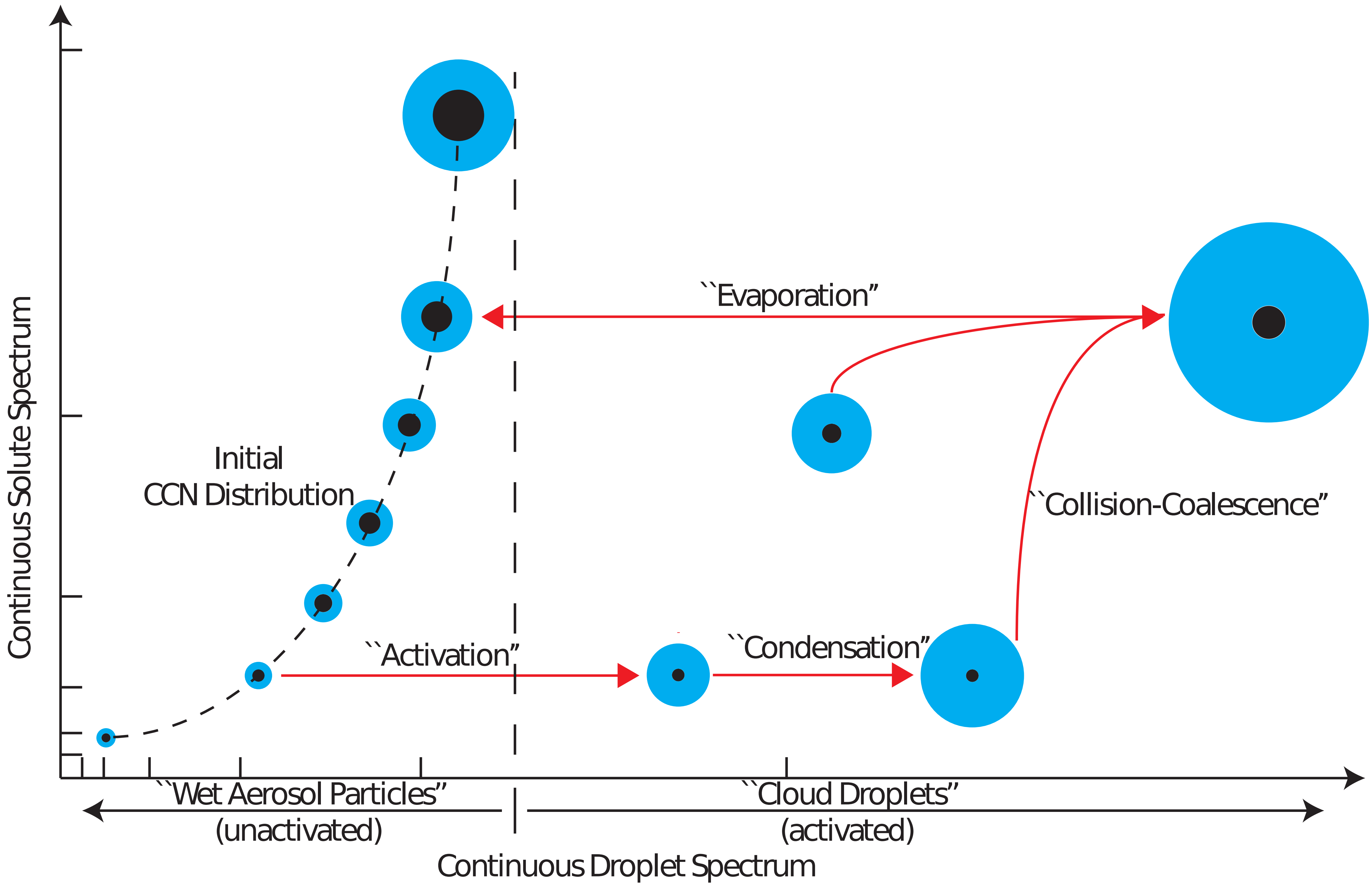
Sources:
- anthropogenic
- phytoplankton
- volcanoes

Sinks:
- oxidation
- dry deposition
- wet deposition

Oxidation reaction:
- in-cloud vs gas-phase
- pH dependant

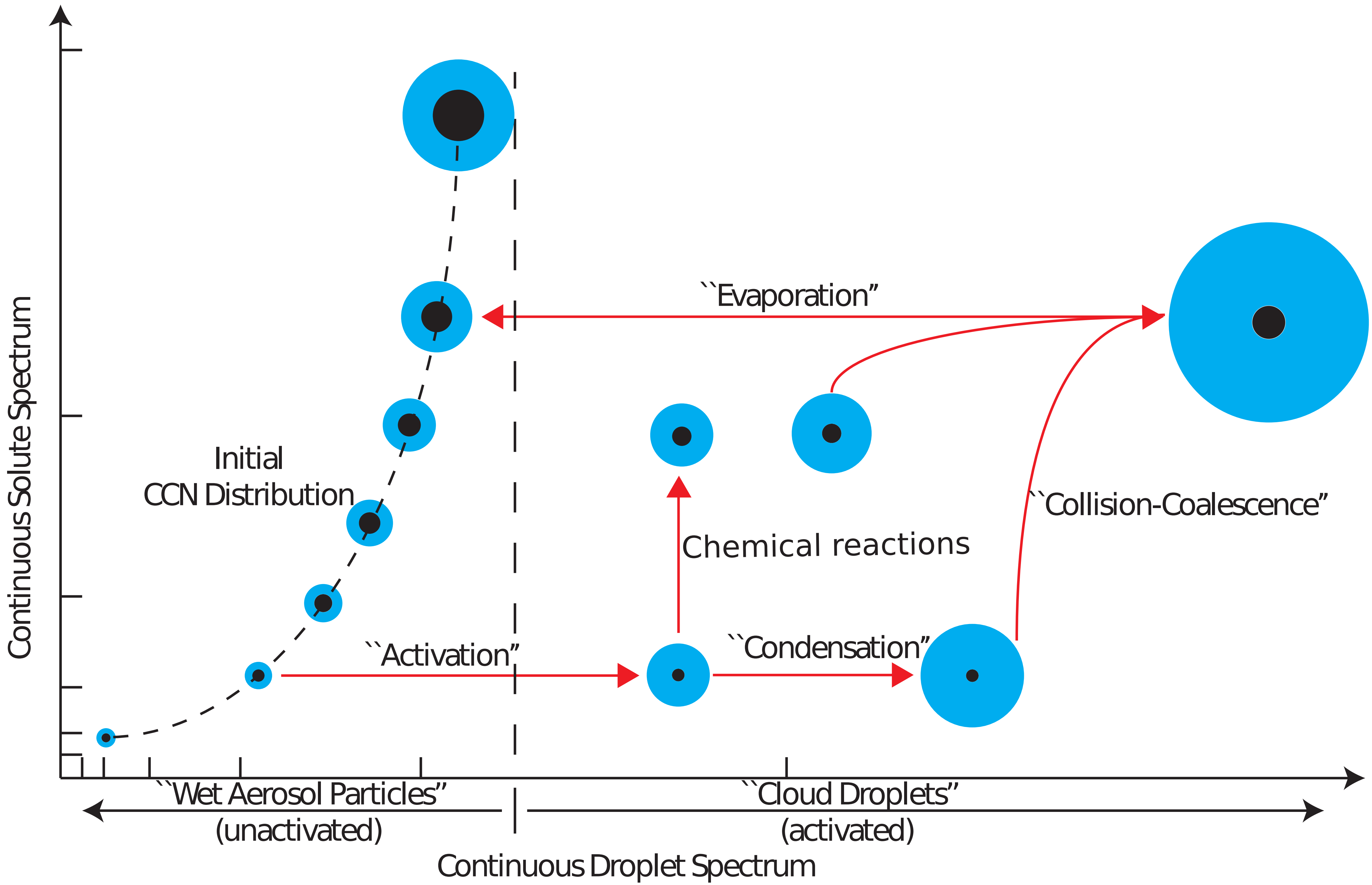


Summary 2/3



adapted from Lebo and Seinfeld (2011)

Summary 2/3



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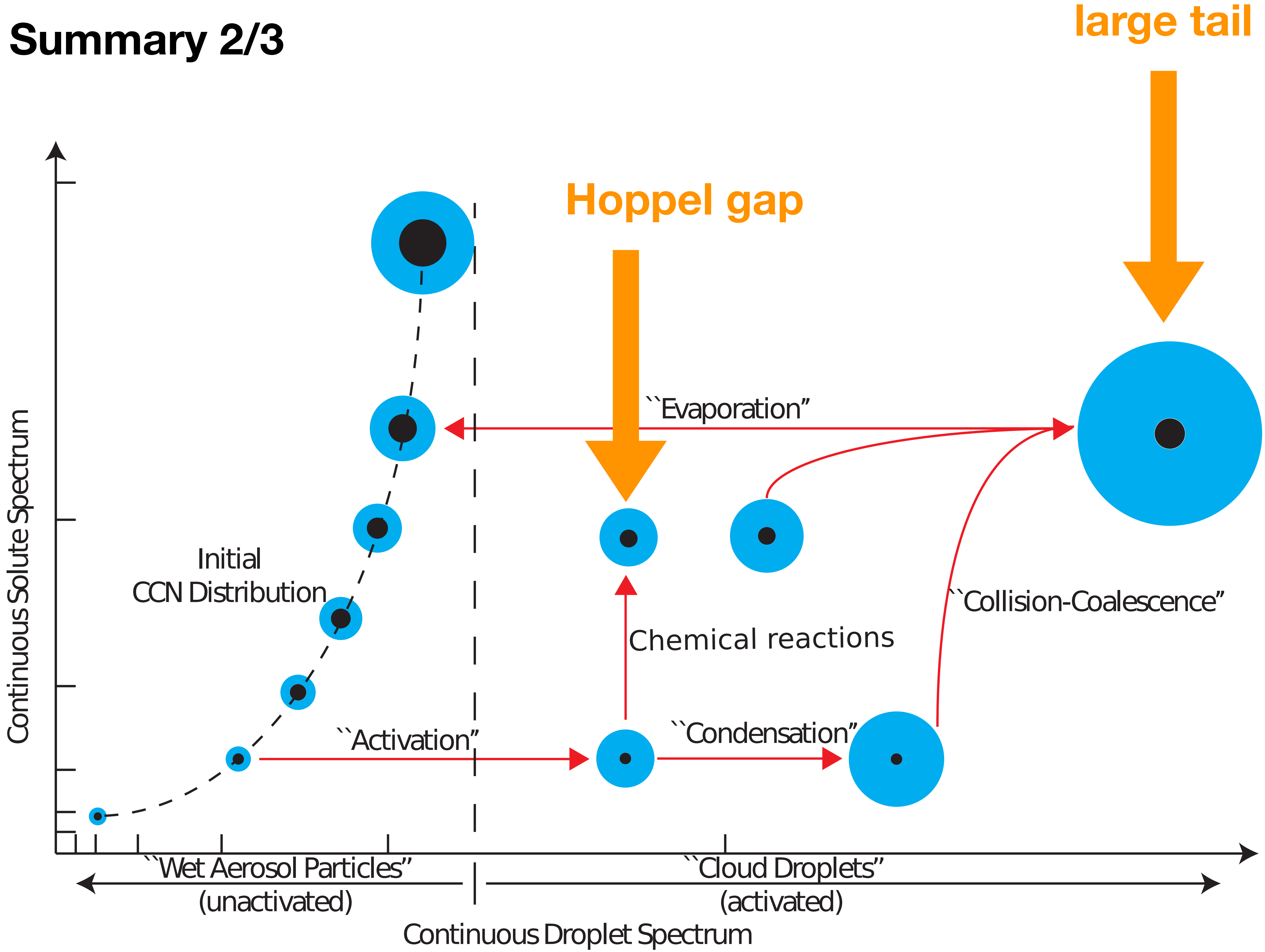
Summary 2/3



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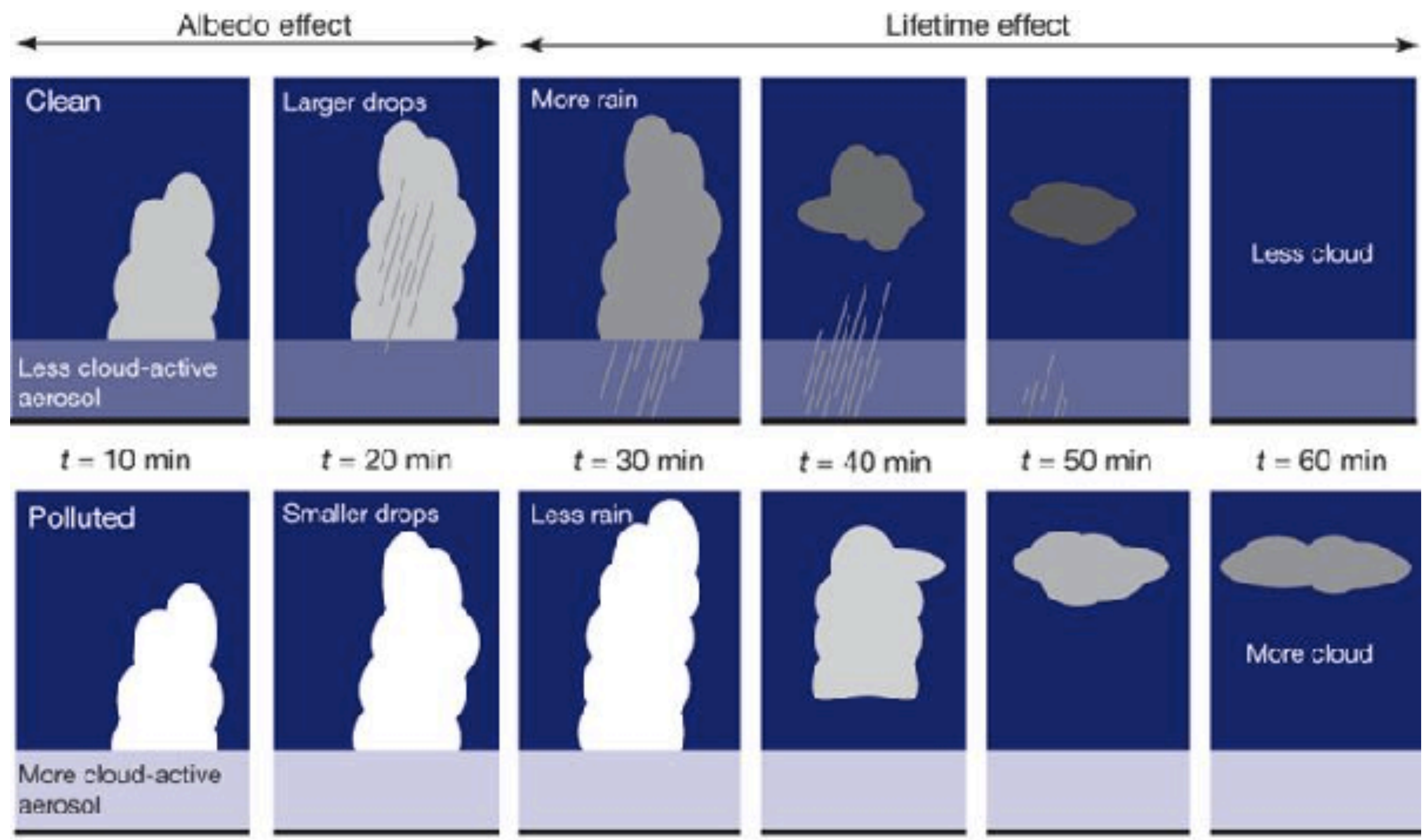
Summary 3/3

Aerosol particles influence clouds

- CCN source
- droplet concentration
- cloud albedo
- rain initiation
- cloud-lifetime effects



Stevens and Feingold 2009

Summary 3/3

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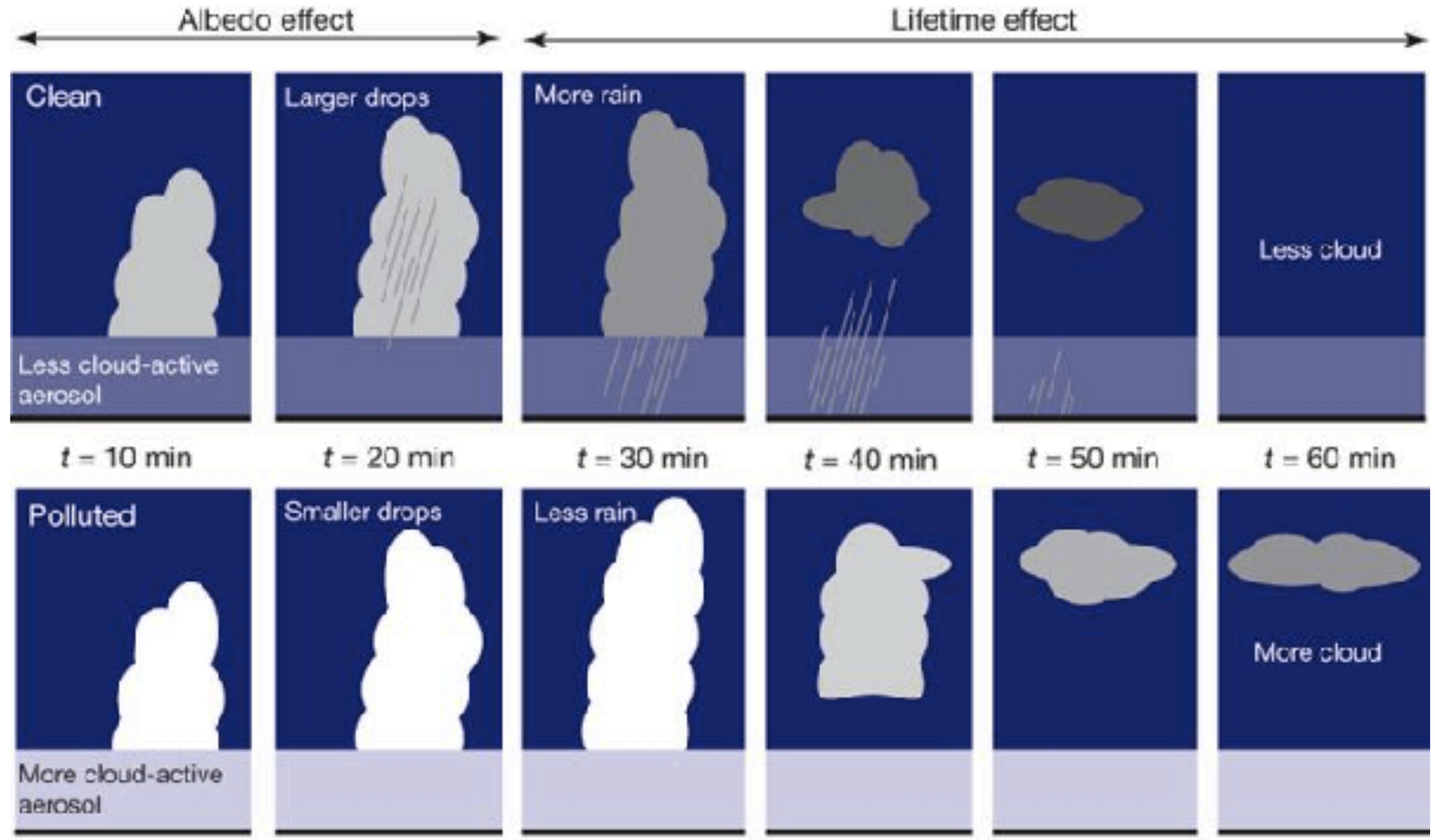

Stevens and Feingold 2009

Clouds influence aerosol particles

- irreversible chemical reactions
- collisions between water drops
- precipitation