‘Sizing’ heterogeneous chemistry in the conversion of gaseous dimethyl sulfide to atmospheric particles

AGUSTIN J. COLUSSI

Linde-Robinson Center for Global Environmental Science

CALIFORNIA INSTITUTE OF TECHNOLOGY



VALENCIA 10/24/ 2016





MESSAGES

- THE DEVIL IS IN THE DETAILS
- CHEMISTRY IN THE ATMOSPHERE:

NOT ONLY IN THE GAS-PHASE!

- IGNORE CHEMISTRY AT YOUR OWN RISK
- CLIMATE RESEARCH:

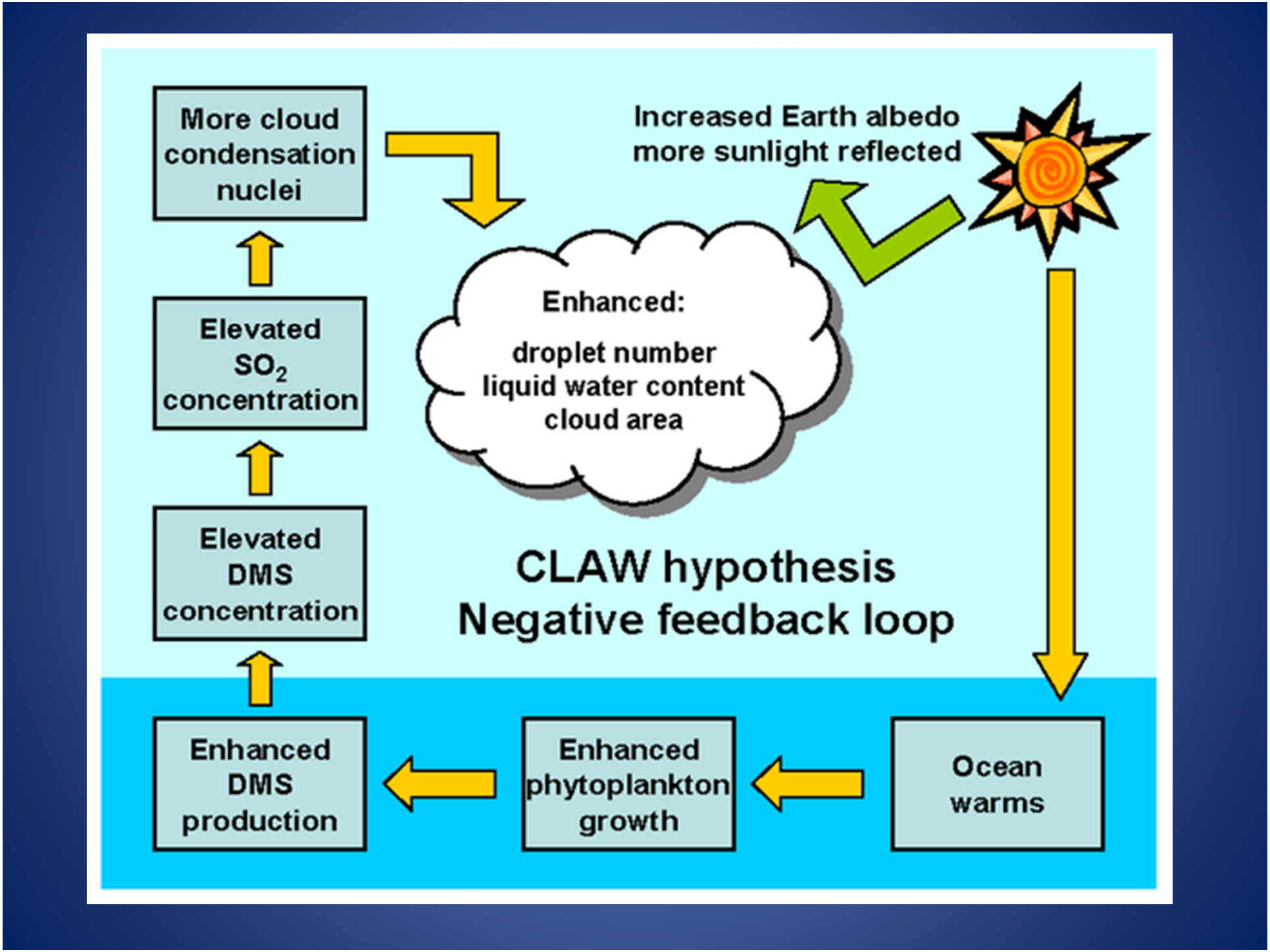
NOT FULLY INTERDISCIPLINARY YET

GAIA HYPOTHESIS

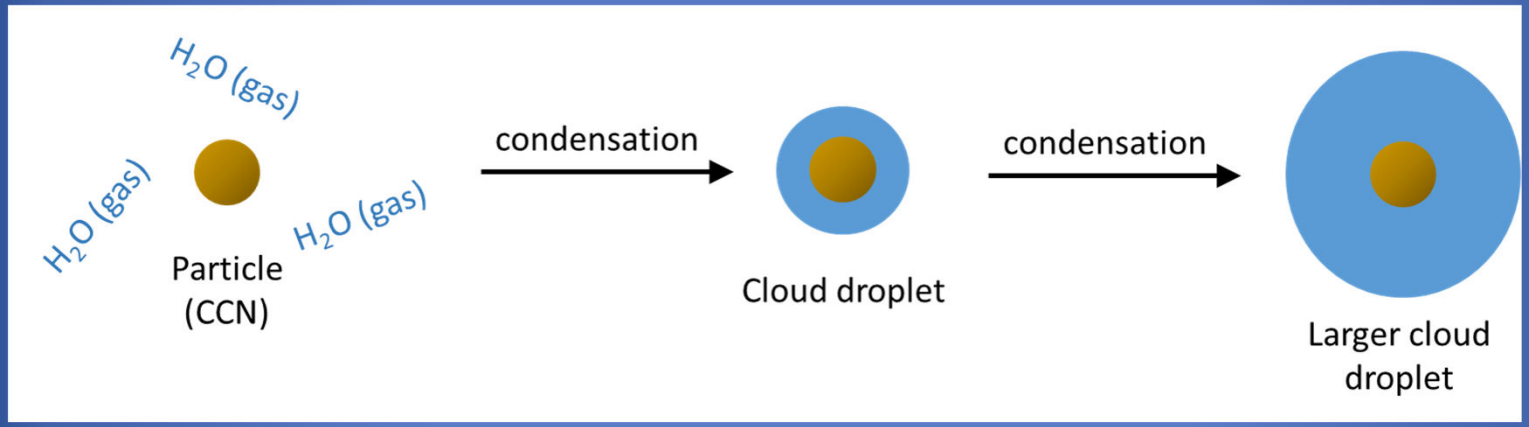
ENVIRONMENTAL HOMEOSTASIS VIA BIOLOGICAL FEEDBACKS

CLAW HYPOTHESIS

"GLOBAL WARMING WILL ENHANCE BIOGENIC DIMETHYL SULFIDE EMISSIONS"


More cloud condensation nuclei
Increased Earth albedo more sunlight reflected
Enhanced:
droplet number
liquid water content
cloud area
Elevated SO_2 concentration
Elevated DMS concentration
CLAW hypothesis
Negative feedback loop
Enhanced DMS production
Enhanced phytoplankton growth
Ocean warms

Clouds form on condensation nuclei CCN



CCN: Sulfuric acid nanodroplets

DMS oxidation ➡ sulfuric acid

STRENGTH OF DMS EMISSIONS

~ 50 MEGATONS OF SULFUR / YEAR

QUESTION

How much CCN from DMS

MSA

- BIOGENIC MARKER

- ONLY FORMED ON AEROSOLS

AEROSOL FIELD MEASUREMENTS

$$\theta = \frac{MSA}{AP\ SULFATE + GP\ SULFATE}$$

Fraction of MSA in the aerosol increases at higher latitudes

Why?

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 117, D10306, doi:10.1029/2011JD016559, 2012

Latitudinal distributions of atmospheric MSA and MSA/nss-SO_4^{2-} ratios in summer over the high latitude regions of the Southern and Northern Hemispheres

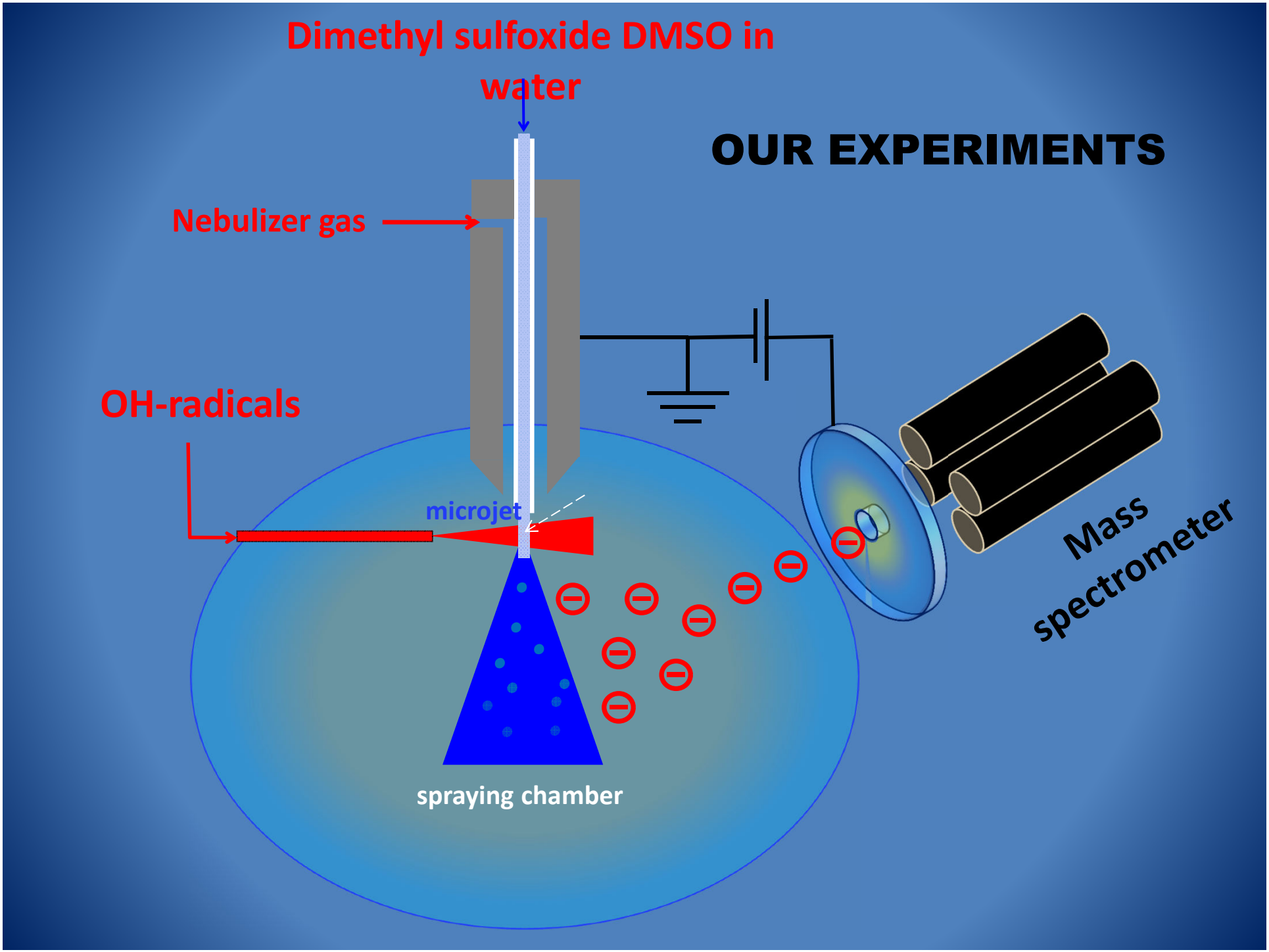
high-latitude regions, bulk aerosol samples were collected during eight cruises

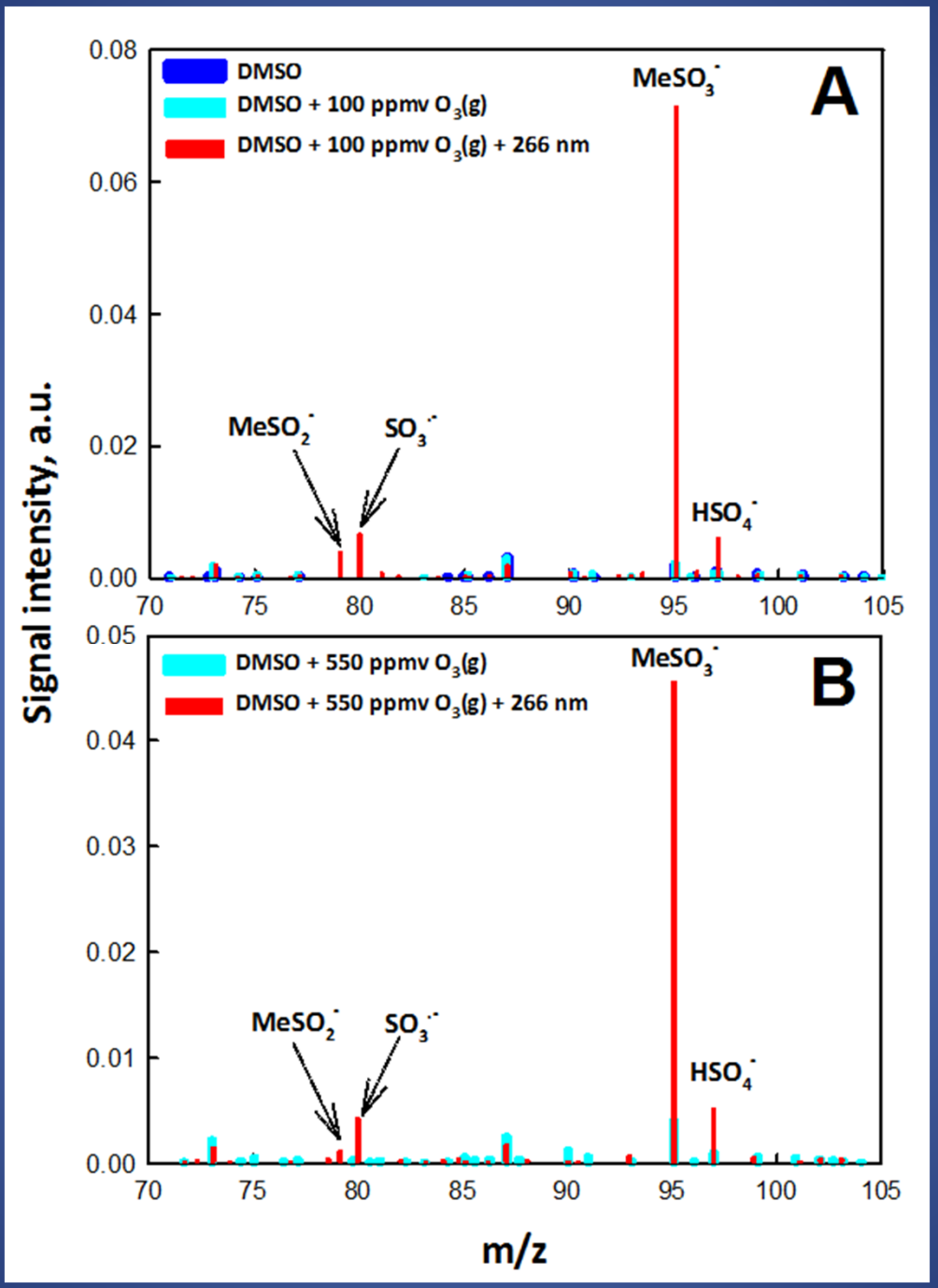
[18] Large population of seabirds, in particular penguins, is a unique feature in the Antarctic ecosystem that is different from that of the Arctic [*Woehler and Croxall*, 1997], and this ecological difference may partially explain the different levels of atmospheric MSA in the two high latitude regions.

Therefore, additional field work and laboratory kinetic studies relating to possible marine animal sources for MSA should be explored to better understand the sulfur chemistry in coastal Antarctica. Additionally, certain environmental factors, such as winds, sea ice coverage, and light intensity, etc., may also contribute to the variability of S-species in the high latitude marine atmosphere and should be considered through future studies.

THE DEVIL IS IN THE DETAILS

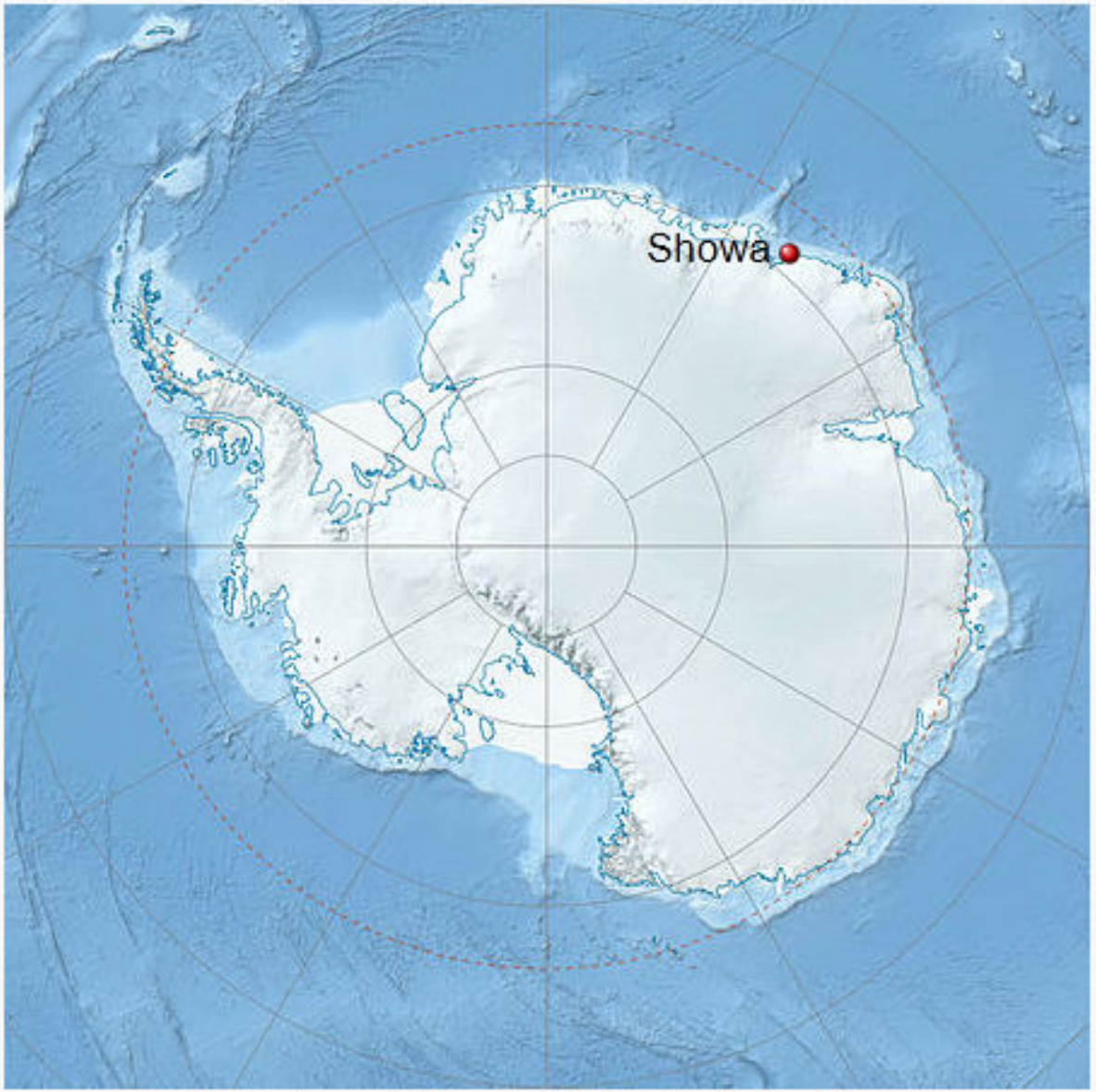
“Ignore chemistry at your own risk”


Dimethyl sulfoxide DMSO in water
OUR EXPERIMENTS
Nebulizer gas
OH-radicals
microjet
Mass spectrometer
spraying chamber


A
DMSO
DMSO + 100 ppmv O3(g)
DMSO + 100 ppmv O3(g) + 266 nm
MeSO3-
MeSO2-
SO3-
HSO4-
B
DMSO + 550 ppmv O3(g)
DMSO + 550 ppmv O3(g) + 266 nm
Signal intensity, a.u.
m/z

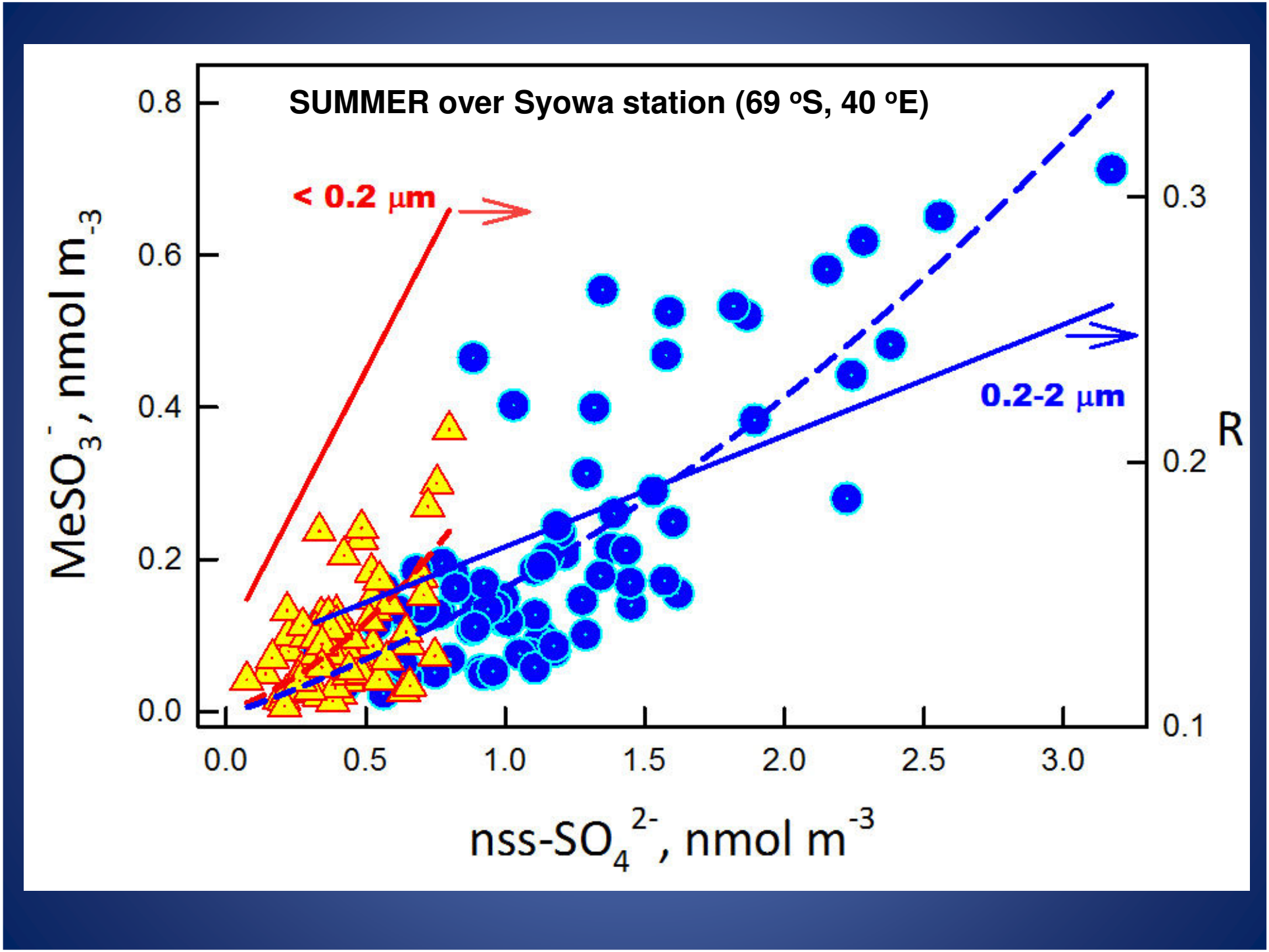
OUR FINDING

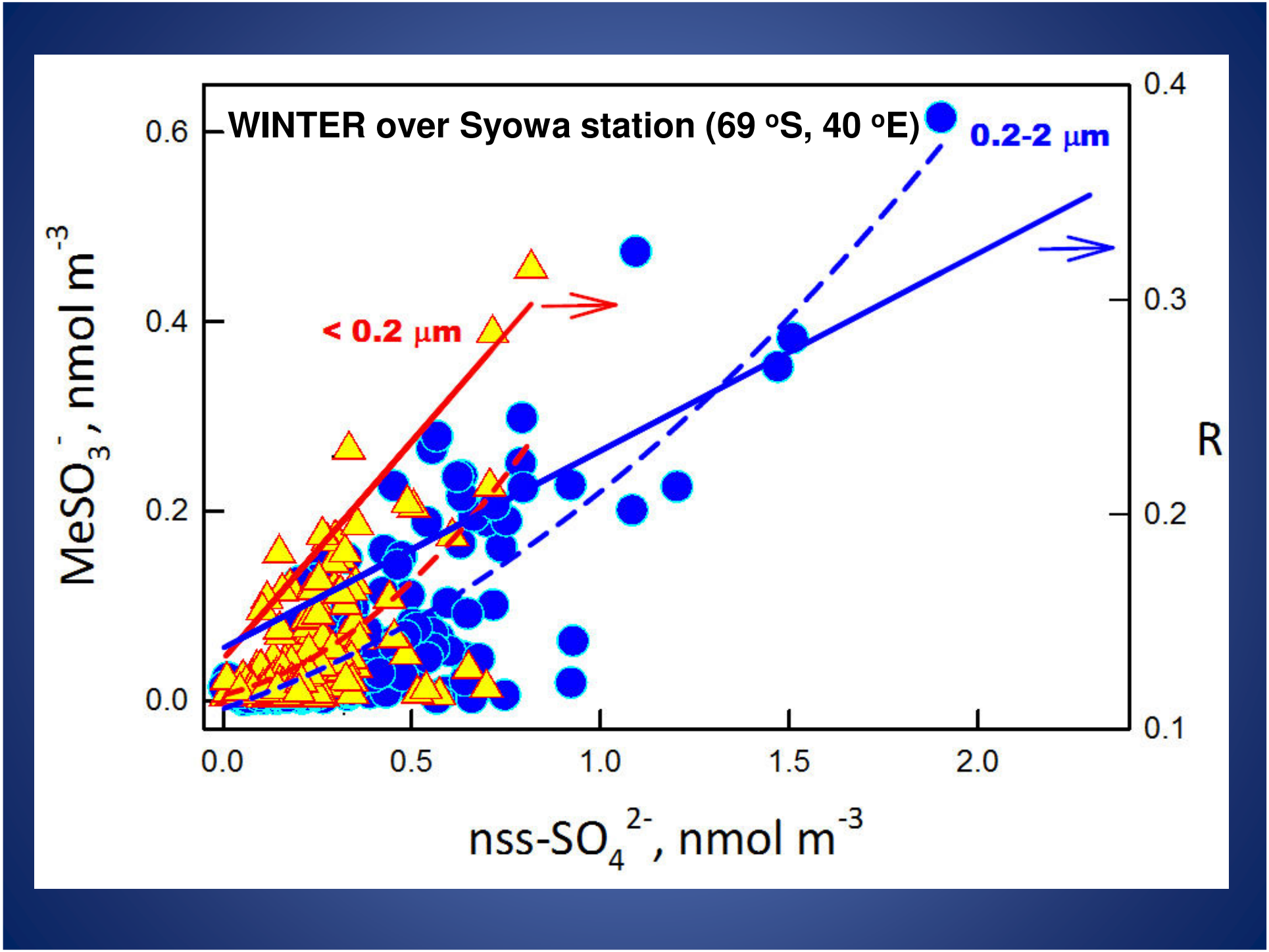
$$R = \frac{MSA}{AP\ SULFATE} = 2.7$$



Location of Showa Station in Antarctica

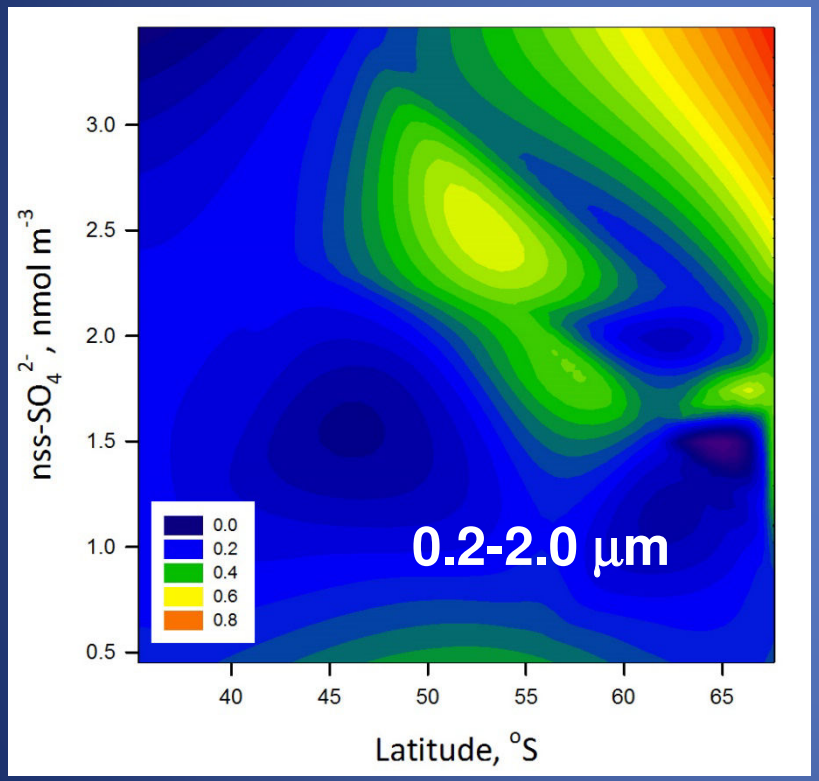
Coordinates: 69°00′S 39°35′E

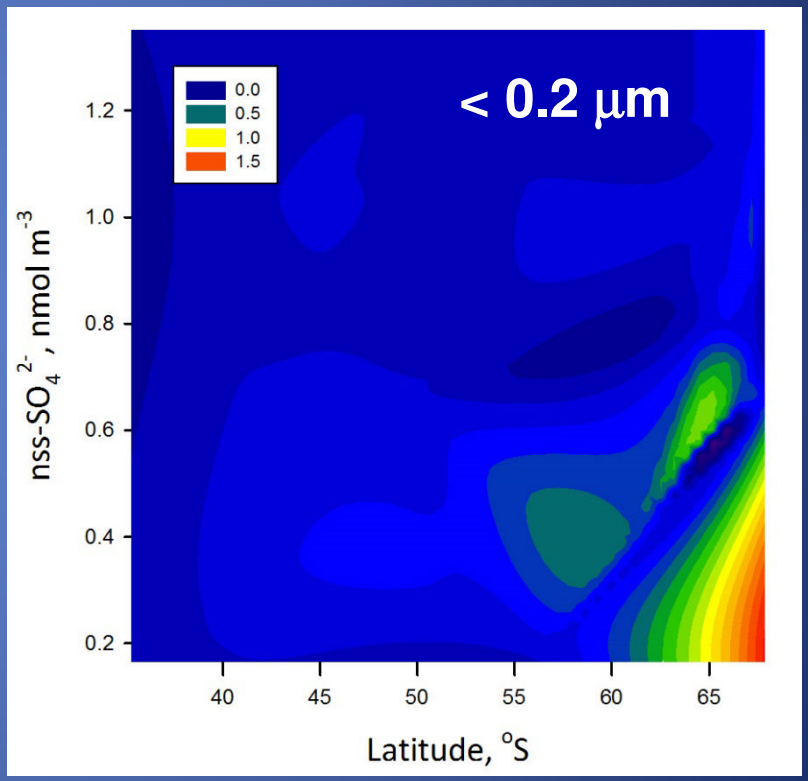

SUMMER over Syowa station (69 ºS, 40 ºE)
< 0.2 μm
0.2-2 μm
MeSO3-, nmol m-3
R
nss-SO4 2-, nmol m-3
0.0
0.2
0.4
0.6
0.8
0.1
0.2
0.3
0.0
0.5
1.0
1.5
2.0
2.5
3.0


WINTER over Syowa station (69 °S, 40 °E)
0.2-2 μm
< 0.2 μm
MeSO3-, nmol m-3
nss-SO4 2-, nmol m-3
R
0.0
0.2
0.4
0.6
0.5
1.0
1.5
2.0
0.1
0.3
0.4

Umitaka-maru expedition

Cape Town (34 °S, 18 °E) to Fremantle (32 °S, 115 °E)



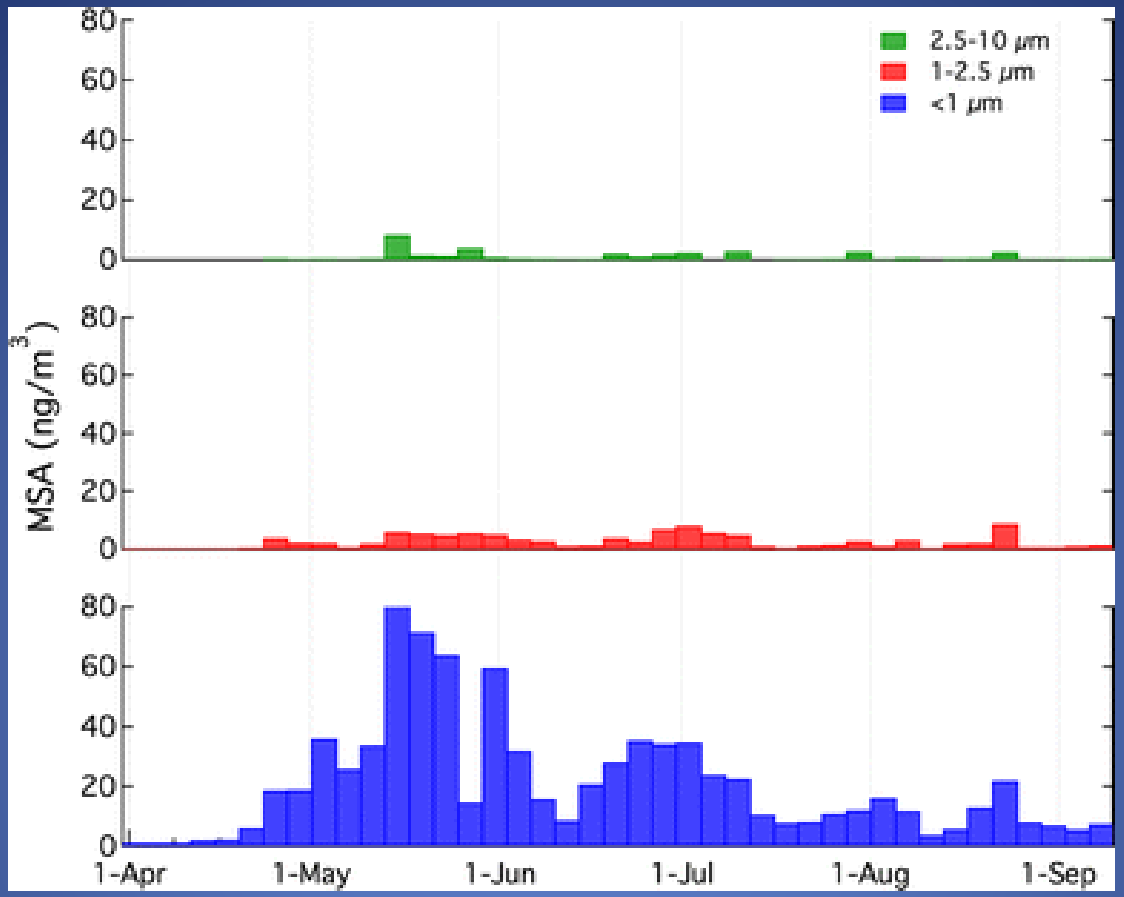


MSA FRACTION IN AEROSOL

- ✓ INTERFACIAL VS GAS-PHASE CHEMISTRY
- ✓ INCREASES WITH AEROSOL SPECIFIC SURFACE AREA
- ✓ ENHANCED ON FINE AEROSOL (LARGER S/V RATIO)

MSA PRODUCTION

CONVOLUTED FUNCTION OF BIOGENIC EMISSIONS



"ratio of biogenic sulfate in MSA depends on latitude, temperature, irradiation intensity, and oxidant concentrations, which promote the formation of sulfate instead of MSA"

SEPTEMBER 2016!

CONCLUSIONS AND RECOMMENDATIONS

- ATMOSPHERIC CHEMISTRY **NOT ONLY** GAS-PHASE CHEMISTRY!
- CHEMISTRY IS NOT AN ADJUSTABLE PARAMETER
- NEED OF **REAL** MULTIDISCIPLINARY APPROACH

- I think that everybody understands, but not all would acknowledge that global warming is an impending catastrophe.
- So at this point the issues seem more political than scientific.
- So real problem in my opinion is to find how to escape the trap of unrelenting growth in a non-disruptive way. How to blend long term issues with short term politics. Change is due for many reasons, global warming being one of them.

Shinichi Enami

The Hakubi Center for Advanced Research, Kyoto University and

Research Institute for Sustainable Humanosphere, Kyoto University

Yosuke Sakamoto

Faculty of Environmental Earth Science, Hokkaido University

Keiichiro Hara

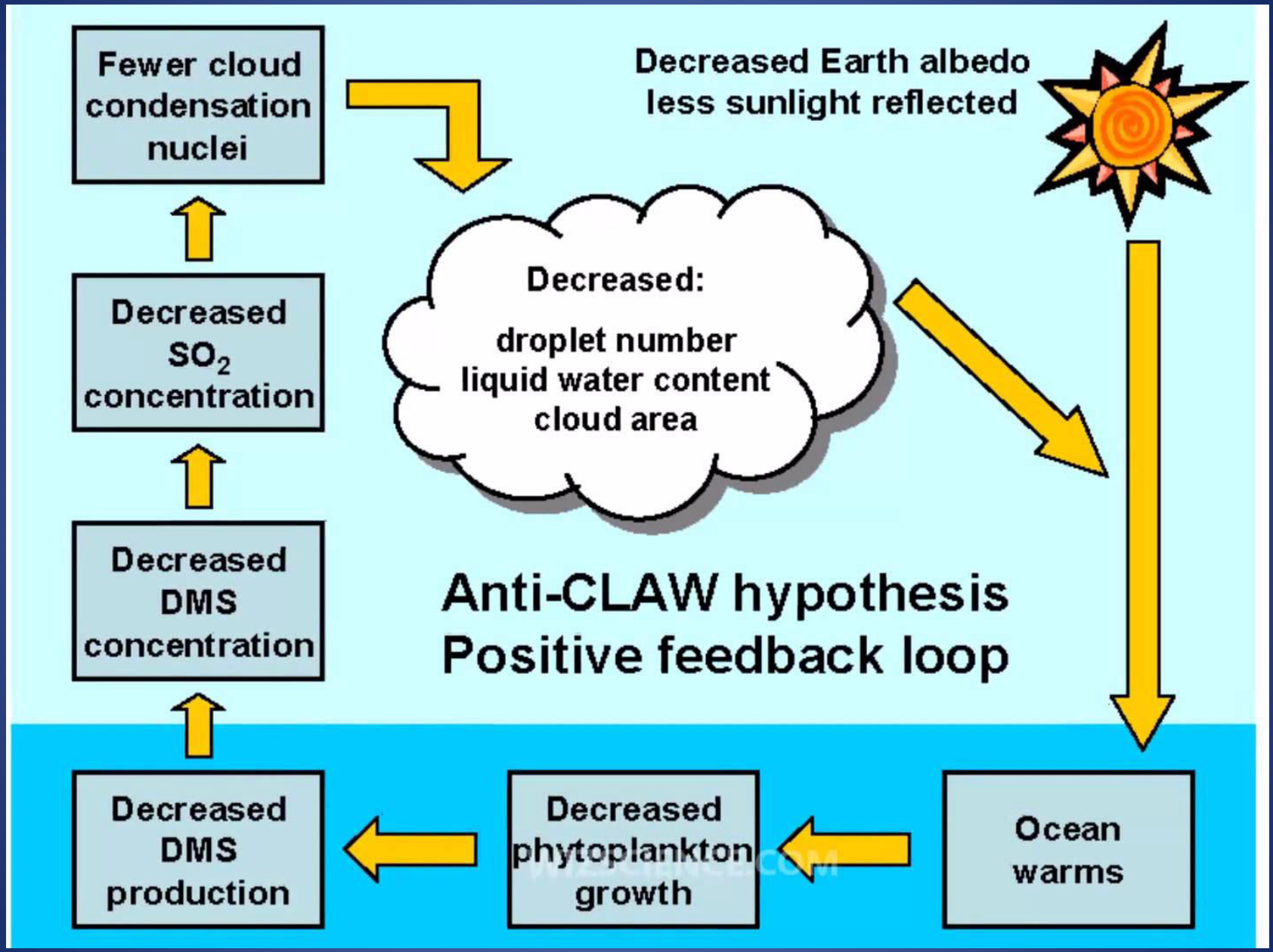
Department of Earth Science System, Fukuoka University

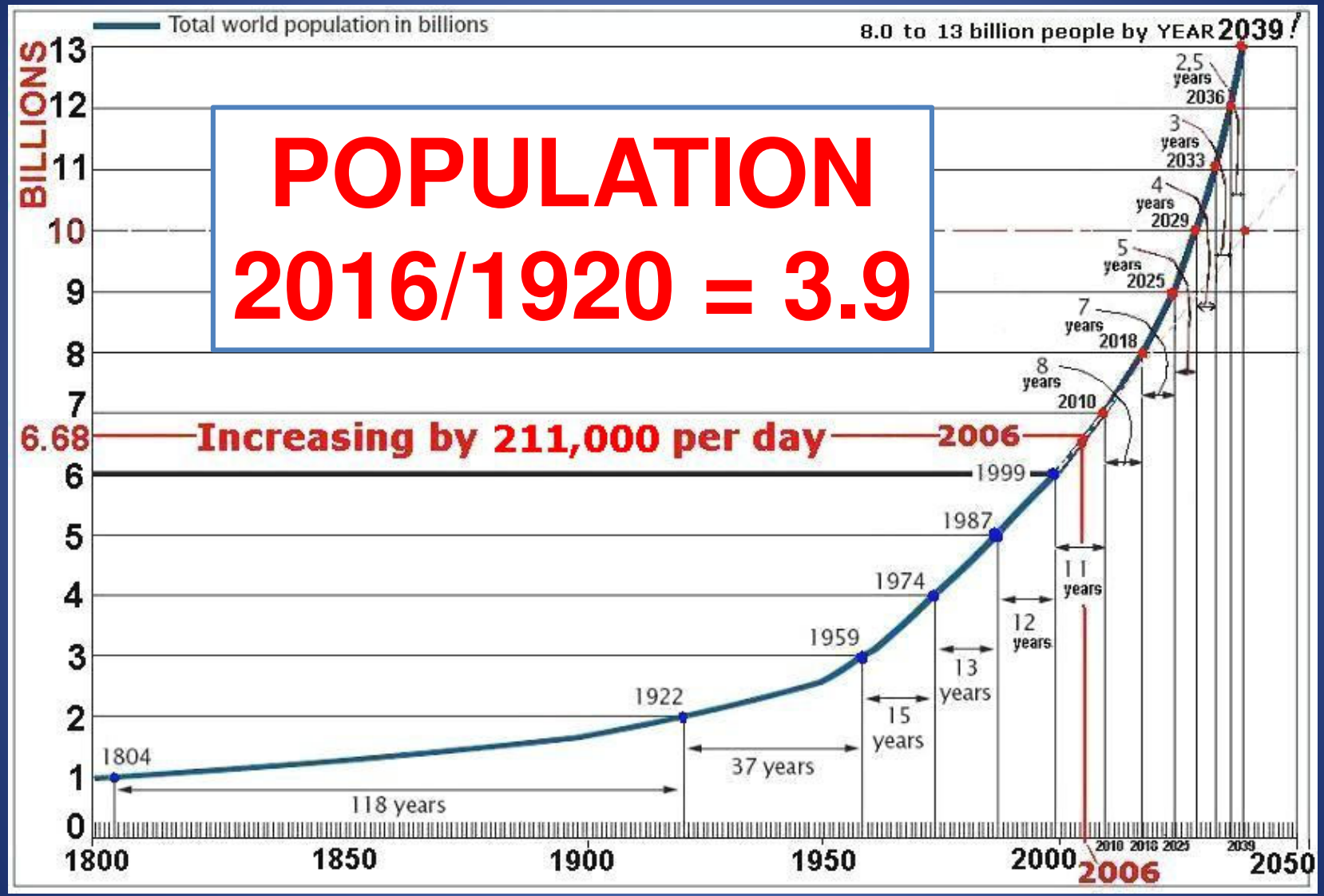
Kazuo Osada

Graduate School of Environmental Studies, Nagoya University

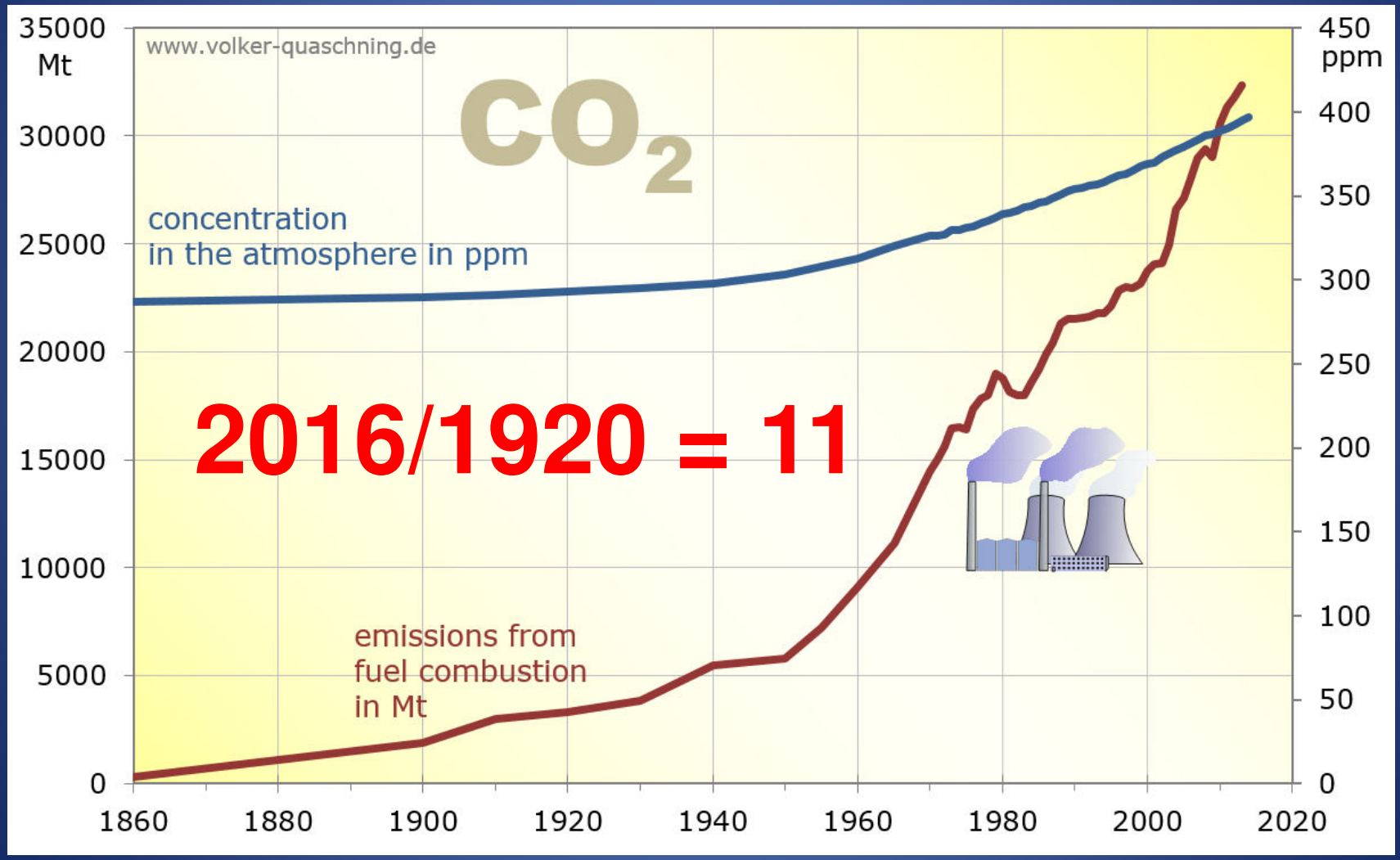
Michael R. Hoffmann and Agustín J. Colussi

Linde Center for Global Environmental Science, California Institute of Technology


Fewer cloud condensation nuclei
Decreased Earth albedo
less sunlight reflected
Decreased:
droplet number
liquid water content
cloud area
Decreased SO_2 concentration
Decreased DMS concentration
Anti-CLAW hypothesis
Positive feedback loop
Decreased DMS production
Decreased phytoplankton growth
Ocean warms


Total world population in billions
8.0 to 13 billion people by YEAR 2039 !
BILLIONS
13
12
11
10
9
8
7
6.68
6
5
4
3
2
1
0
POPULATION
2016/1920 = 3.9
Increasing by 211,000 per day
2006
1999
1987
1974
1959
1922
1804
118 years
37 years
15 years
13 years
12 years
11 years
8 years 2010
7 years 2018
5 years 2025
4 years 2029
3 years 2033
2.5 years 2036
1800
1850
1900
1950
2000
2050
2006

CO_2 EMISSIONS VS CONCENTRATION




東京海洋大学
Tokyo University of Marine Science and Technology
JPAT
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The debate about whether enhanced CCN generation due to the stronger DMS emissions expected at higher temperatures would create a negative feedback to global warming (the CLAW conjecture)[6] has underscored the fact that the strength of natural DMS emissions, their geographical and seasonal distributions and, particularly, the chemistry involved in their atmospheric processing remain uncertain.

The outstanding issue at present is how to quantify biogenic contributions to particle nucleation and growth from the composition of the aerosol