Review of the IMPROVE Equation for Estimating Ambient Light Extinction

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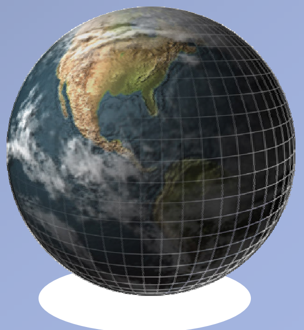
OUTLINE

- Introduction
- Sampling Biases
- Chemical forms of species in IMPROVE equation
- Mass scattering efficiency- methods for deriving and recent literature survey



Recall:

$$PM_{2.5} = (NH_4)_2SO_4 + NH_4NO_3 + POM + LAC + Soil$$

$$Soil = 2.2Al + 2.49Si + 1.94Ti + 1.63Ca + 2.42Fe$$

$$POM = R_{oc} \cdot OC$$

Recall:

- Light extinction includes contributions from gases and particles

$b_{ext} = b_{sp} + b_{ap} + b_{sg} + b_{ag}$

$b_{sp} = 3.0f(RH)[(NH_4)_2SO_4] +$

$3.0f(RH)[NH_4NO_3] +$

$4.0R_{oc}[OC] +$

$1.0[Soil] +$

$0.6[CM]$

$b_{ap} = 10.0[LAC]$

BIASES

- Artifact: any increase or decrease in the material being sampled that results in a positive or negative bias in the ambient concentration measured
- Positive: contamination, adsorption of gases on filter
- Negative: volatilization of gases from disassociated particles on the filter medium (during sampling or handling)
- Biases affect aerosol species differently; applying corrections is not always straightforward

BIASES

- Nitrate

  Teflon-implications for gravimetric mass

- Carbonaceous aerosols

  Artifact contributions to organic mass can range from -80 % to + 50 %, Turpin et al., 2000).

- Coarse mass and elemental species

  Lower Z elements have higher MDLs

  $CM = PM_{10} – PM_{2.5}$

    Uncertainties in flow rates can significantly affect coarse mass as well as fine mass (more later)

CHEMICAL FORMS: Particulate Organic Matter (POM)

- POM = $R_{oc} \cdot [OC]$
- Current algorithm: $R_{oc} = 1.4$

(Based on measurements from the late 70s in Pasadena, CA)

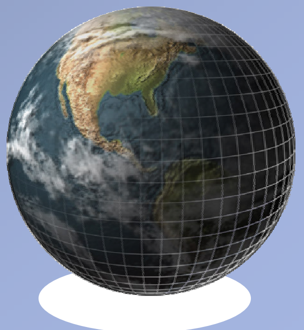
- R_{oc} (as suggested by Turpin and Lim, 2001)
  - 1.6±0.2 for urban organic aerosols
  - 2.1±0.2 for non-urban organic aerosols
  - 2.2-2.6 for samples with biomass burning influences

CHEMICAL FORMS: Particulate Organic Matter (POM)

- Observations:
  - Biomass burning observations: R_{oc} ~ 1.8 (aged) (Malm et al., 2005; Poirot and Husar, 2004)
  - Fresh smoke R_{oc} ~ 1.1-1.2 (Day et al. 2005)
  - El-Zanan et al. (2005) performed extractions on IMPROVE filters from 5 sites (1998-2000): estimated R_{oc} from these data ranging from 1.58±0.13 (Grand Canyon) to 2.58±0.29 (Mount Rainier)

    →Average: 1.92±0.40

    (Median 1.78)



CHEMICAL FORMS: Estimating R_{oc}

$PM_{2.5} = a_1[(NH_4)_2SO_4] + a_2[NH_4NO_3] + a_3[OC] + a_4[LAC] + a_5[Soil] + a_6[sea\ salt]$

Issues:

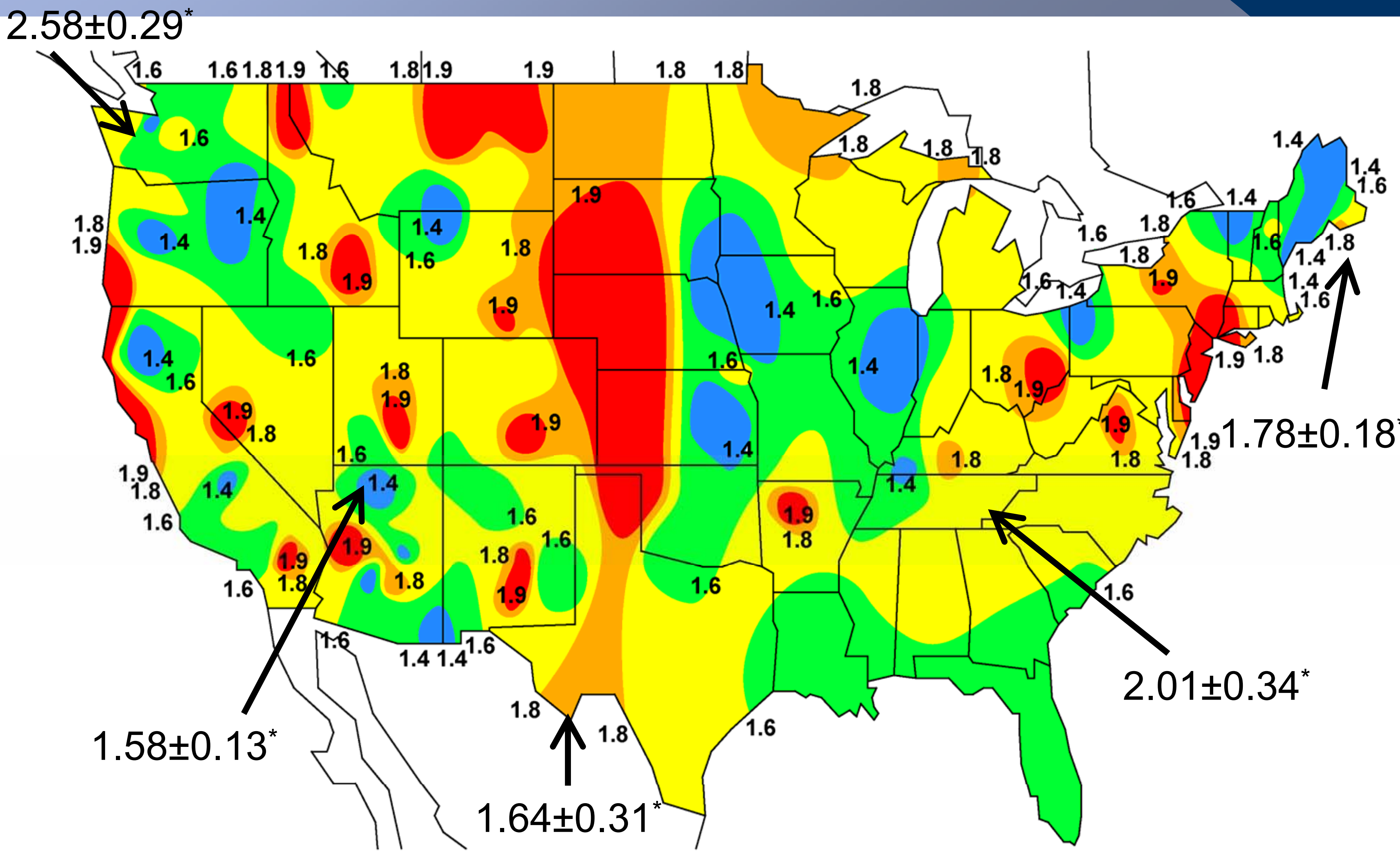
•chemical forms of species (e.g., ammonium sulfate, soil)

•water retention on Teflon filter

•sampling artifacts

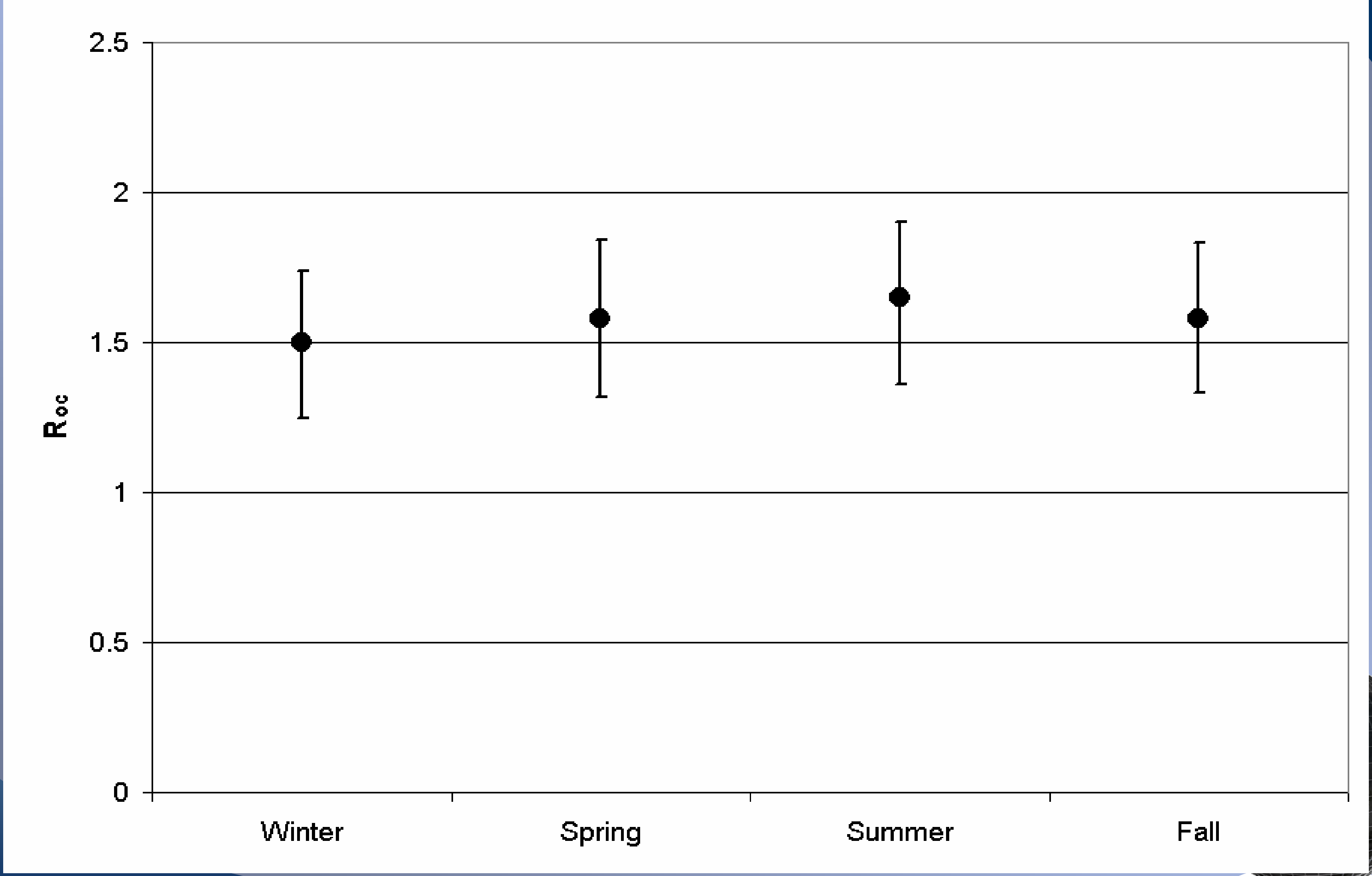
•collinearity

Annual average R_{oc} factor



*El-Zanan et al., 2005

Seasonal variation in R_{oc}



CHEMICAL FORMS: Nitrate

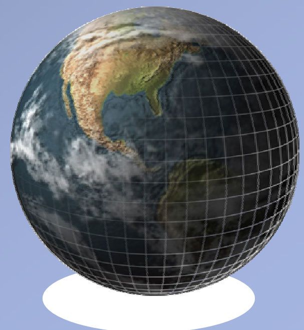
a2 = 0.8 ± 0.3

$HNO_3(g) + NH_3(g) \leftrightarrow NH_4NO_3(p)$

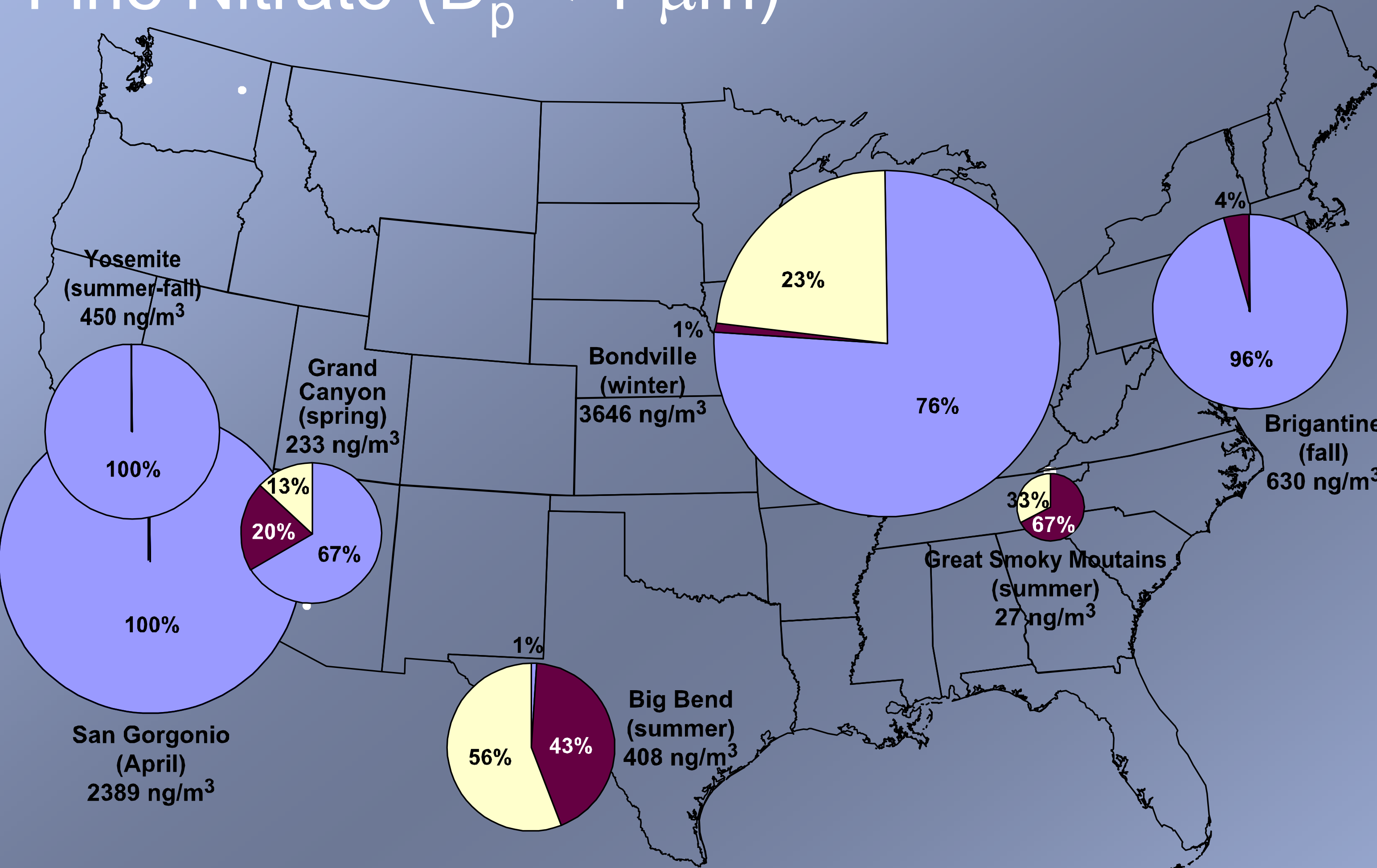
$HNO_3(g) + NaCl(p) \rightarrow NaNO_3(p) + HCl(g)$

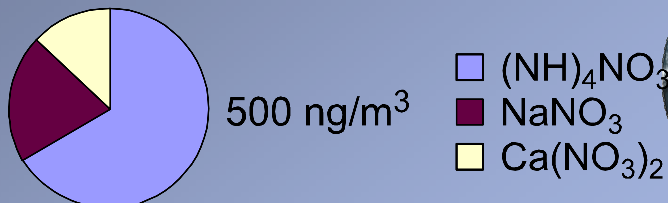
$2\ HNO_3(g) + CaCO_3(p) \rightarrow Ca(NO_3)_2(p) + CO_2 + H_2O$

} coarse particles



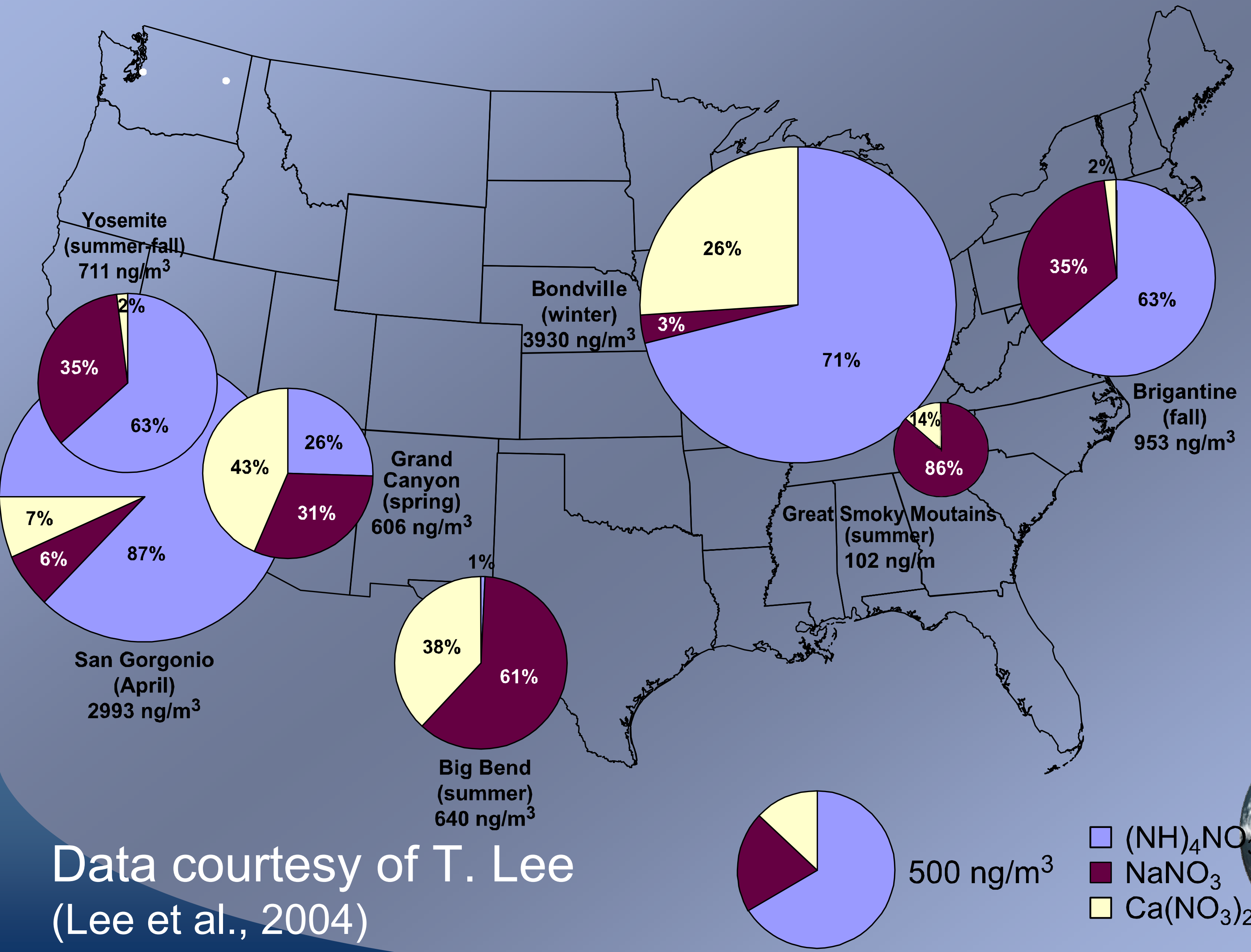
Fine Nitrate (D_p < 1 μm)





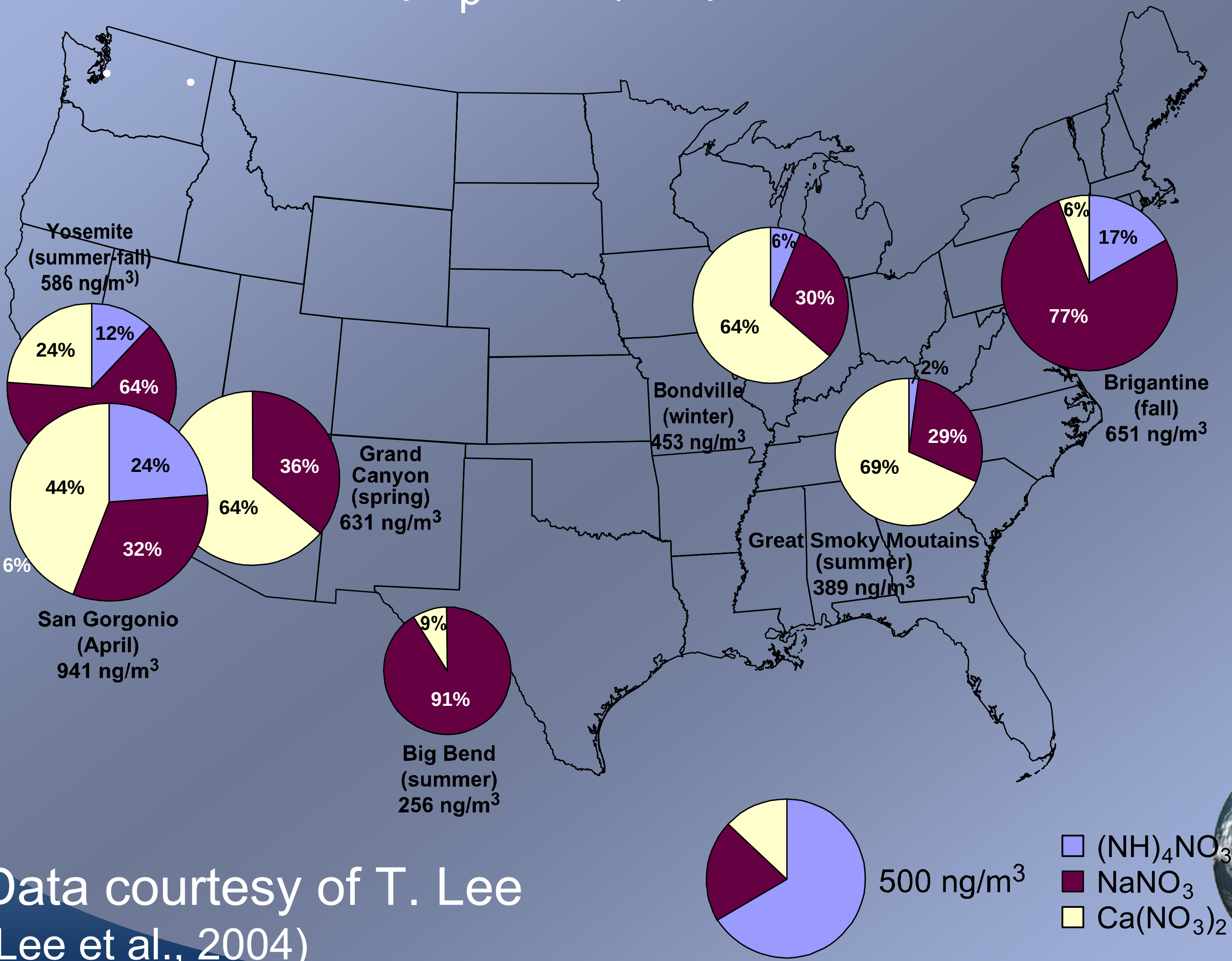
Data courtesy of T. Lee
(Lee et al., 2004)

Fine Nitrate (D_p < 3.2 μm)



Data courtesy of T. Lee
(Lee et al., 2004)

Coarse Nitrate (D_p > 1 μm)



Data courtesy of T. Lee

(Lee et al., 2004)

CHEMICAL FORMS - Sulfate

a1 = 1.2 ± 0.2

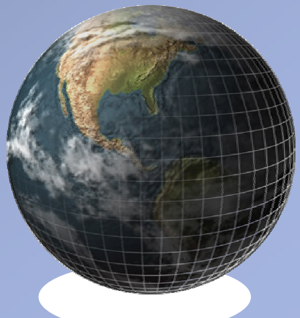
- Fully neutralized ammonium sulfate is assumed
- SO_4^{-2}
  - as $(NH_4)_2SO_4$: $1.375 \cdot [SO_4^{-2}]$
  - as $(NH_4)_3H(SO_4)_2$: $1.29 \cdot [SO_4^{-2}]$
  - as NH_4HSO_4: $1.2 \cdot [SO_4^{-2}]$

- NH_4^+ is not measured regularly at IMPROVE sites
- More acidic forms of sulfate have been measured at many locations

CHEMICAL FORMS- Soil

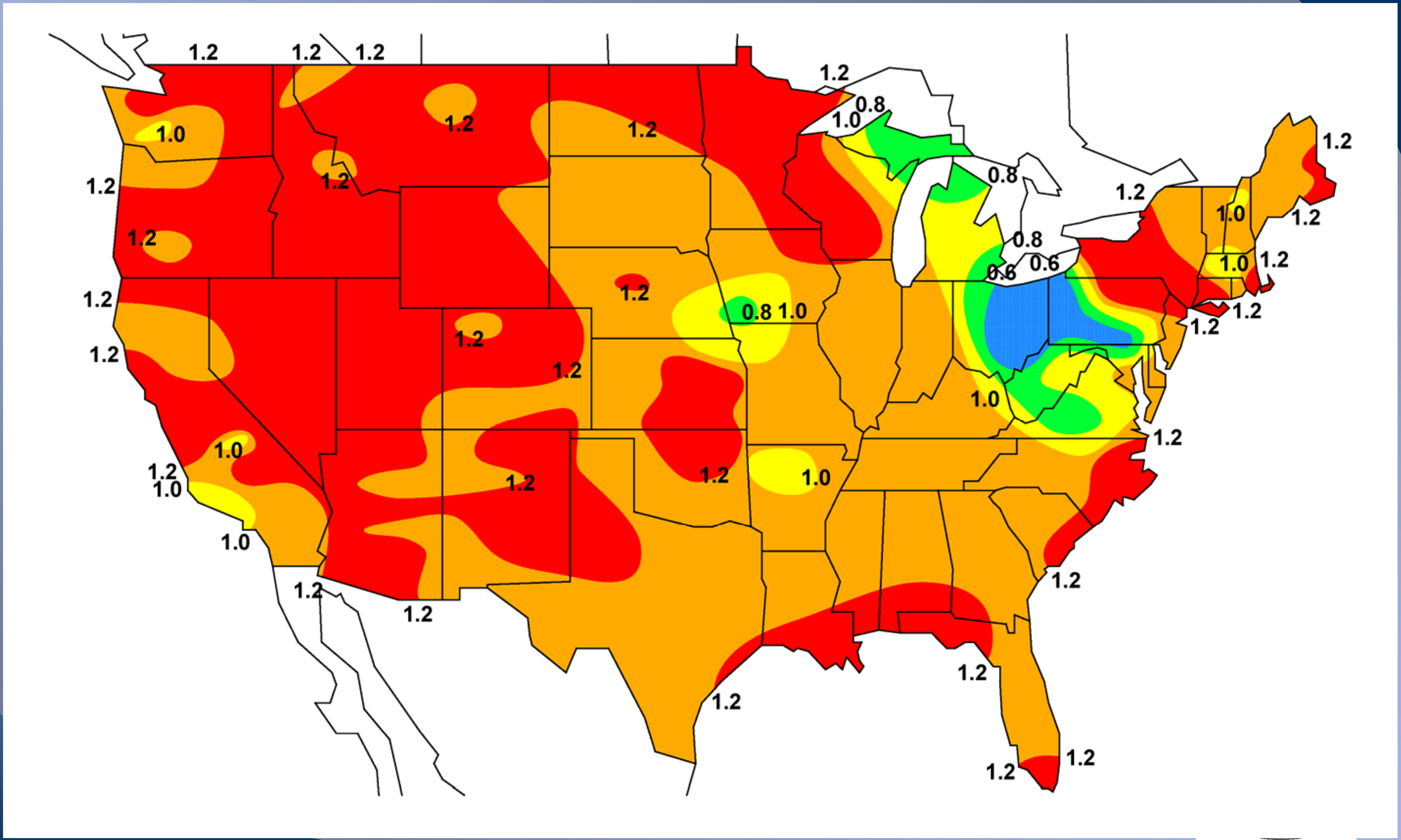
a5 = 1.2 ± 0.3

- Soil composition varies as a function of location and is further complicated by intercontinental and transcontinental transport (Asia, Africa, Mexico)
- Soil mass concentrations are computed by assuming oxides of elements typically associated with soil



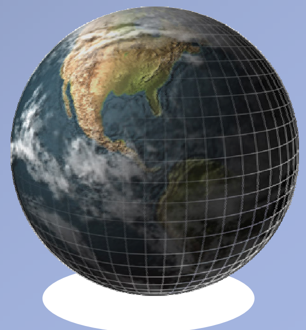
Annual average soil coefficient

a5 = 1.2 ± 0.3



CHEMICAL FORMS- Coarse mass
$CM = PM_{10} – PM_{2.5}$

- Coarse mass speciation at nine IMPROVE sites in 2003 for ~ year
- Preliminary results: over 50 % of CM is soil, with higher soil concentrations in the west than east
- POM is next highest contributor (15-35 %)- homogeneous spatial distribution
- Nitrate (5-15%) –associated with sea salt on the coast
- Sulfate is minor except at some coastal sites in NE (~ 10 %)



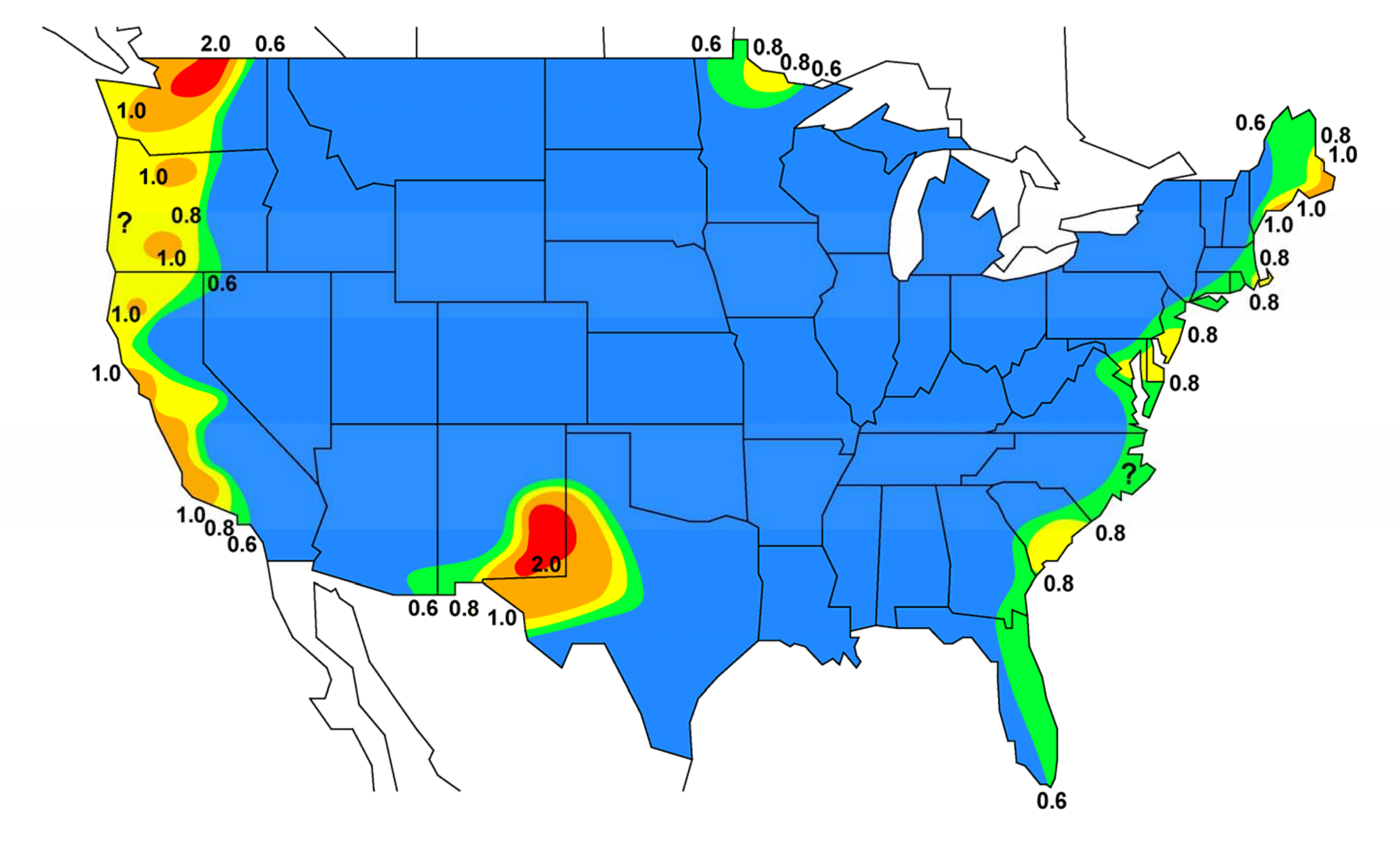
Mount Rainier
54%
37%
0% 6%
3%
Sequoia
70%
23%
0% 7%
0%
San Gorgonio
75%
14%
0% 10%
1%
Bridger
69%
15%
8%
7%
1%
Grand Canyon
78%
15%
2% 4%
1%
Bond
63%
26%
3% 5%
3%
Upper Buffalo
58%
21%
8%
11%
2%
Brigantine
58%
17%
9%
15%
1%
Great Smoky Mountains
52%
34%
0% 12%
2%
Aerosol Concentration
Month
Jan Mar May Jul Sep Nov
Over Unexplained
Under Unexplained
Soil
Elemental Carbon
Organics
Nitrate
Sulfate

CHEMICAL FORMS- sea salt

a6 = 1.12 ± 0.5

- Sea salt is not currently included in the IMPROVE algorithm
- Usually computed from sea salt markers like Na^+, Cl^- or combinations
- Difficulties arise because positive ions are not analyzed as part of the IMPROVE network, elemental Na data have large uncertainties, depletion of Cl^- due to reactions of HNO_3 with sea salt
- Could be important at coastal sites
- Compute from $1.8 \cdot Cl^-$ (sea salt is 55 % Cl by weight)

Annual average sea salt coefficient



Methods for deriving mass extinction efficiencies (α_{ext}, $m^2\ g^{-1}$)

- Measurement method
- Theoretical method
- Multi-linear regression method (MLR)
- Partial scattering method

Measurement method

Specific mass scattering efficiency can be defined as the ratio of light scattering coefficient (b_{sp}) to mass concentration (M):

$$\alpha_{sp\_spec} = \frac{b_{sp}}{M}$$

Either the average b_{sp} is divided by the average mass, or a linear regression is performed on the data and the slope is interpreted as the specific mass scattering efficiency

Represent an average aerosol that could be changing due to variations in RH, size distribution and composition

Theoretical method

$$b_{ext} = \int_0^{\infty} \alpha_{ext} \frac{dM}{d\log Dp} d\log Dp$$

$$\alpha_{ext} = \frac{3}{2} \frac{Q_{ext}(n, D_p, \lambda)}{\rho_p D_p}$$

ρ_p=particle density

λ=wavelength of incident light

Q_{ext}=Mie extinction efficiency

D_p = particle diameter

Multi-Linear Regression method (MLR)

$$b_{ext} = \Sigma \alpha_{Mj} M_j$$

Assumptions:

- All aerosol components (M_j) contributing to b_{ext} are included
- large number of samples
- uncorrelated species (collinearities)
- biased by random uncertainties in measurements: species with lower uncertainties are over-predicted and vice-versa

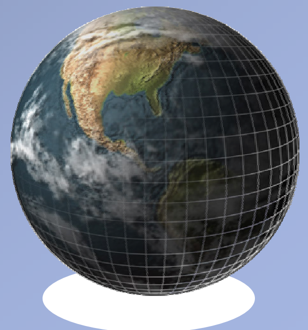
Partial Scattering

$$\alpha_{ext,part} = \left(\frac{\partial b_{ext}}{\partial M_j} \right)$$

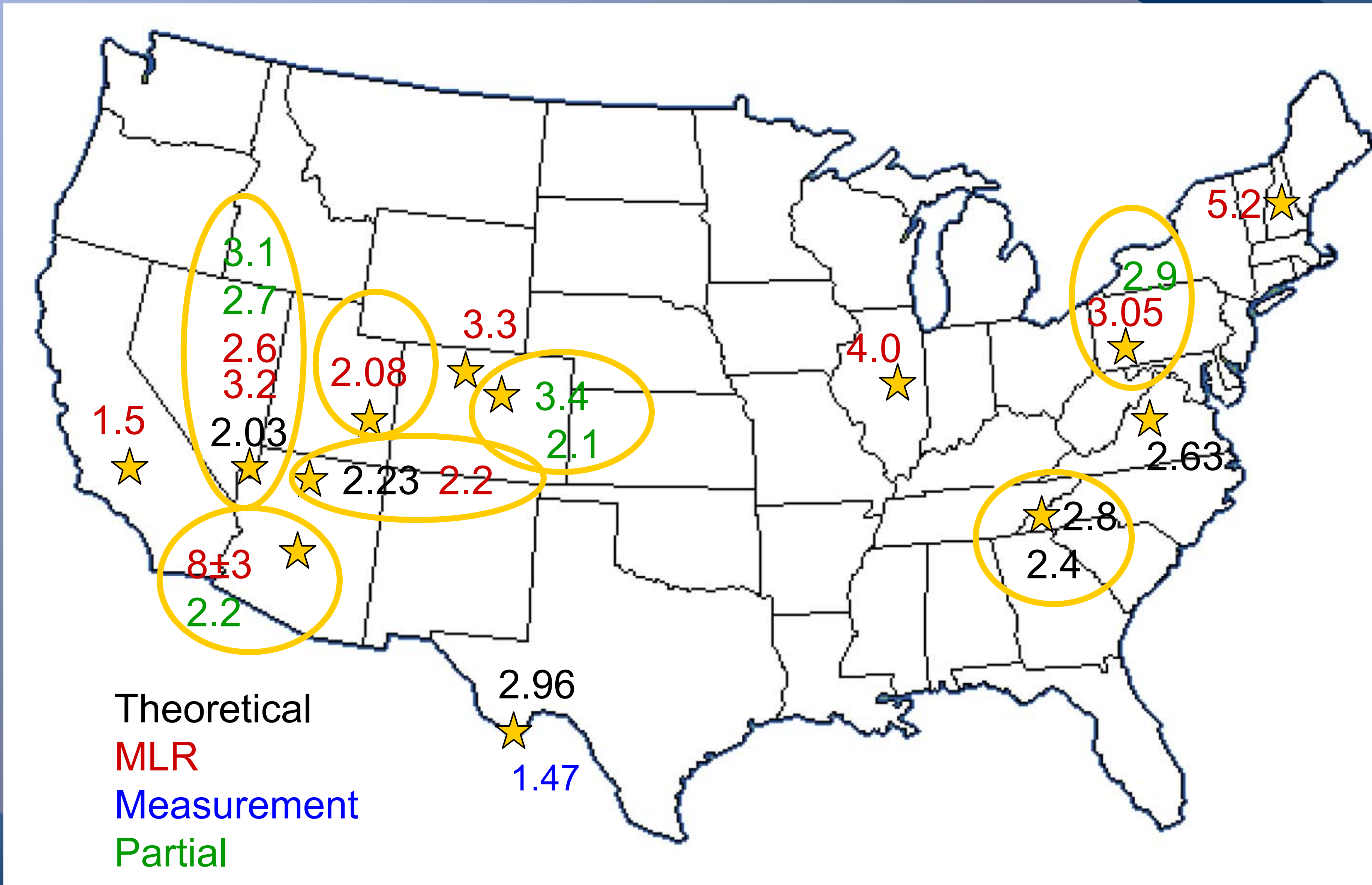
- Depends on change in concentration as species M_j is added or removed- either by changing particle number or size
- useful for regulatory purposes, difficult to implement in practice

Literature Survey

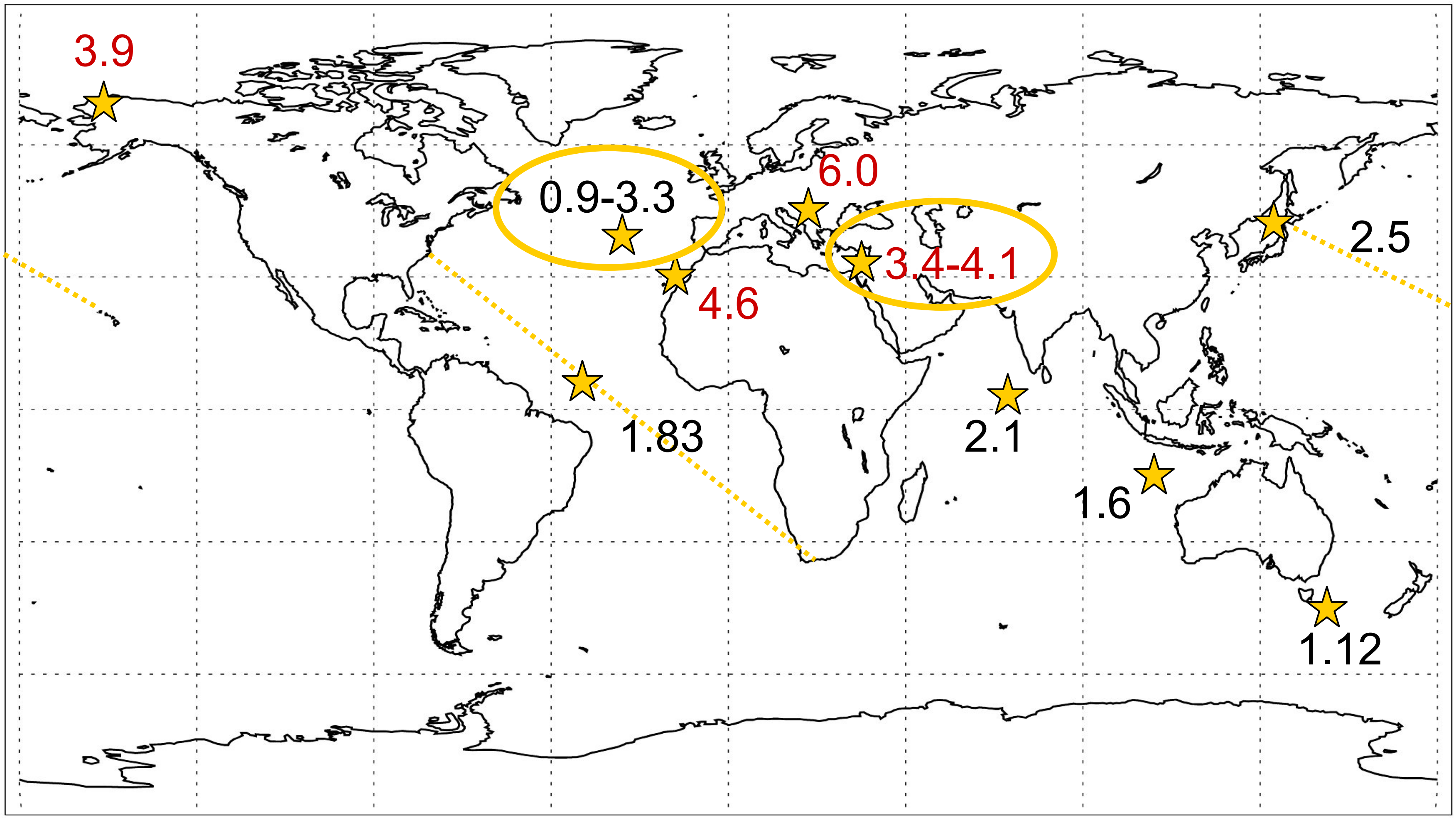
- ~ 60 peer-reviewed journal articles since 1990: focus on ground-based measurements
- Results separated into methods used, also for species and size modes
- Corrections to sulfate and POM applied



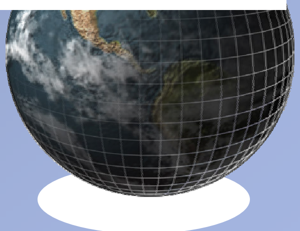
Dry Fine $(NH_4)_2SO_4$ ($m^2\ g^{-1}$)



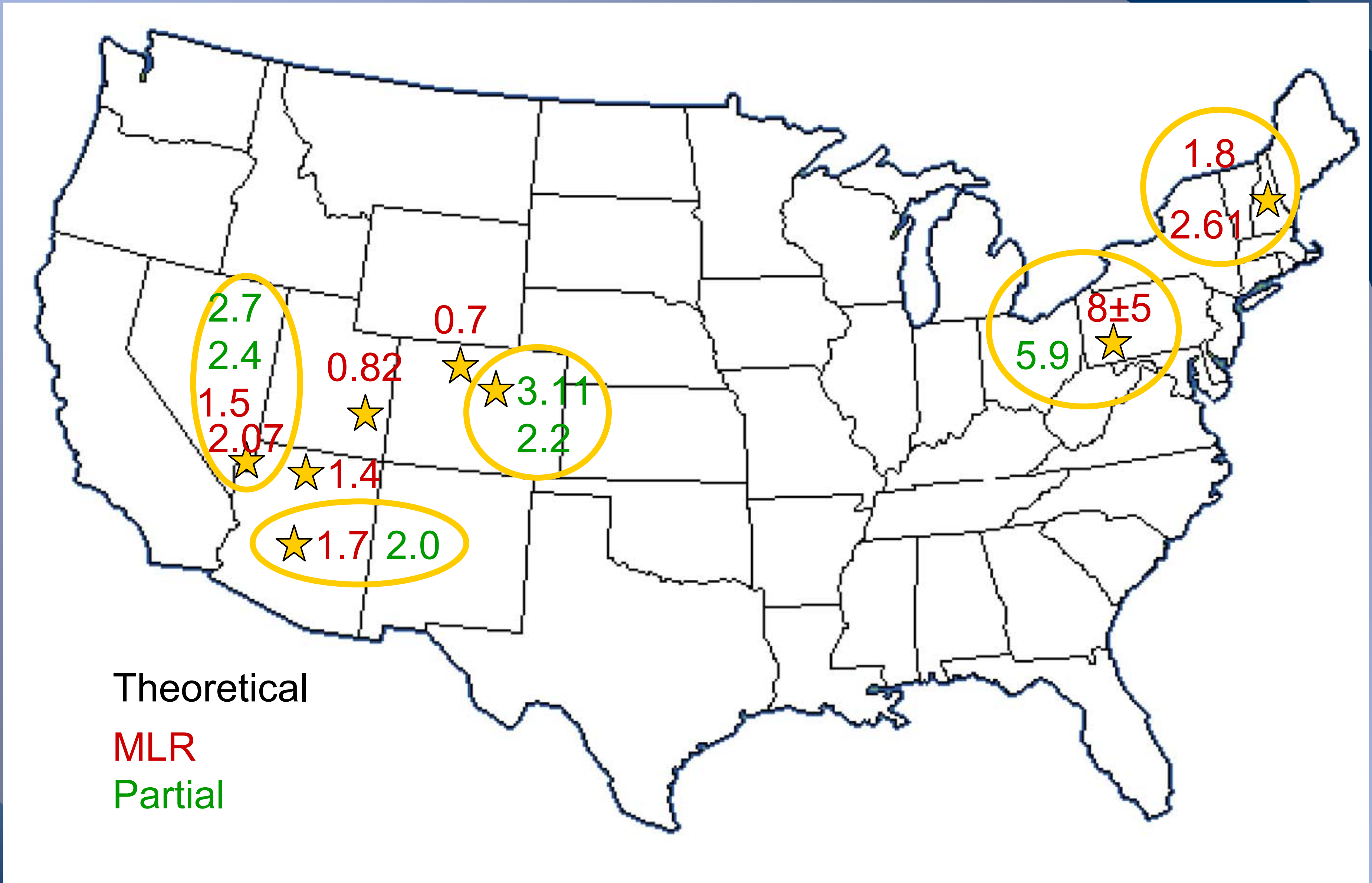
Global Fine Dry $(NH_4)_2SO_4$ ($m^2\ g^{-1}$)



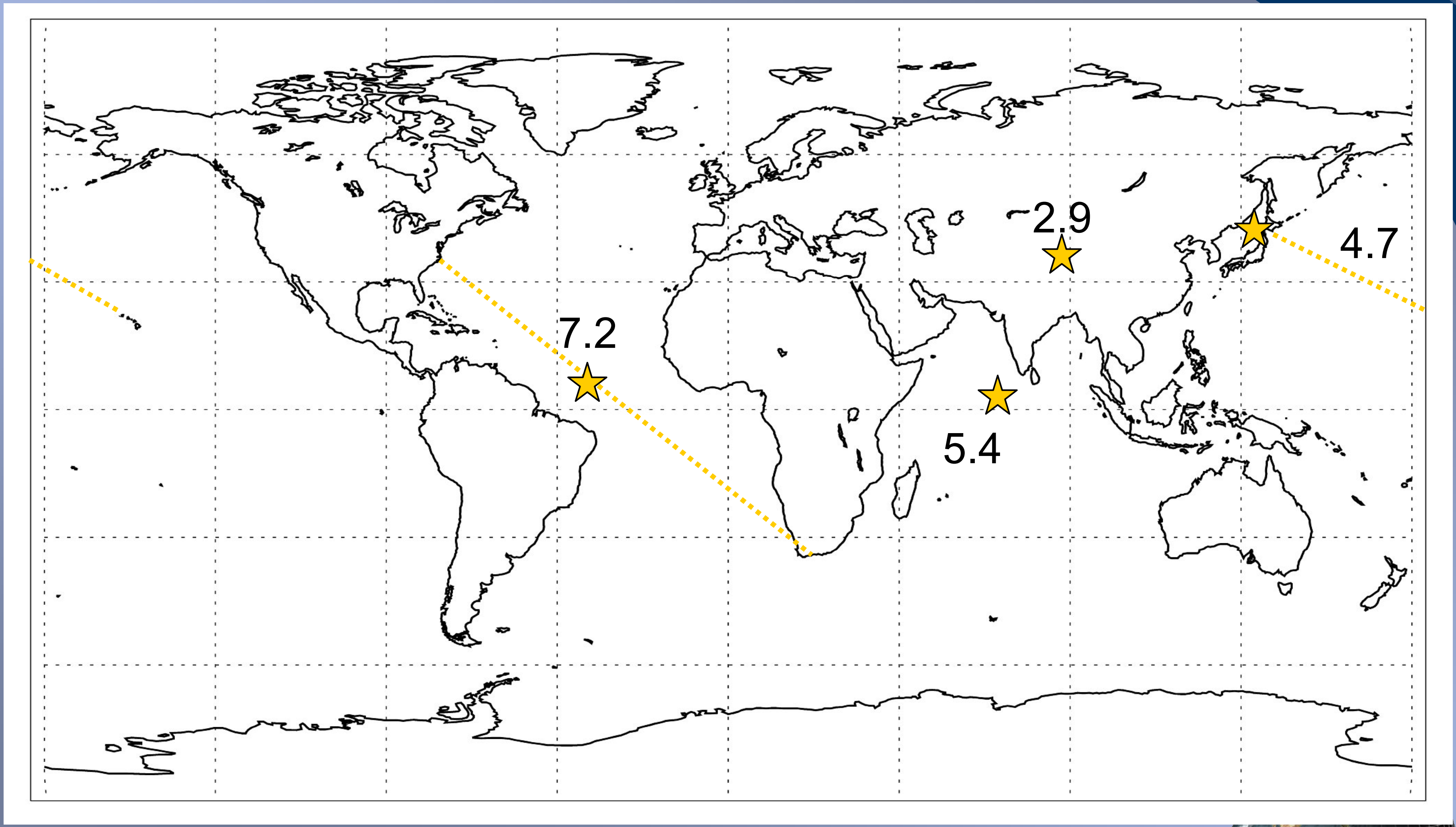
Theoretical MLR



Fine POM (R_{oc} =1.8) ($m^2\ g^{-1}$)



Global Fine POM (R_{oc} =1.8) ($m^2\ g^{-1}$)



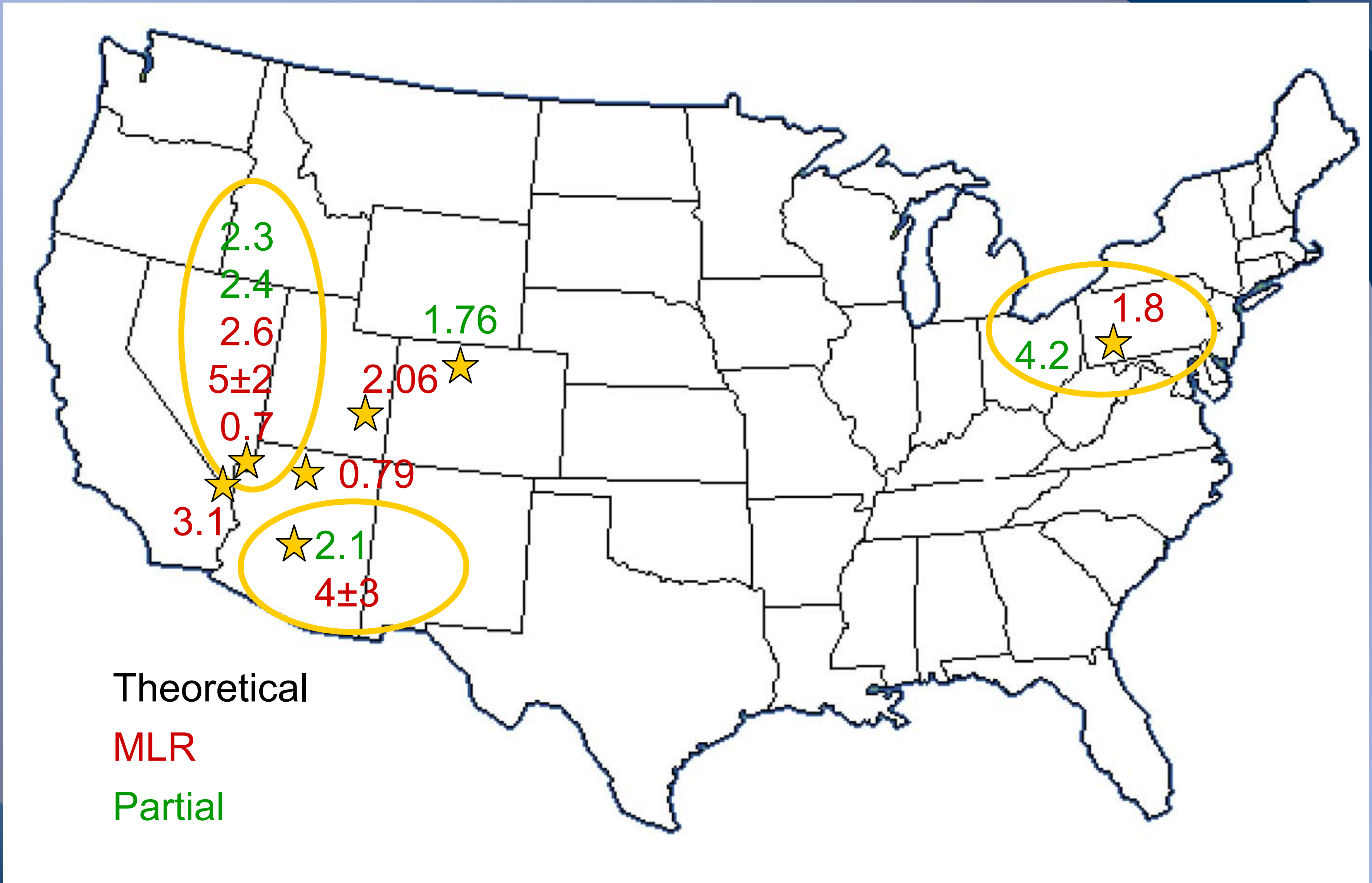
Theoretical

Summary of Mass Scattering Efficiencies from All Methods (m^2 g^{-1})

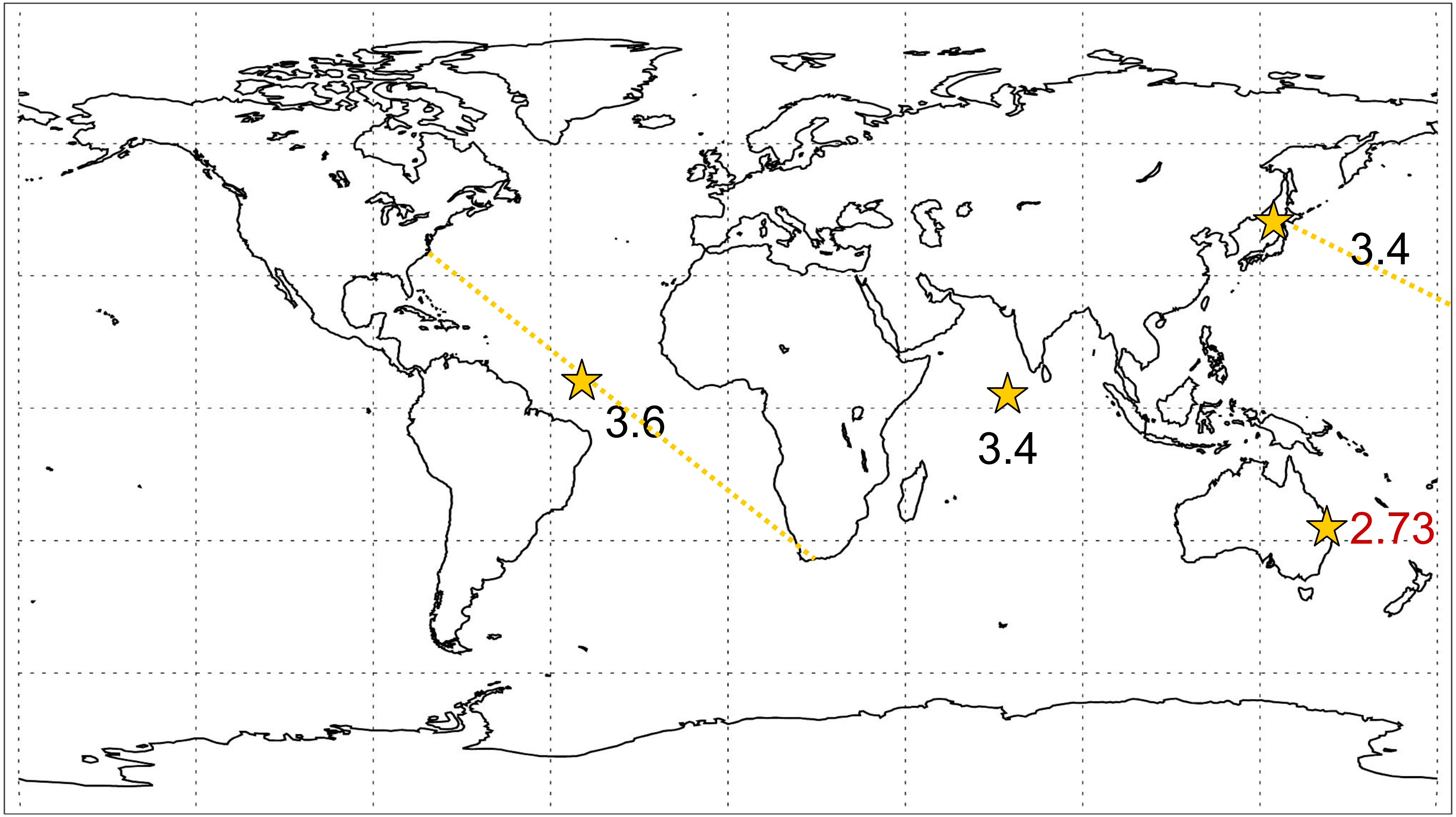
Species/mode	Theoretical	MLR	Partial	IMPROVE
Fine	4.3 ± 0.7 (*26*)	3.1 ± 1.5 (*17*)		
Coarse	1.6 ± 1.0 (*21*)	0.7 ± 0.6 (*13*)		0.6
Total	2.2 ± 1.0 (*9*)			
Sulfate	2.5 ± 1.1 (*16*)	3.2 ± 1.2 (*24*)	2.8 ± 0.7 (*24*)	3
Nitrate		4 ± 2 (*16*)	3.8 ± 1.6 (*11*)	3
POM	5.9 ± 1.0 (*20*)	2.3 ± 1.0 (*23*)	5.4 ± 1.8 (*26*)	4
Fine dust	3.4 ± 0.5 (*19*)	3 ± 2 (*19*)	3 ± 1 (*9*)	
Coarse dust	0.7 ± 0.2 (*21*)	0.40 ± 0.08 (*2*)		1
Total dust	1.2 ± 0.3 (*9*)	0.7 ±0.2 (*3*)		
Fine sea salt	5.3 ± 0.8 (*22*)	4.0 ± 1.6 (*3*)		
Coarse sea salt	1.2 ± 0.3 (*20*)	1.6 ± 1.2 (*3*)		
Total sea salt	2.3 ± 0.9 (*9*)	2.2 (*1*)		

Discussion…

Fine Dust ($m^2\ g^{-1}$)

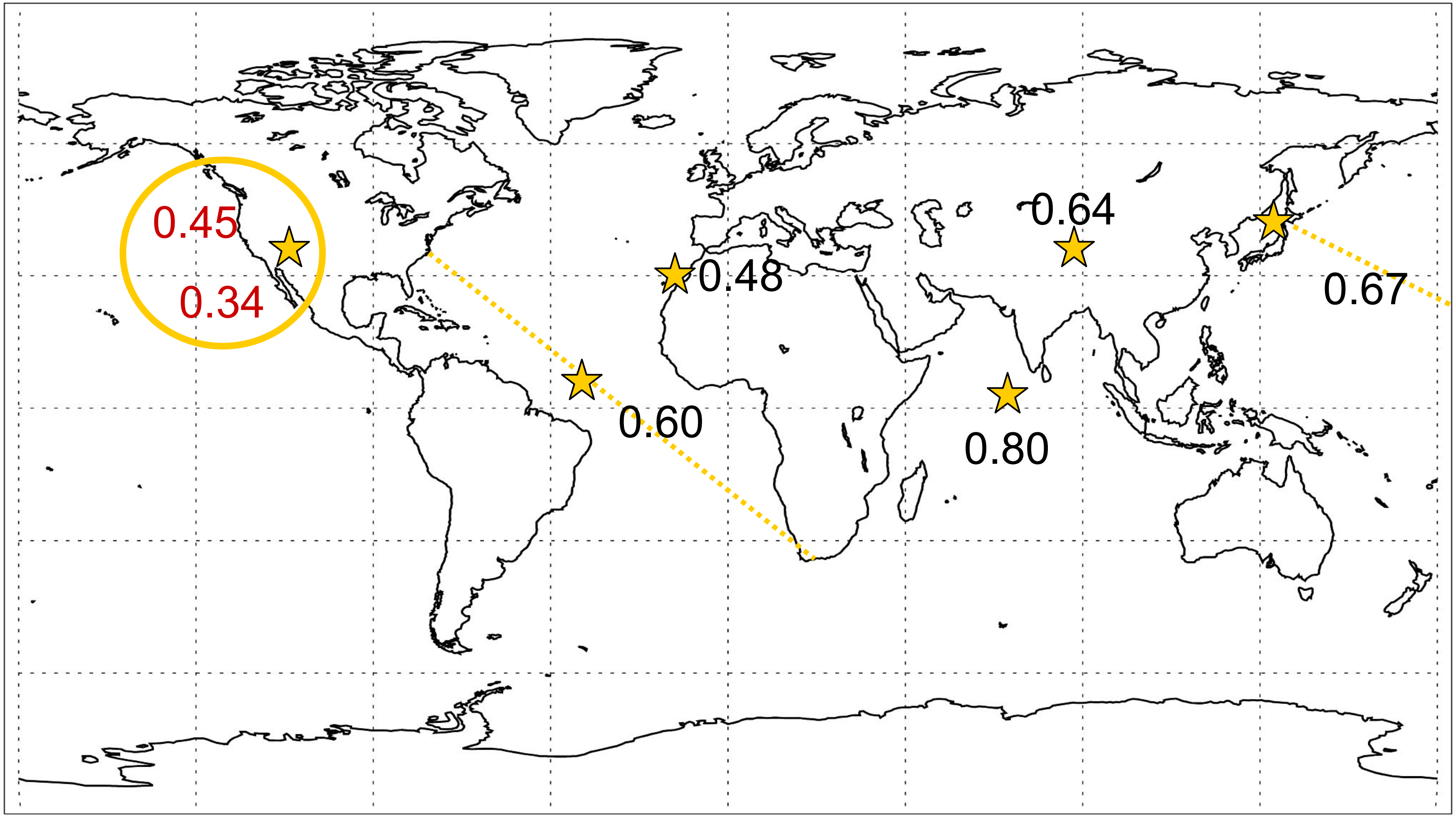


Global Fine Dust ($m^2\ g^{-1}$)



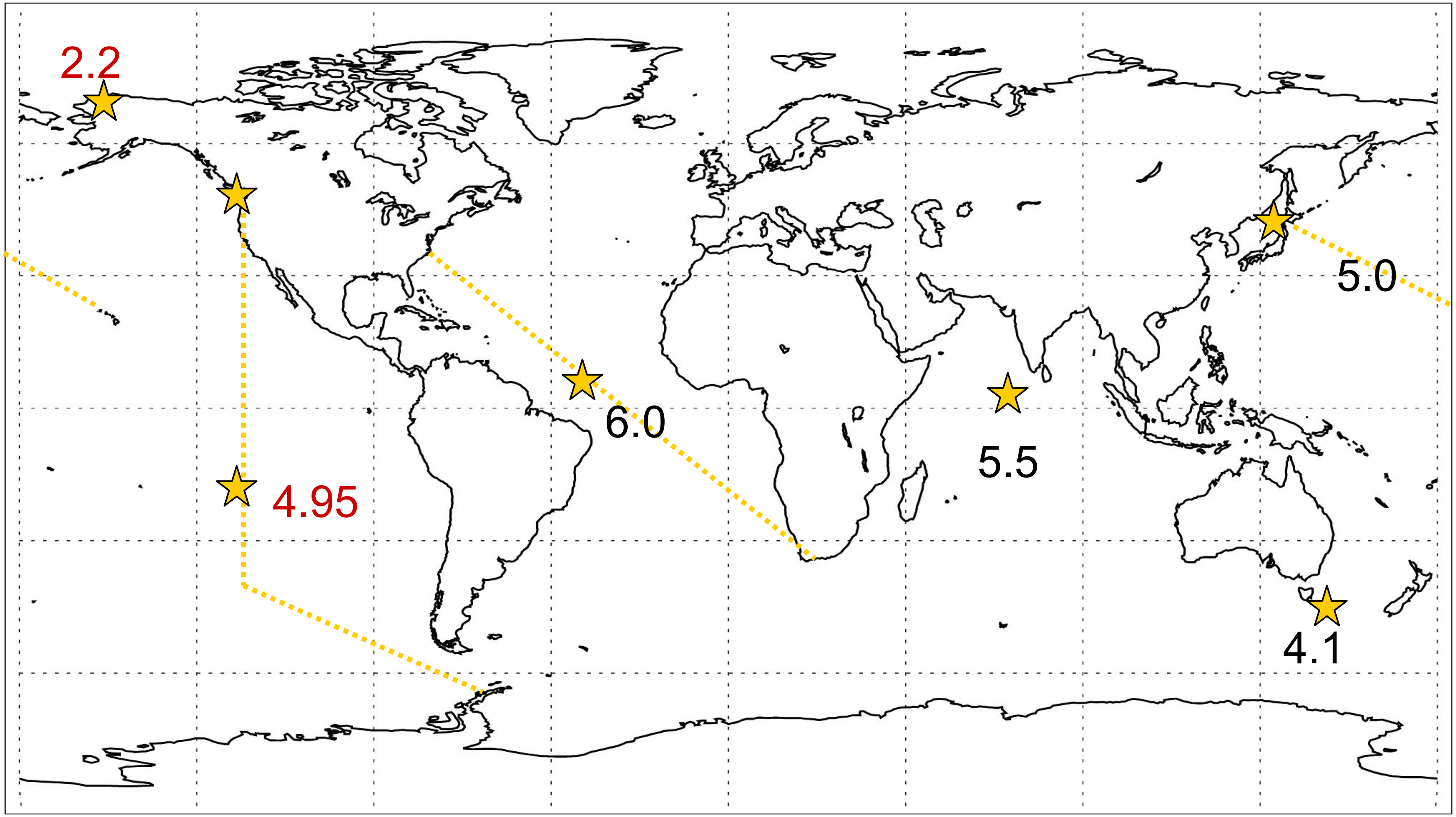
Theoretical MLR

Global Coarse Dust ($m^2\ g^{-1}$)



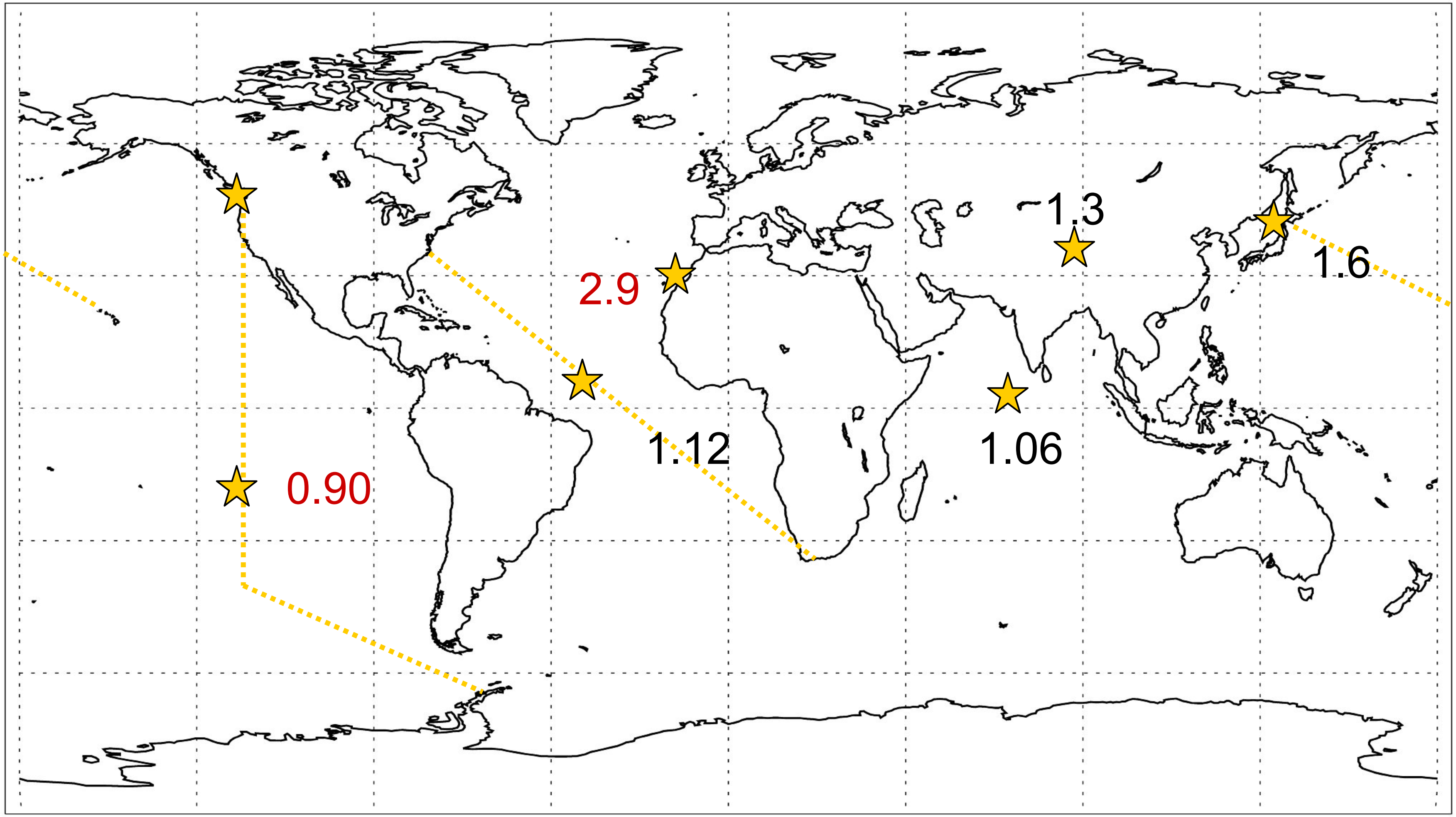
Theoretical MLR

Global Fine Sea Salt (m^2 g^{-1})



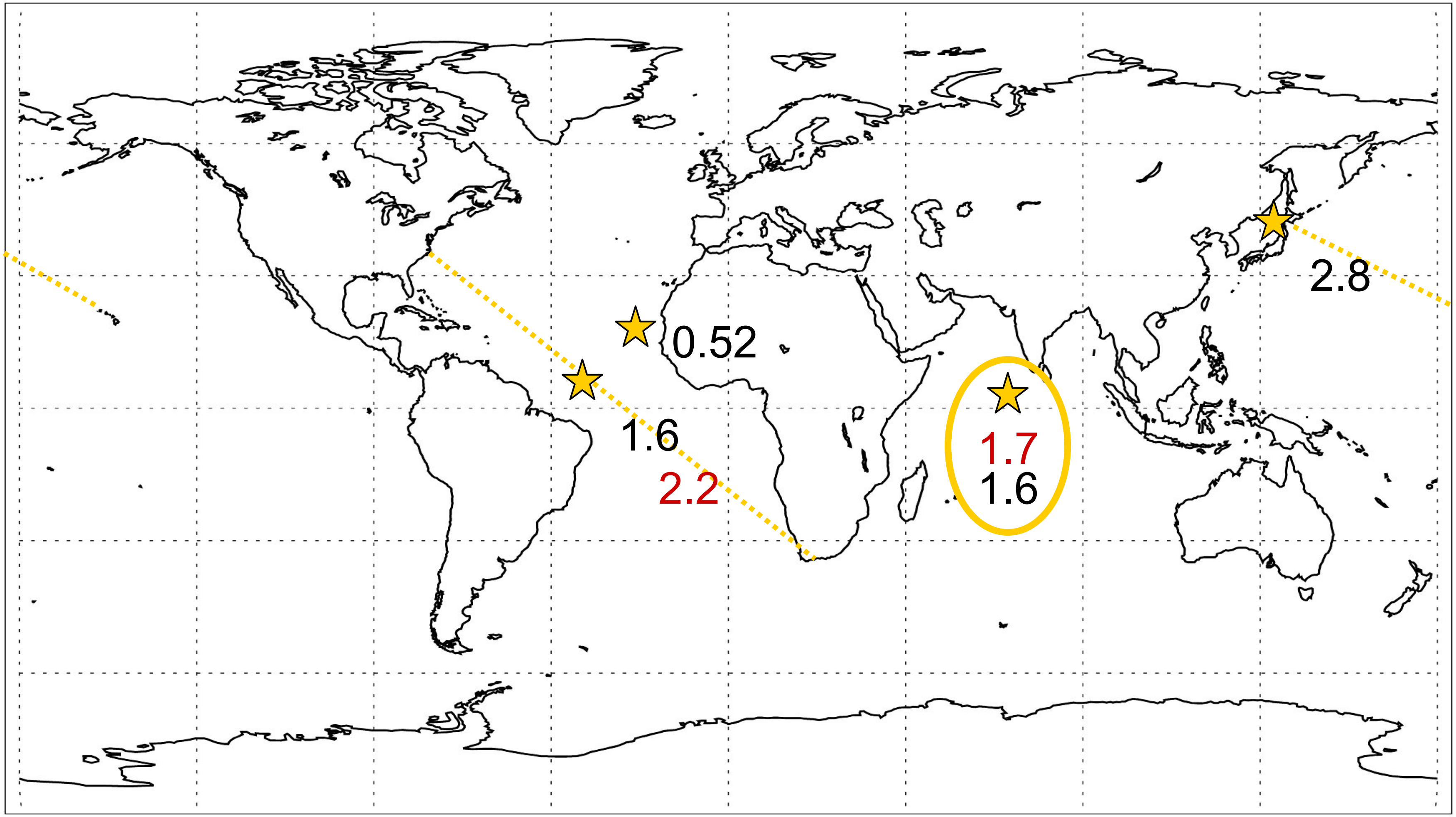
Theoretical MLR

Global Coarse Sea Salt ($m^2\ g^{-1}$)



Theoretical MLR

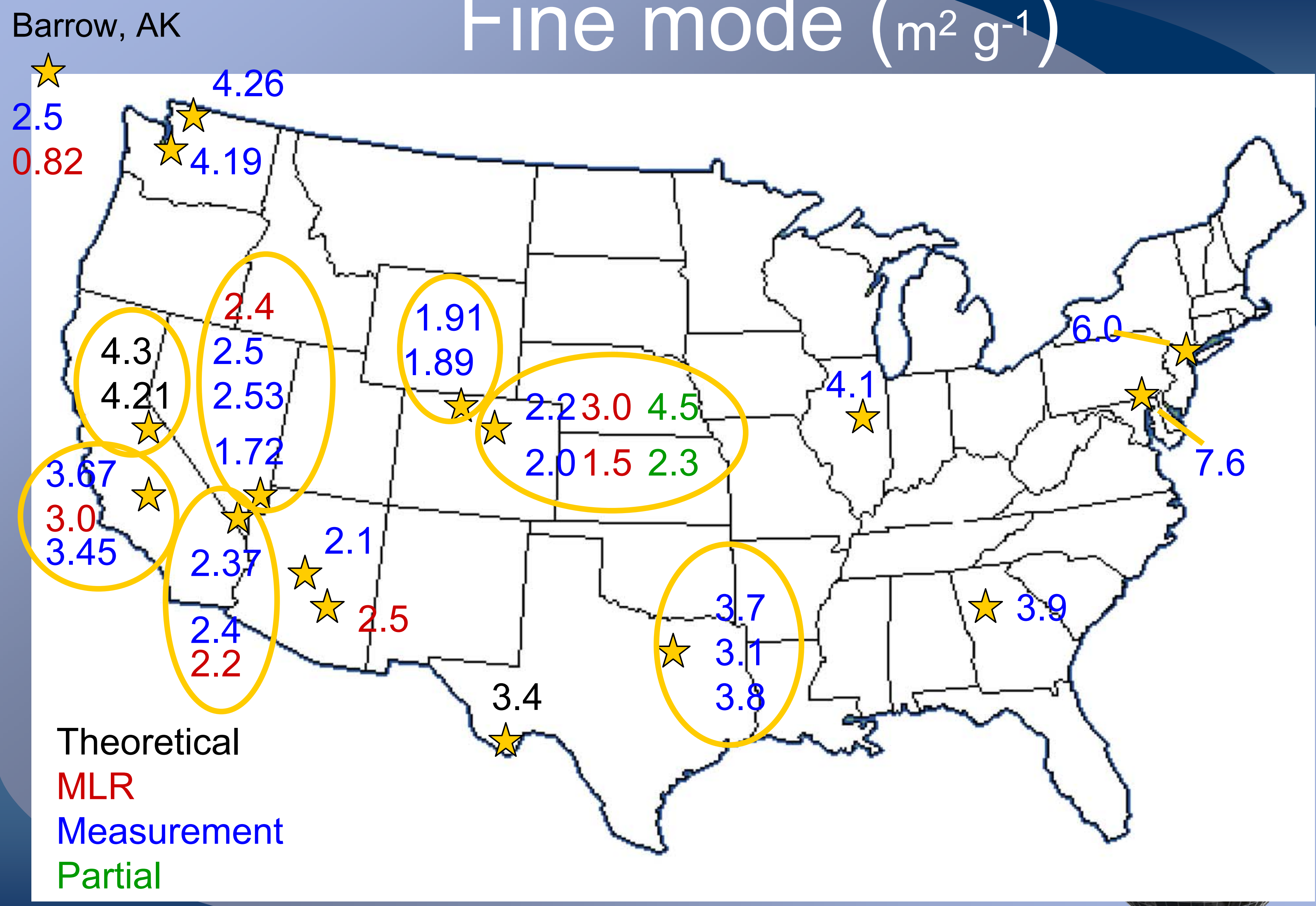
Global Total Sea Salt ($m^2\ g^{-1}$)



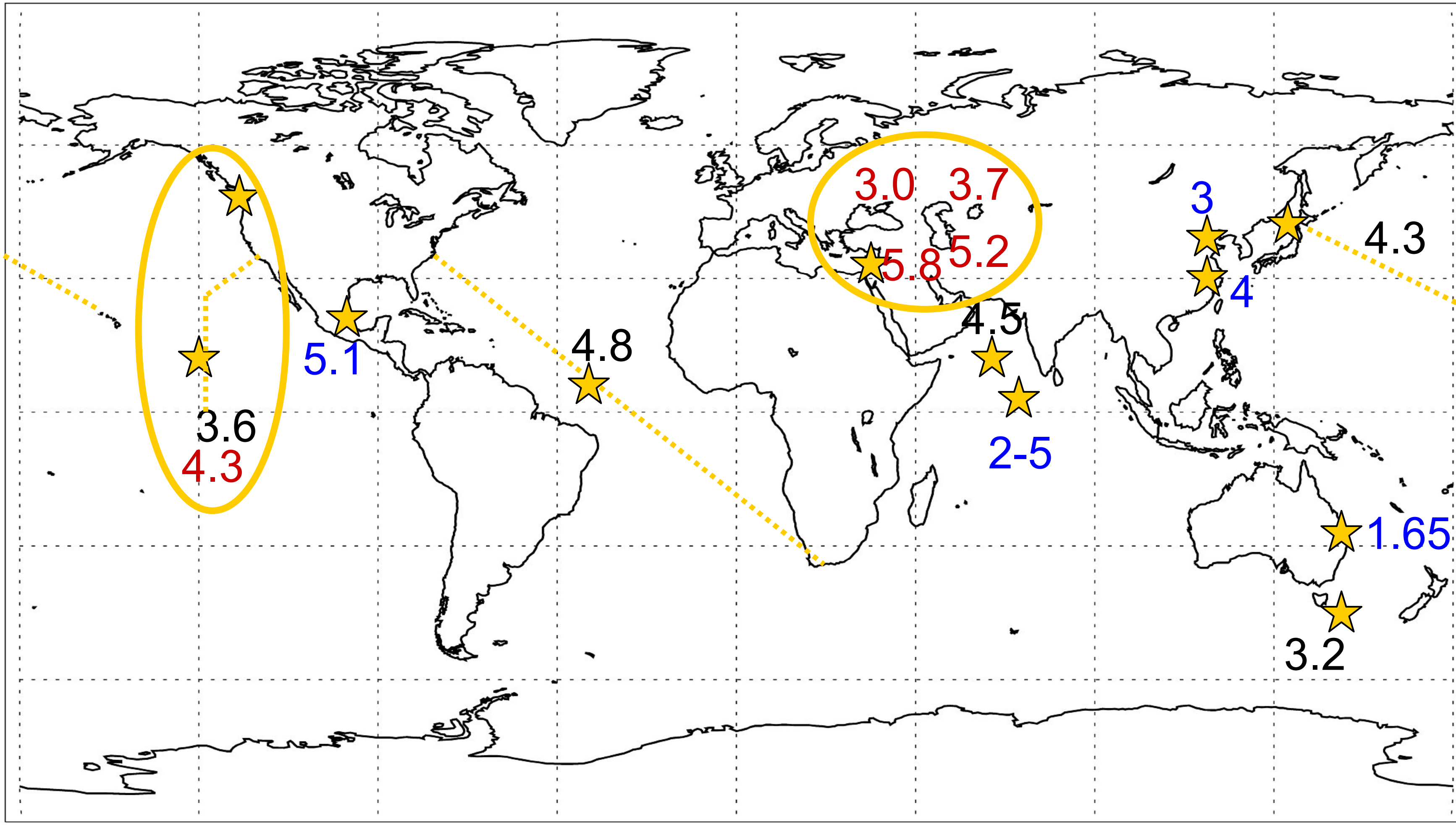
Theoretical

MLR

Fine mode ($m^2\ g^{-1}$)

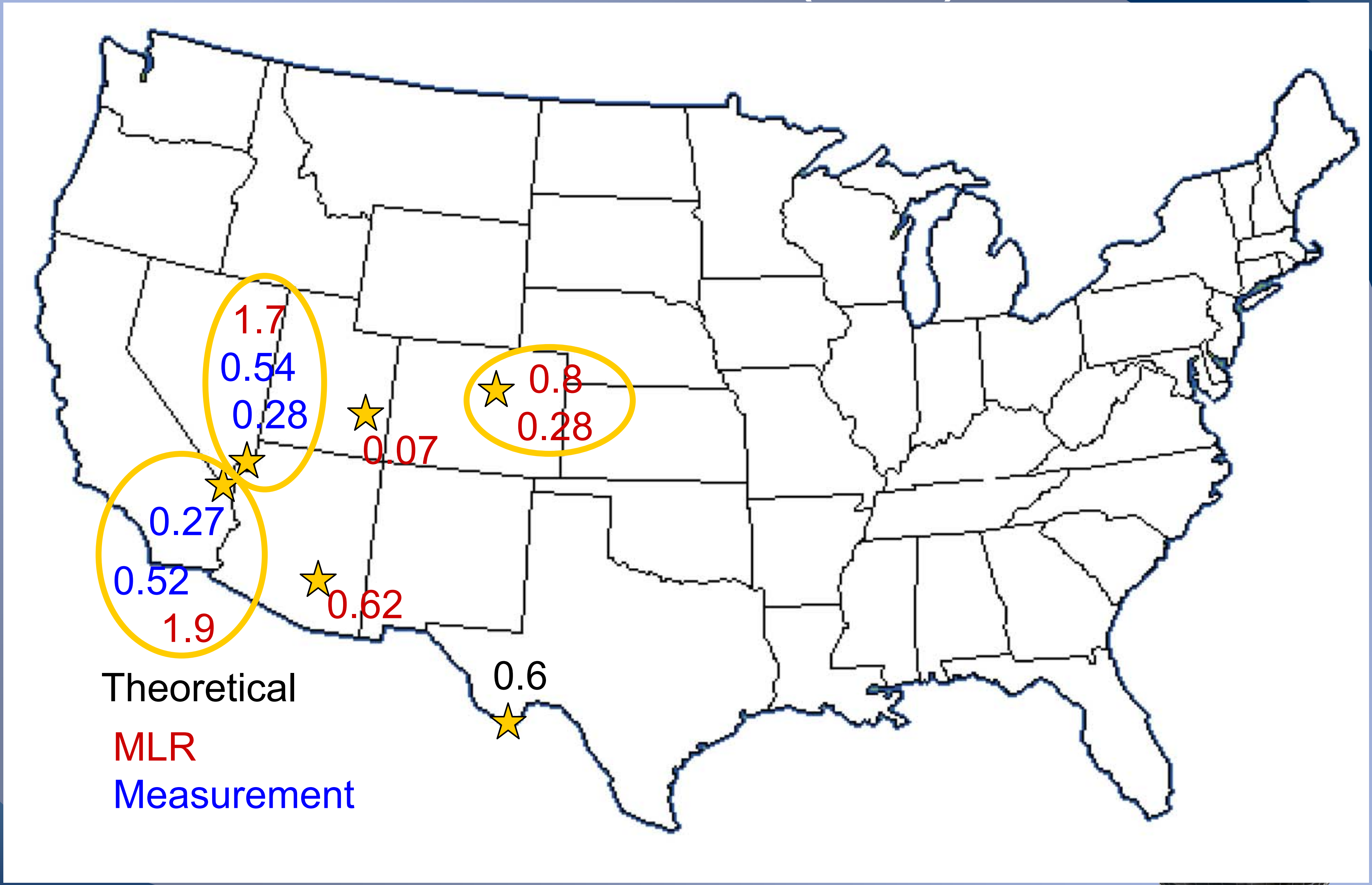


Global Fine Mode ($m^2 g^{-1}$)

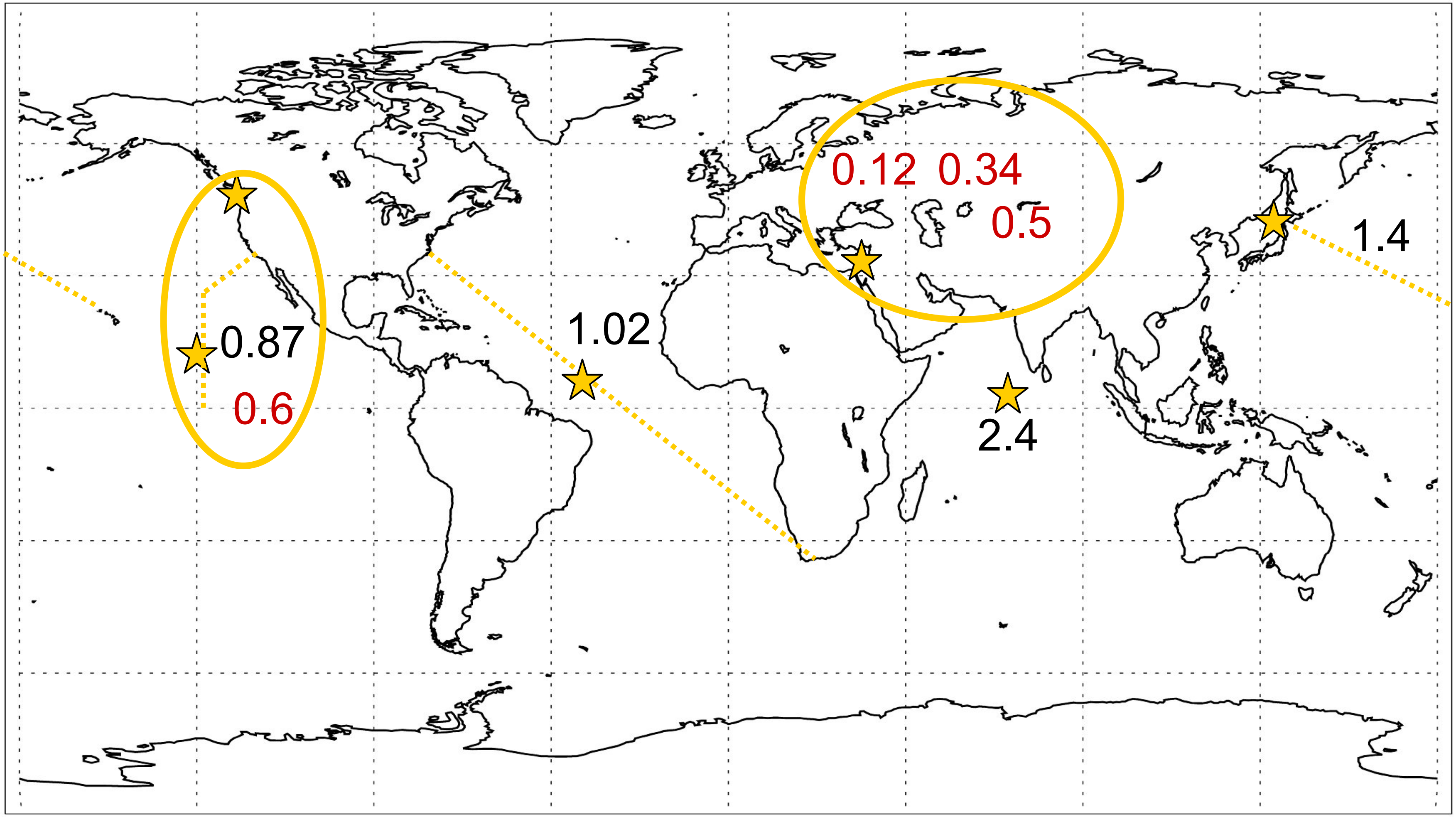


Theoretical MLR Measurement

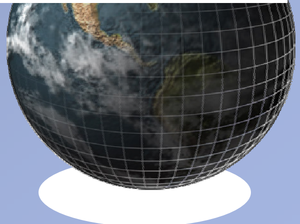
Coarse mode ($m^2\ g^{-1}$)



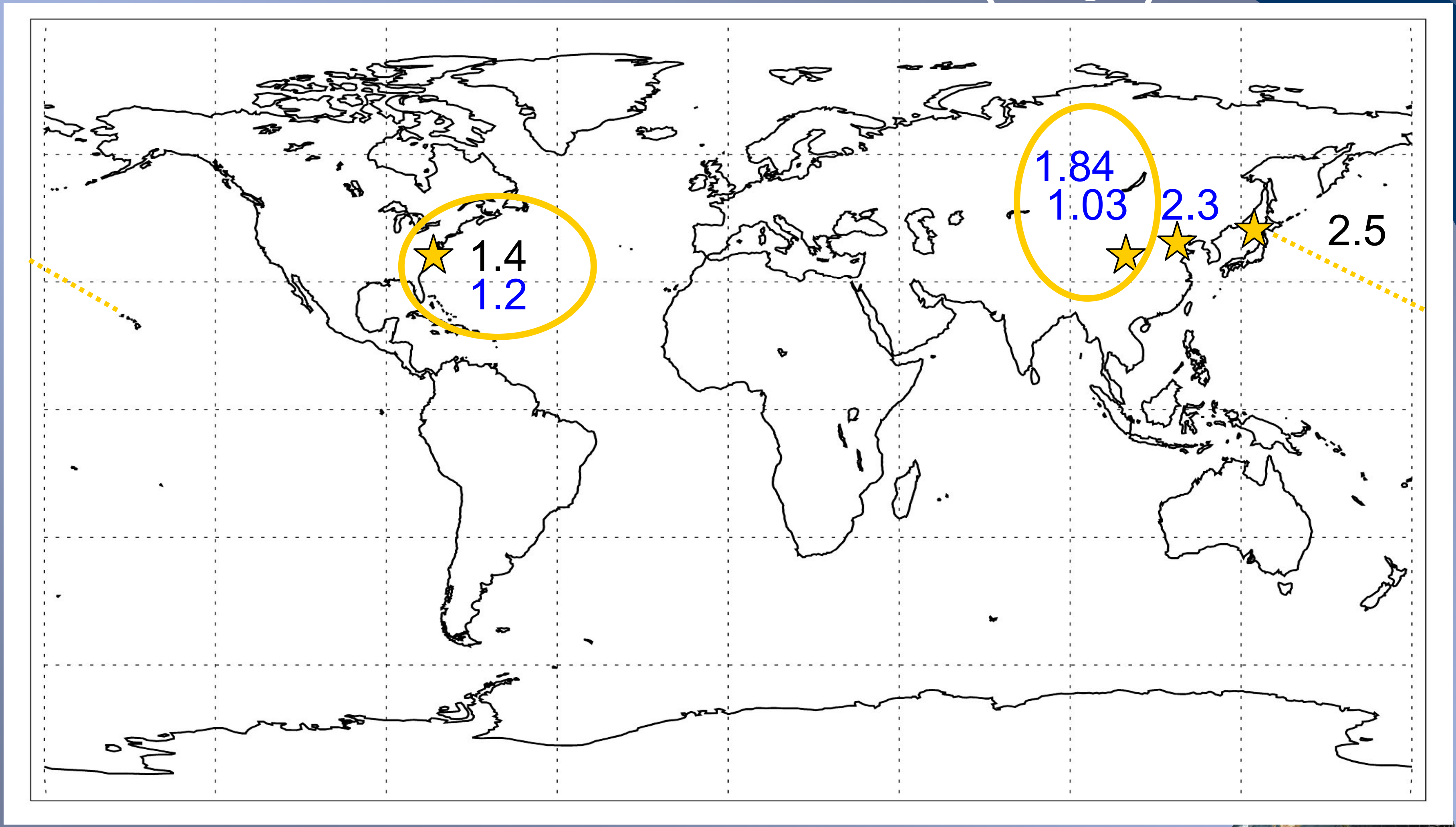
Global Coarse Mode ($m^2 g^{-1}$)



Theoretical MLR

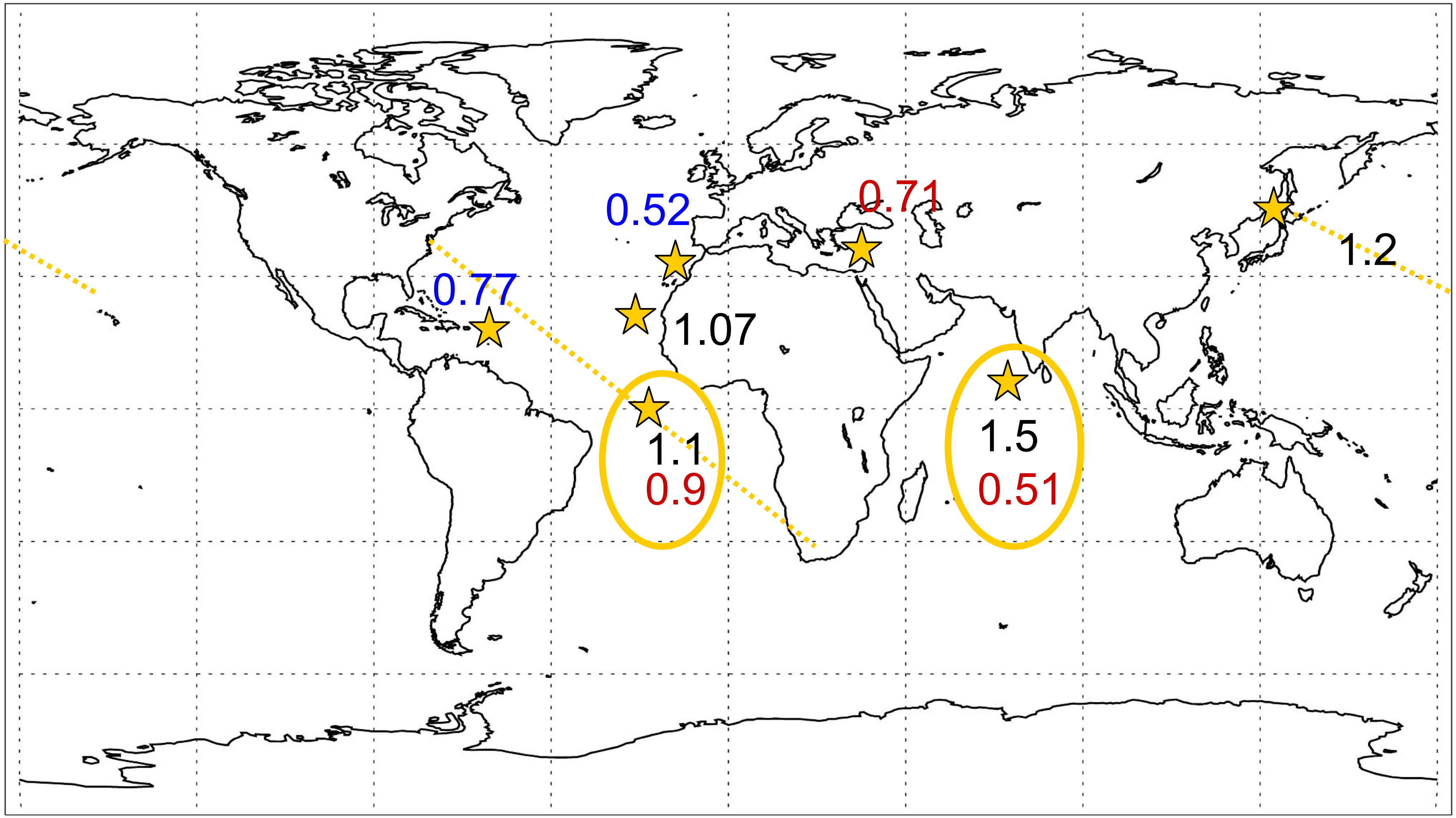


Global Total Mode ($m^2\ g^{-1}$)



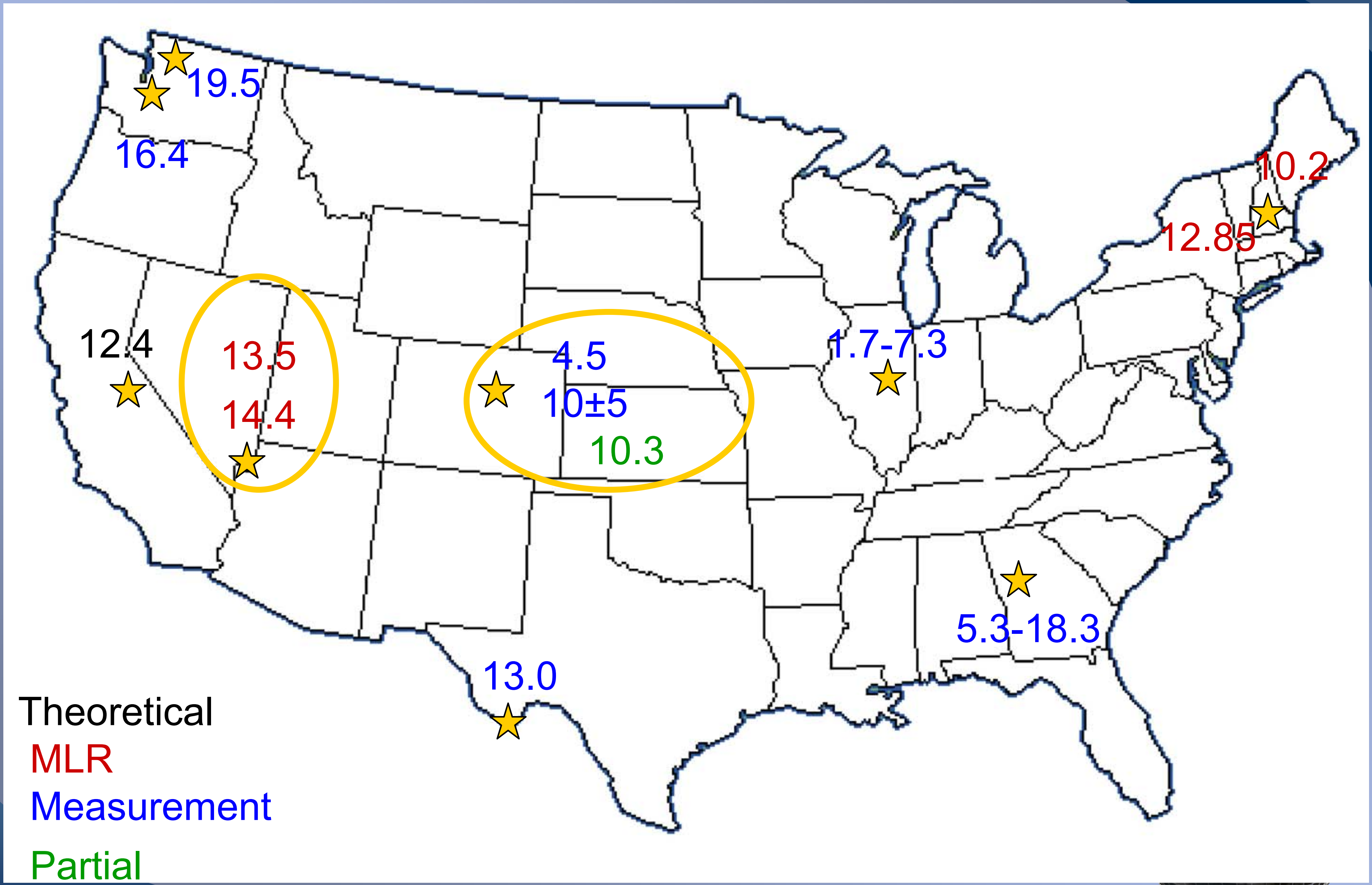
Theoretical Measurement

Global Total Dust (m² g⁻¹)

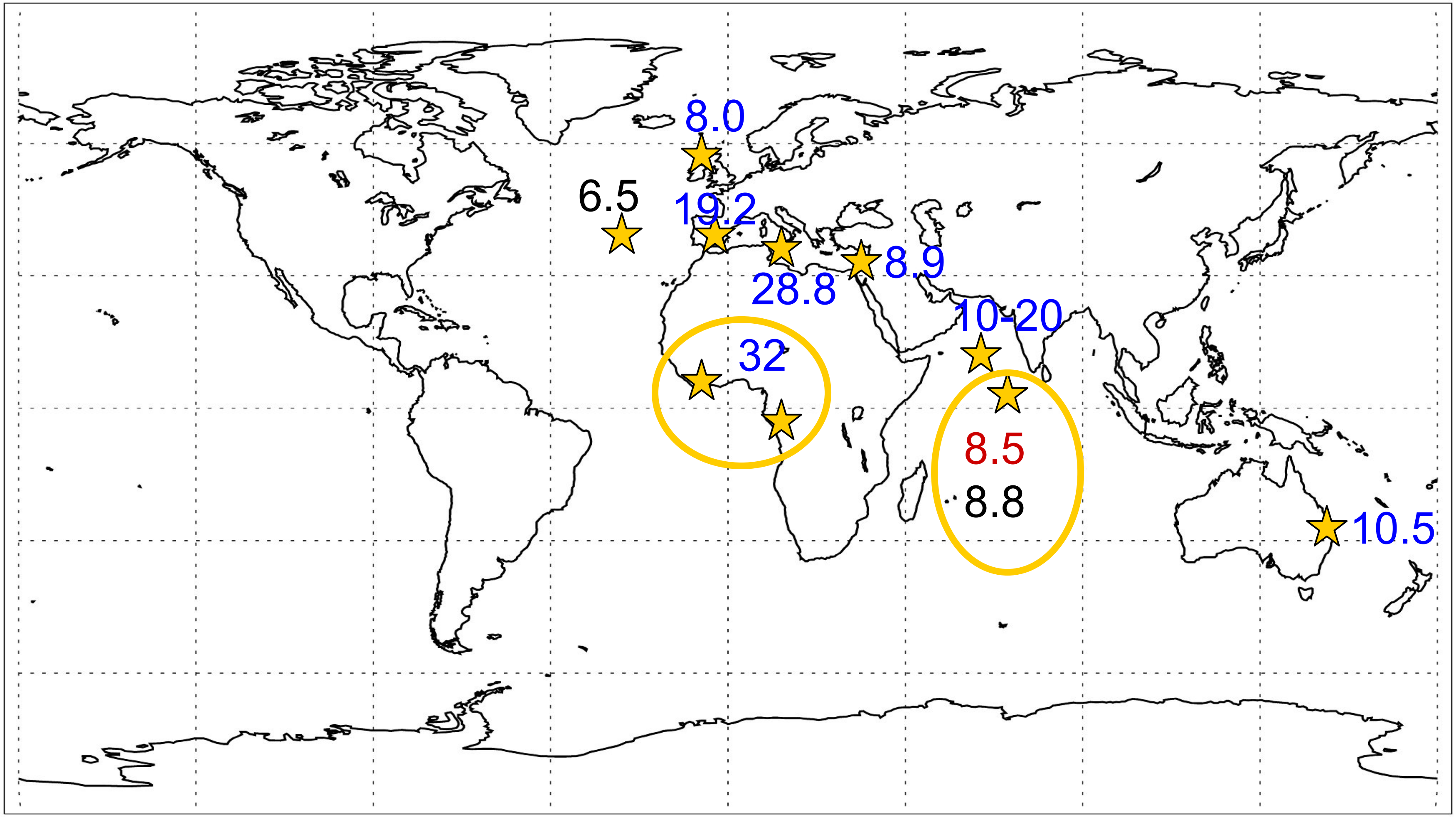


Theoretical MLR Measurement

LAC ($m^2\ g^{-1}$) (corrected to λ=550 nm)



Global LAC ($m^2 g^{-1}$) (corrected to λ=550 nm)



Theoretical MLR Measurement

Species	density	Refractive index	RH(D)	RH(E)
$(NH_4)_2SO_4$	1.76	1.53	80	37-40
$(NH_4)_3H(SO_4)_2$	1.83	1.51	69	35-40
NH_4HSO_4	1.78	1.473	40	0.05-20
H_2SO_4	1.8	1.41	-	-
NH_4NO_3	1.725	1.554	62	25-32
$NaNO_3$	2.261	1.587	74.5	0.05-30
NaCl	2.165	1.544	75.3	46-48
Na_2SO_4	2.68	1.48	84	57-59

IMPROVE Network Regions
Puget Sound (Seattle)
Northwest
Columbia River Gorge
Oregon & Northern California
Hells Canyon
Northern Rockies
Northern Great Plains
Boundary Waters
Northeast
Great Basin
Sierra Nevadas
California Coast
Central Rockies
Central Great Plains
Ohio River Valley
Appalachia
Washington DC
East Coast
Colorado Plateau
Mogollon Plateau
Southern California
Phoenix
Southern Arizona
West Texas
Mid South
Southeast
Alaska
Hawaii
Virgin Islands
IMPROVE Sites

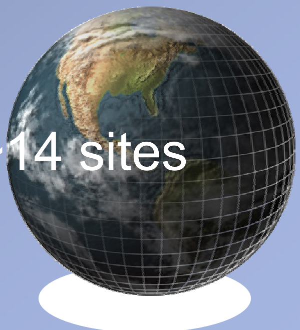
BIASES

- Corrections to IMPROVE data for sampling artifacts have been applied as part of routine methodology since 1988
- Dynamic field blanks for Teflon and nylon filters are collected at all sites by being placed in the sampler with no air drawn through
- Teflon field blanks are insignificant- no corrections
- Nylon field blanks- concentrations are subtracted from measured filters (monthly median artifact corrections applied separately for each ion)
- Quartz after-filters are collected at 6 sites- designed to capture organic gases (positive artifacts)

Aerosol Species measured by IMPROVE

Module	Substrate	Measured Variables
A (≤ 2.5 μm)	Teflon	Fine mass, Elements
B (≤ 2.5 μm)	Nitric acid denuder plus nylon filter	NO_3^-, NO_2^-, Cl^-, SO_4^{-2}
C (≤ 2.5 μm)	Prefired quartz substrates	Organic and elemental carbon
D (≤ 10 μm)	Teflon	Total mass

Nephelometers (b_{sp}) at ~24 sites and Transmissometers (b_{ext}) at ~14 sites

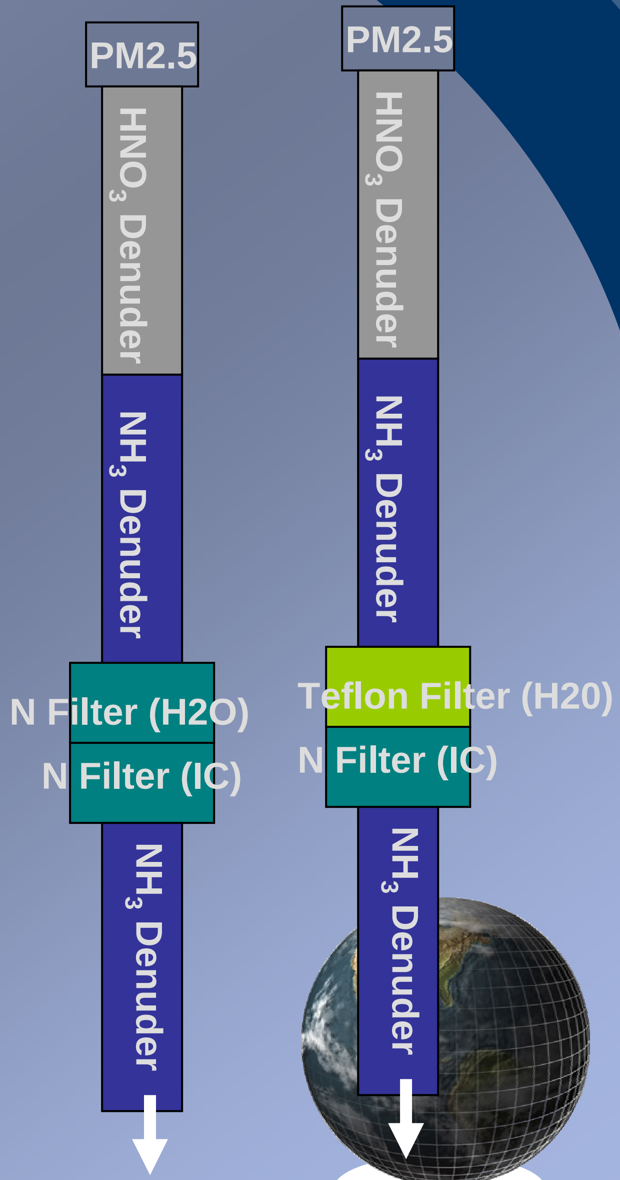


BIASES: Nitrate (NO_3^-)

- NO_3^- sampled with nylon filters (corrections < 10 %, McDade et al., 2004)
- Denuders precede the filters to capture acidic gases (HNO_3); positive artifacts could occur if the denuder efficiency degrades with time
- Recent studies suggest that no differences in nitrate concentrations were observed due to different denuder configurations (Ashbaugh et al., 2004; Yu et al., 2005a)
- Nitrate loss from Teflon filters remains an issue- disassociation of NH_4NO_3 particles- Teflon does not retain nitrate as nylon filters do-important implications for gravimetric mass

BIASES: Ammonium (NH_4^+)

- Recent work by Yu et al. (2005b at 4 IMPROVE sites
- NH_4^+ losses ranging from 9.7% - 52%
- Disassociation of NH_4NO_3: nitrate is retained but NH_4^+ is not
- N-N and T-N performed about the same

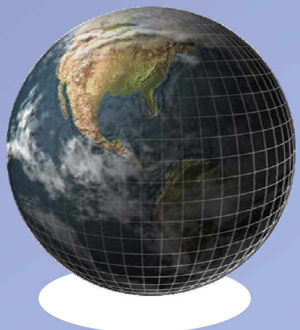


BIASES: Carbonaceous aerosols

- Carbonaceous aerosol concentrations are determined with the DRI thermal/optical reflectance (TOR) technique
- Organic carbon (OC) is separated into fractions based on temperature regimes in the measurement protocol (O1, O2, O3, O4, OP)
- Elemental carbon (LAC) determined in the high temperature regime (E1, E2, E3)
- OC/EC split is method dependent

BIASES: Carbonaceous aerosols

- Sampling carbonaceous particles is tough…
- Positive artifacts due to adsorption of organic acids on the filter
- Negative artifacts occur due to volatilization of particulate organics
- Artifact contributions to organic mass can range from -80 % to + 50 % (Turpin et al., 2000).
- Huebert and Charlson (2000) suggest systematic errors on the order of ±80 % are possible with thermal methods



BIASES: Carbonaceous aerosols

- IMPROVE network assumes negative artifacts are insignificant
- Positive artifacts: estimated from quartz after-filters at 6 sites, determined separately for each fraction of OC and EC
- O3 artifact represents nearly half of ambient concentration
- E2 artifact is less than 10 % of ambient concentration (since 2000) McDade et al. (2004)
- Some spatial and seasonal differences:

-Okefenokee site has higher O3 artifacts than the other sites
-Summer has higher O3 and E2 artifacts than winter

- The same median value is applied to the entire network

BIASES: Coarse mass and elemental species

- Elemental species are determined by XRF
- Lower Z elements have higher MDLs
- $CM = PM_{10} – PM_{2.5}$
  - Uncertainties in flow rates can significantly affect coarse mass as well as fine mass (more later)