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23 - 25 September 2010

An analysis of chemical particles related to the sulfur cycle and the meteorological effects of sulfate aerosols over Europe and the Mediterranean region

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An Analysis of Chemical Particles related to the Sulfur Cycle and the Meteorological Effects of Sulfate Aerosols over Europe and the Mediterranean Region

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MedCLIVAR Workshop, ICTP, Trieste
23rd – 25th September 2010

Outline

- PRECIS & Physical Parameters
- Why the Mediterranean Basin?
- The Sulfur Cycle & Aerosols
- Aerosol Impacts
- Sulfur Cycle Validation
- Data Analysis
- Atmospheric Sulfur Chemistry
- Conclusions

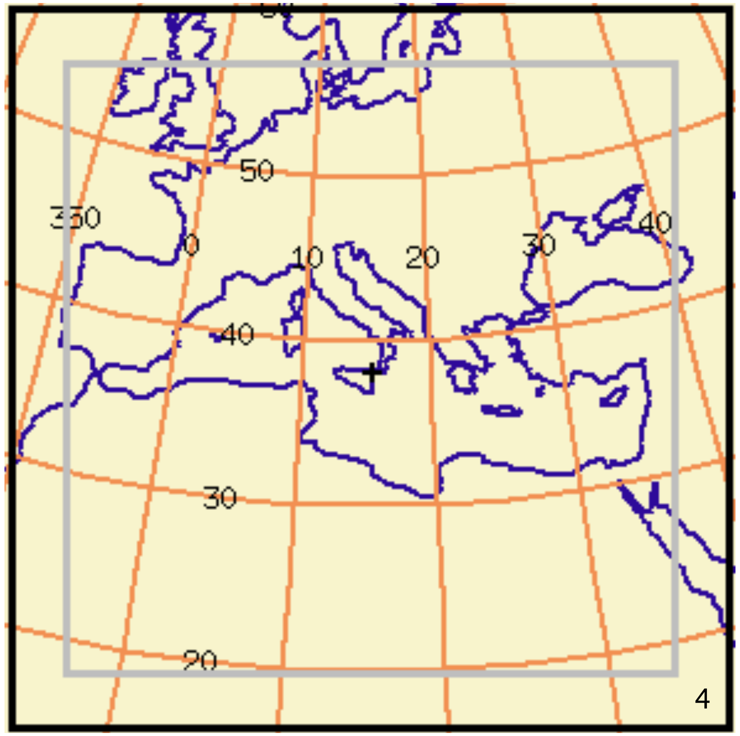
PRECIS & Physical Parameters

- The PRECIS (Providing REgional Climates for Impact Studies)
  - RCM is driven by the GCM HadAM3P. (Gordon *et al*, 2000)
- Clouds & precipitation
- Radiation includes the seasonal and diurnal cycles of solar radiation
- Land Surface characteristics are prescribed according to climatological surface types
- Surface exchanges
  - Land surface scheme is MOSES (Met Office Surface Exchange Scheme). (Cox *et al*, 1999)

Why the Mediterranean Basin?

- Enclosed by 3 major continents.
- Surrounded almost entirely by mountains.
- Very unique and sensitive to climate changes.

- Simulation details
  - GCM-HadAM3P-150km
  - PRECIS (v 1.7.2) used
  - 1960-1990 (1-year spin up)
  - Resolution: 0.44° x 0.44°
  - 100 cells x (50 km x 50 km)
  - 57°N-18°N, 16°W-46°E



The Sulfur Cycle & Aerosols

Mode	Diameter (μm)	Lifetime	Removal Process
Nucleation	<0.01	Minutes-Hours	Coagulation
Aitken	0.01-0.1	Hours-Days	Coagulation
Accumulation	0.1-1	Weeks	Nucleation
Coarse	1-10	Hours-Days	Gravitation
Giant	>10	Hours-Days	Gravitation

- The Sulfur Cycle is based 5 variables:
  - SO_2, DMS and 3 modes of SO_4^{2-} (1 dissolved & 2 free modes)
- Model simulates transport of above, via horizontal and vertical advection, convection and turbulent mixing
- Aerosols act as CCN
- Increase in aerosol causes climate impacts

Aerosol Impacts

- With increasing aerosol activity:

- Direct: Scattering effect
  - Decreased: SW, Skin T
- Indirect: Cloud albedo (Twomey) effect
  - Decreased: Diurnal Temperature Range (DTR)
- Indirect: Cloud lifetime effect
  - Decreased: Precipitation, DTR

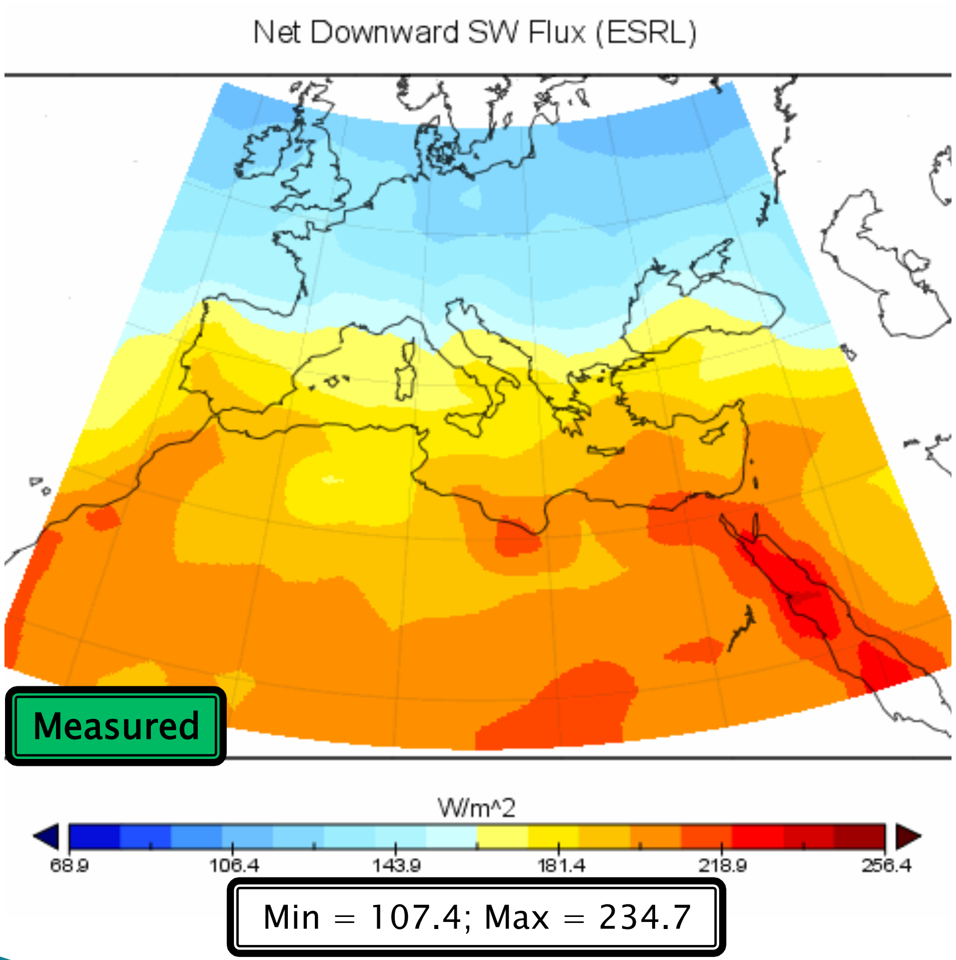
Sulfur Cycle Validation

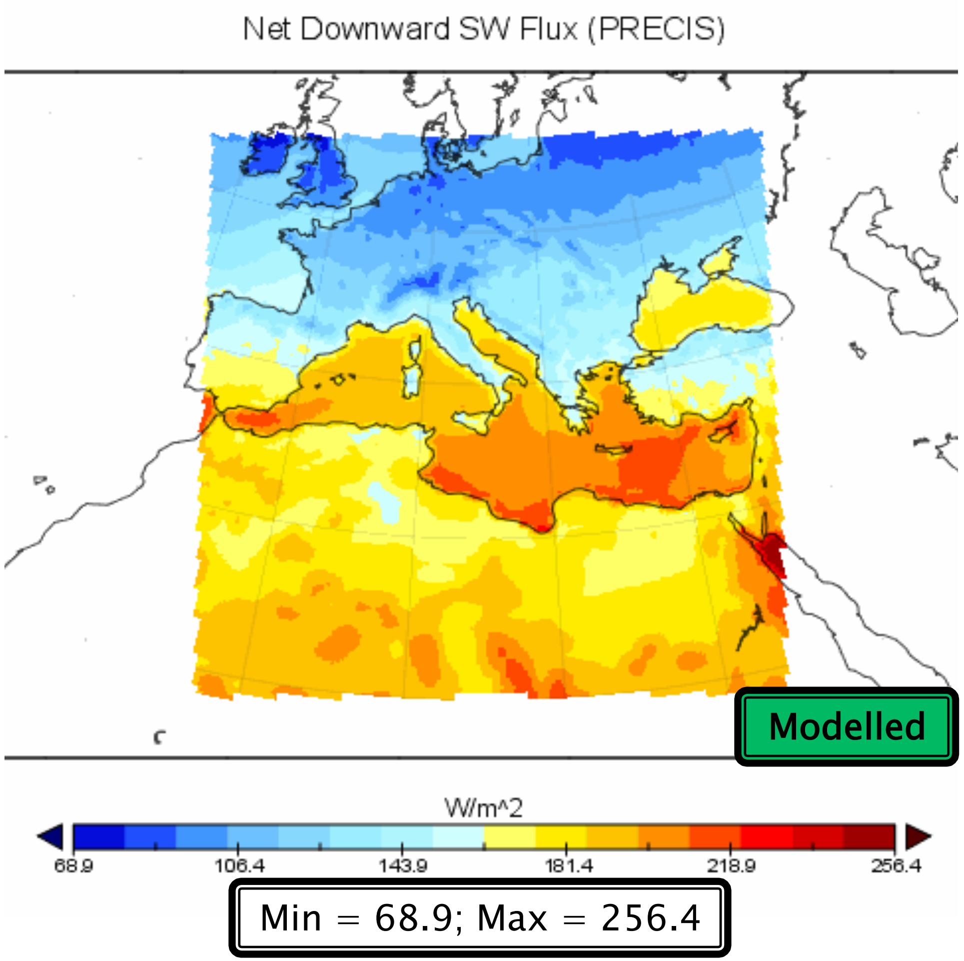
Aerosol Impacts within the PRECIS output:

- Studied through correlation between aerosol-sensitive parameters.
- Direct effect:
  - Correlations between 0.60-0.82
- Indirect effects:
  - Correlations between 0.18-0.82
  - Complex interactions
  - Cannot isolate Cloud albedo effect from the Twomey

Effect		Correlation
Indirect	Diss v Skin T	-0.77
Indirect	Diss v SW	-0.82
Indirect	SW v DTR	0.50
Indirect	CLW v DTR	-0.59
Indirect	Diss v CLW	0.39
Indirect	CLW v SW	-0.28
Indirect	Diss v DTR	-0.40
Cloud lifetime	Diss v PPN	0.43
Cloud lifetime	CLW v PPN	0.18
Indirect	CLW v LW	-0.26
Indirect	Diss v LW	-0.60
Indirect	LW v DTR	0.47

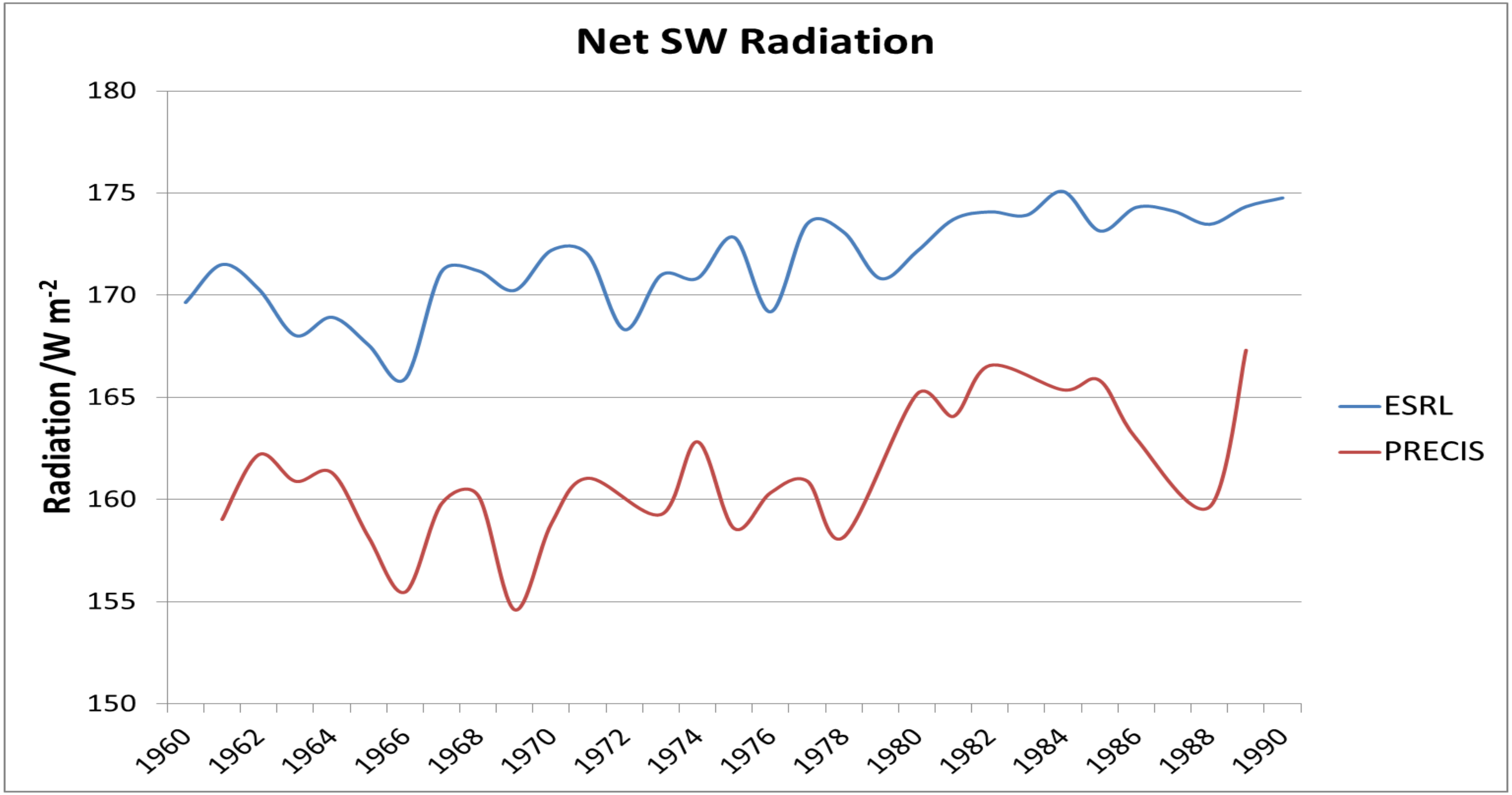
Data Analysis



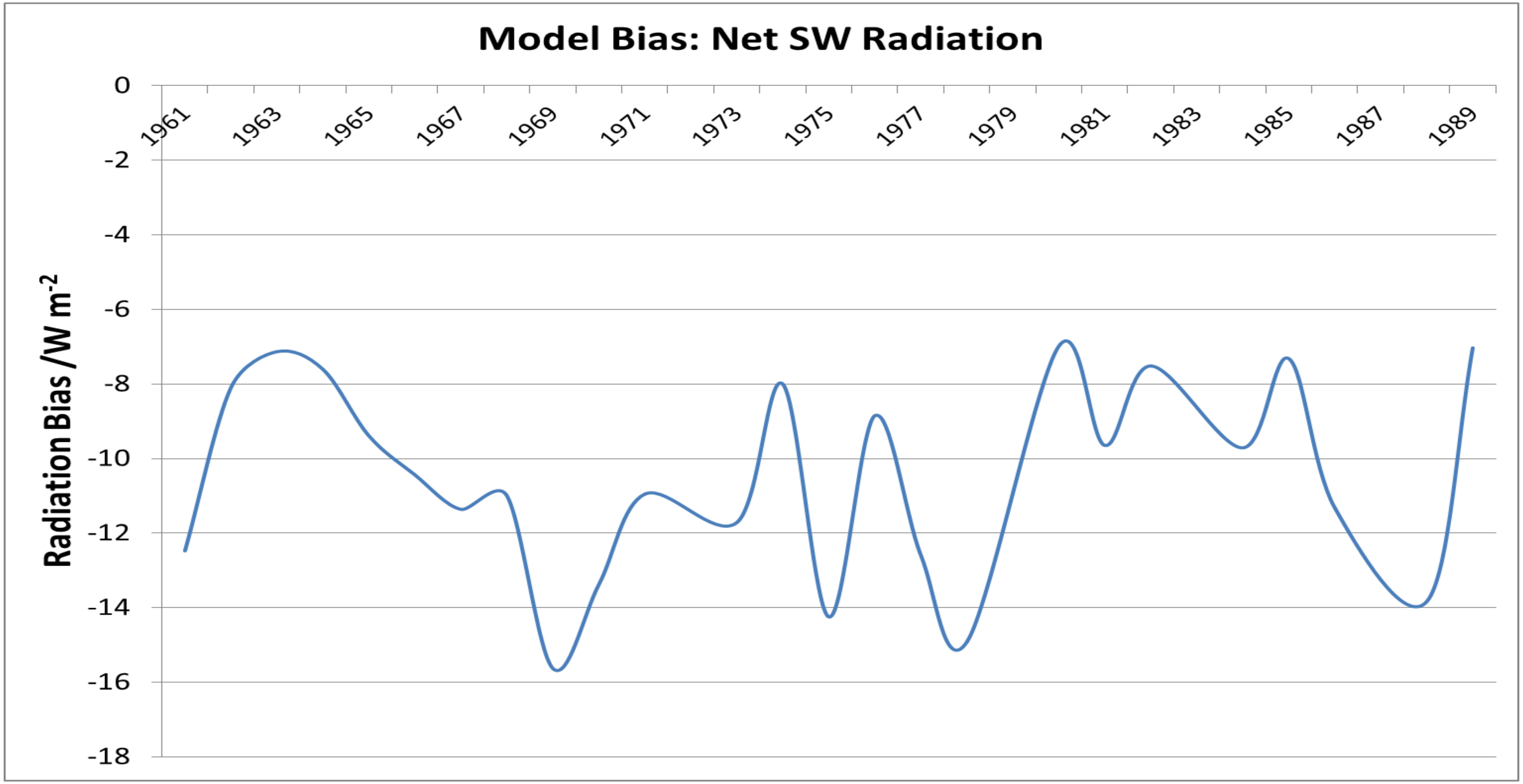


1961-1990

Data Analysis



Data Analysis



Data Analysis

Statistics of Parameters

Parameter	Correlation	Average Bias	Max Bias	Min Bias
Conv PPN ($x10^{-6}$)	0.47	-3.08	-1.48	-5.80
DTR	-0.11	-1.98	-0.32	-3.52
Net LW	0.48	1.01	3.77	-1.37
Net SW	0.59	-10.45	-6.99	-15.63
RH	0.43	-5.46	-3.01	-8.38
Surface T	0.13	0.82	1.59	0.05

- Bias of Conv PPN, DTR, Net LW, Net SW, RH:
  - Suggest SO_4^{2-} over-prediction
- Bias of Surface Temperature:
  - Possible result of Net LW over-prediction

Atmospheric Sulfur Chemistry

- PRECIS
  - STOCHEM Model
    - UK Meteorological Office Global Three-Dimensional Lagrangian

- Bacterial Reduction of Sulfate:

$$SO_4^{2-} + H^+ + 2CH_2O \rightarrow HS^- + 2H_2O + 2CO_2$$

- Gaseous Oxidation of Sulfide: (Andreae *et al*, 2008)

$$2H_2S + 3O_2 \xrightarrow{HO\cdot} 2SO_2 + 2H_2O$$

- <u>Oxidation of DMS:</u> (Norris, 2003)

$$CH_3SCH_3 + HO\bullet \rightarrow SO_2 \text{ (unbalanced)}$$

Atmospheric Sulfur Chemistry

- Ammonic Oxidation of Sulfur Dioxide:

$$NH_3 + SO_2 + H_2O \rightarrow NH_4^+ + HSO_3^-$$

- Gaseous Oxidation of Sulfur Dioxide: (Harrison, 1999)

$$HO\bullet + SO_2 \rightarrow HSO_3\bullet \xrightarrow{O2} SO_3 + HO_2\bullet \xrightarrow{H2O} H_2SO_4$$

- Aqueous oxidation Sulfur (IV) compounds:

$$\{O\} + \{S\} \rightarrow 2H^+ + SO_4^{2-} \text{ (unbalanced)}$$

  - $\{O\} = H_2O_2, HO\bullet, O_3, O_2$
  - $\{S\} = SO_2, HSO_3^-, SO_3^{2-}$

- Aqueous Oxidation of SO_2 via H_2O_2:

$$SO_2 + H_2O_2 \rightarrow SO_3 + H_2O \rightarrow H_2SO_4$$

Chemistry Module

- PRECIS yearly average concentrations:
  - HO• – constant.
    - HO• causes no variation in DMS and SO_2 oxidation

- Using Pearson Correlation:
  - SO_2 is correlated to dissolved SO_4^{2-}
  - DMS is negatively correlated to dissolved SO_4^{2-}
  - H_2O_2 is negatively correlated to Aitken & accumulation SO_4^{2-}
  - Aitken is correlated to accumulation SO_4^{2-}
  - Accumulation is correlated to dissolved SO_4^{2-}

[All correlations are statistically significant ($p<0.01$), except the first, which is $p<0.05$]

Conclusions

- Sulfur Cycle Validation:
  - Direct: High evidence
  - Indirect: Varying evidence

- Results suggest problems with the Sulfur cycle:
  - Possible over-estimation of SO_4^{2-} concentrations

- Correlation of SO_4^{2-} and H_2O_2 shows the SO_2 to H_2O_2 reaction is the most important within PRECIS

- Correlations show evidence of conversion between:
  - Aitken and accumulation SO_4^{2-} ;
  - Accumulation and dissolved SO_4^{2-} ;
  - DMS and dissolved SO_4^{2-} ;
    - Negative correlation of DMS not yet understood
  - SO_2 and dissolved SO_4^{2-}

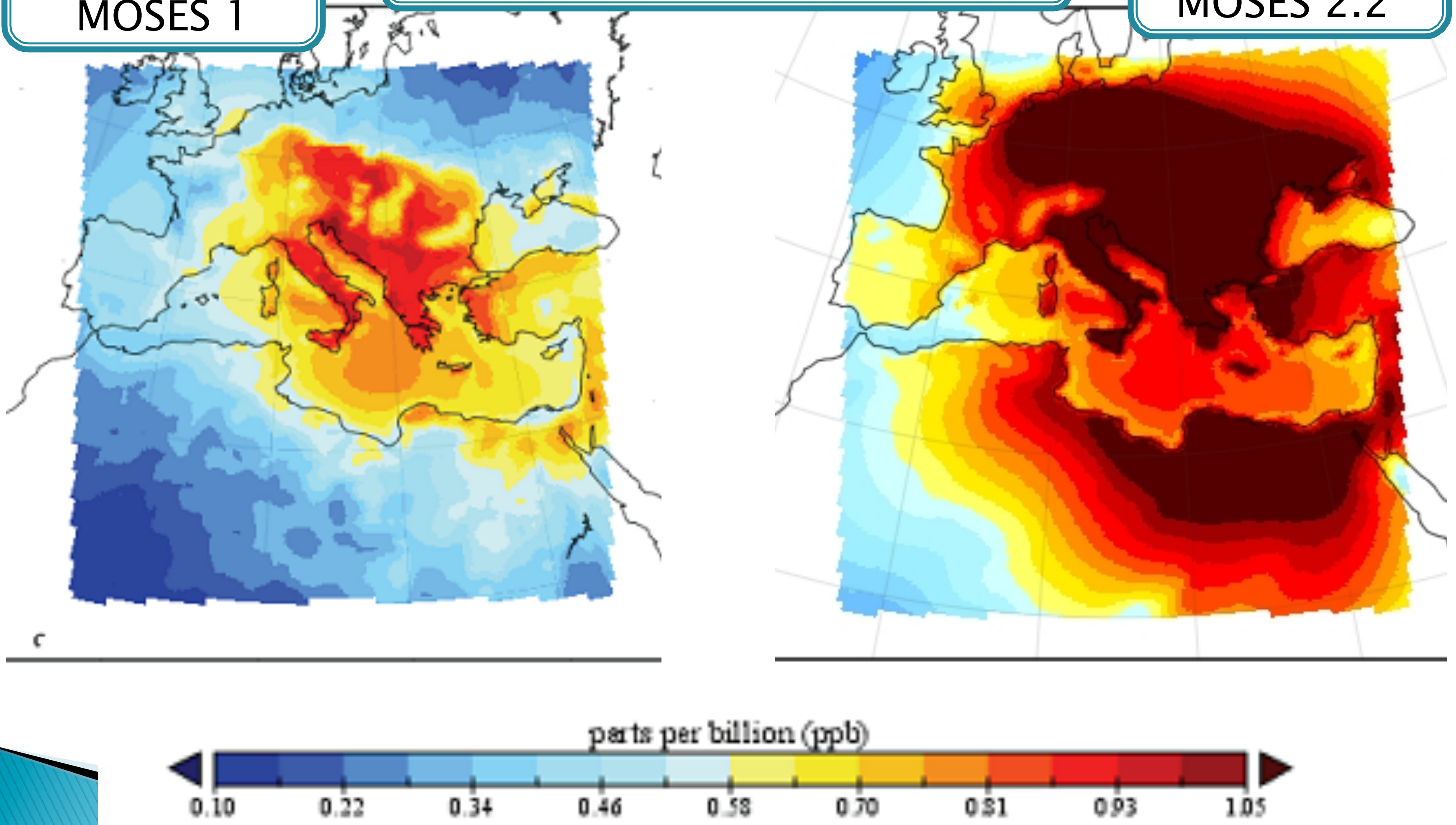
- More detailed chemical analysis is needed within PRECIS.

Further Work

PRECIS 1.7.1
MOSES 1

1961–1990 Sulfate Aitken mode

PRECIS 1.9.1
MOSES 2.2



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http://precis.metoffice.com/

Met Office

UNDP

defra Department for Environment Food and Rural Affairs

UK Air Quality Archive

NOAA Earth System Research Laboratory Physical Sciences Division

DFID Department for International Development

Thank you for your attention

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What is PRECIS?

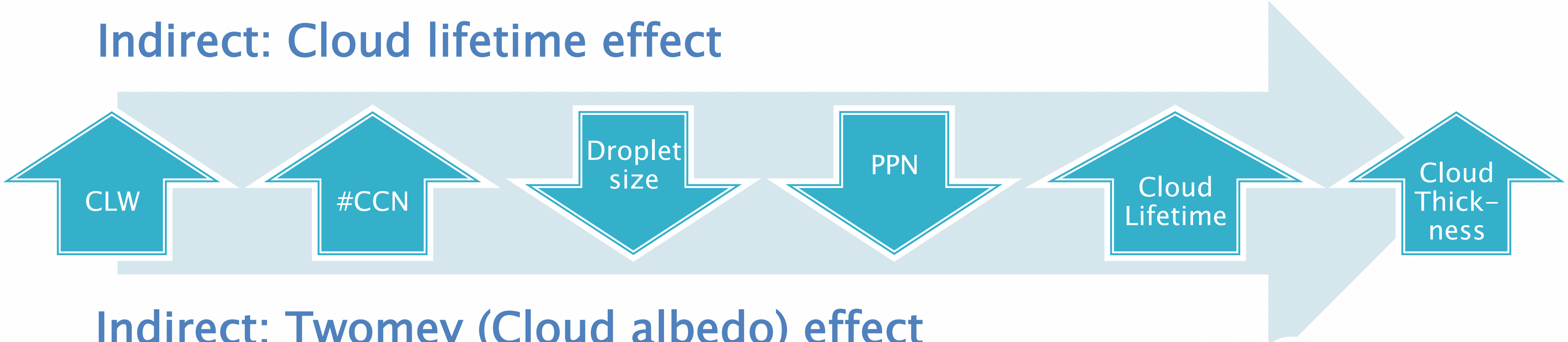
- It is an Atmospheric and LSM of limited area.
- The model is described in 3 units:
  - The dynamics
  - The physical parameterizations
  - The Sulfur cycle

Boundary Conditions

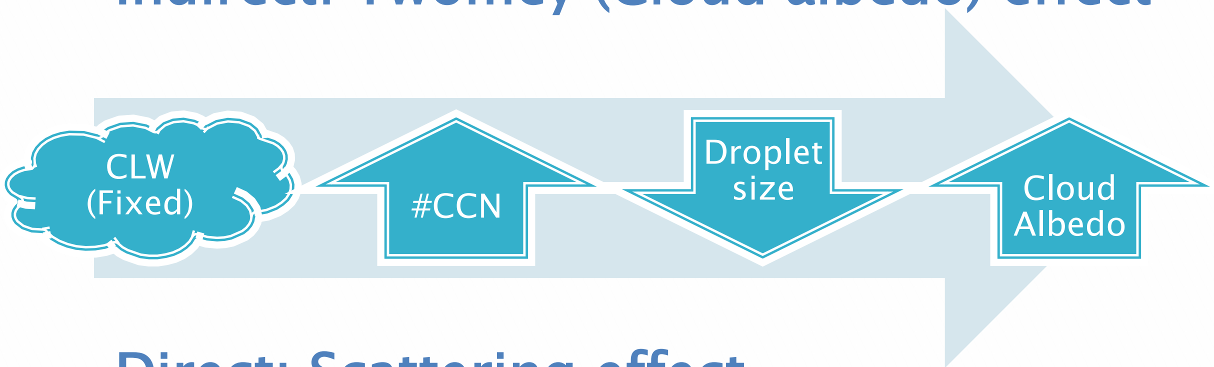
- Model requires **surface boundary conditions** from surface temperatures and ice extents.
- Dynamical atmospheric information at the boundary of the model's domain are obtained from the **LBCs** which include
  - standard atmospheric variables of surface pressure
  - horizontal wind components
  - atmospheric temperature and humidity measures
- LBCs are updated every 6 hours of the model simulation time.
- Surface boundary conditions are updated every day.

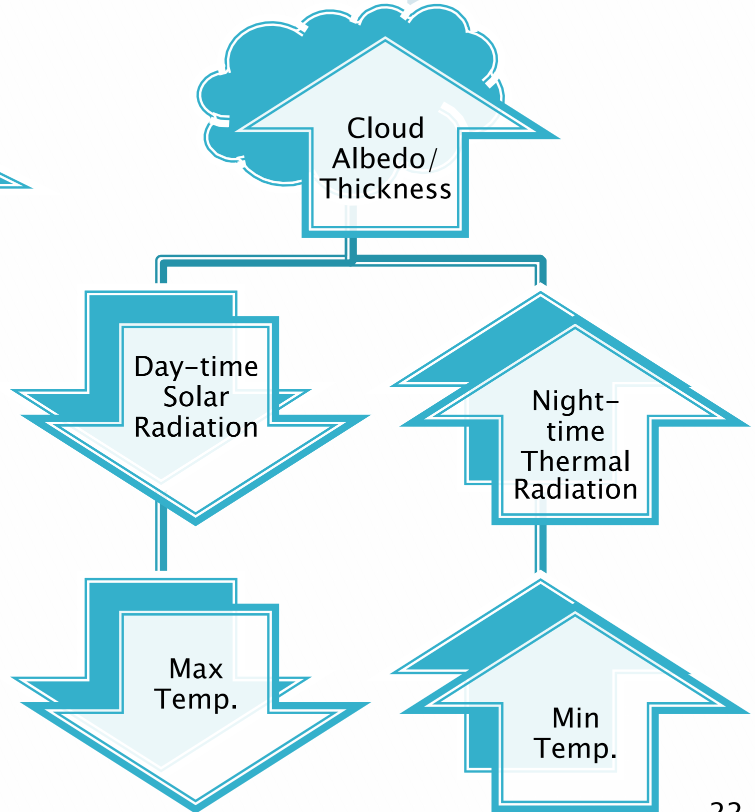
Aerosol Impacts

Indirect: Cloud lifetime effect



Indirect: Twomey (Cloud albedo) effect





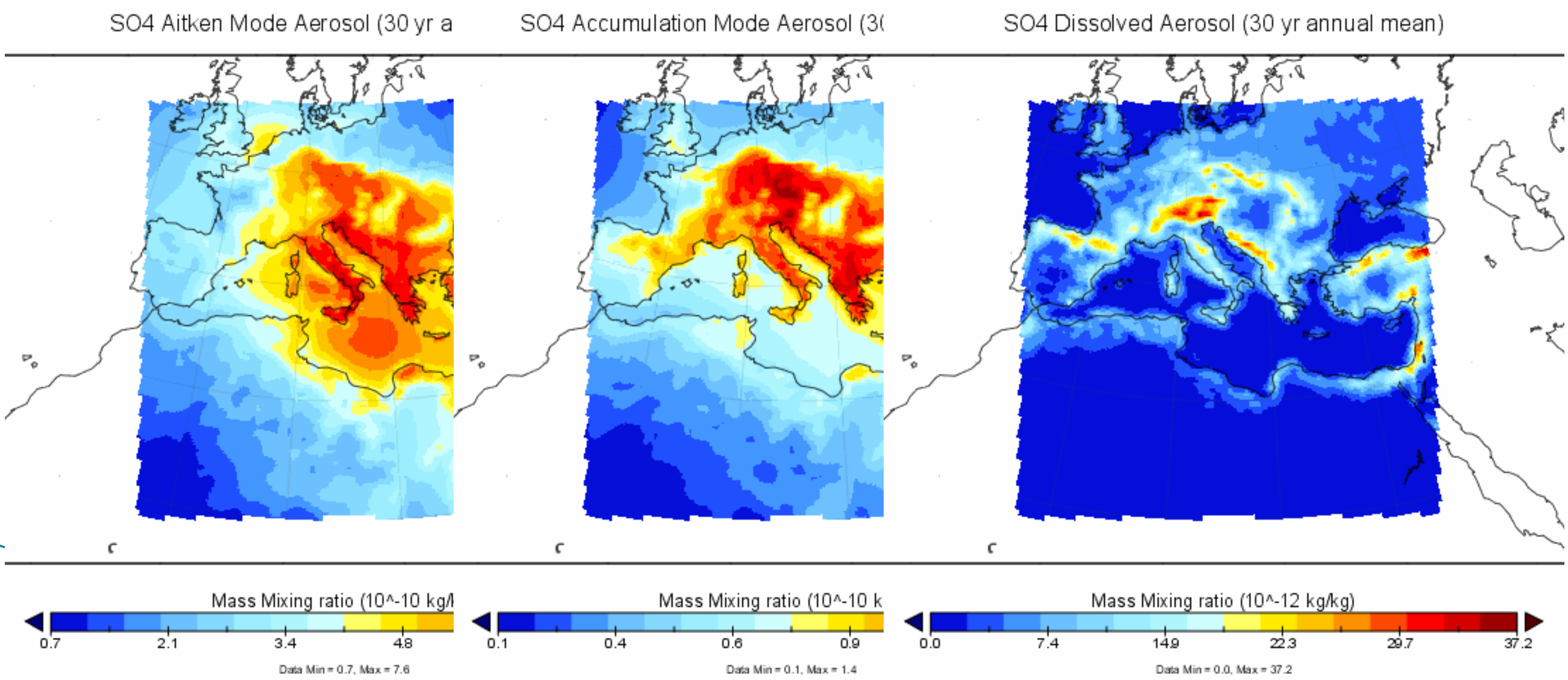
Direct: Scattering effect

- Direct: *LW* unaffected: *Aerosol Opacity*↓ as *λ*↑
- Indirect: *RH* decreased: *water vapour* ↓ as *condensation* ↑

Sulfur Cycle Validation

Sulfate Abundance:

1. Aitken
2. Accumulation
3. Dissolved



Sulfur Cycle Validation

- *Aerosol-sensitive parameters*

Effect		Correlation	Expected Relationship
Direct	Aitken v SW	-0.76	Negative
Direct	Accum v SW	-0.82	Negative
Direct	SW v Skin T	0.69	Positive
Direct	Aitken v Skin T	-0.60	Negative
Direct	Accum v Skin T	-0.64	Negative

- *Direct Effect*
  - Strong correlations
  - Expected relationships
  - Strong evidence of effect

Sulfur Cycle Validation

- ***Aerosol-sensitive parameters***

- *Indirect Effects*:
  - Low detectability of effect
  - Expected due to complex interactions

- "Incorrect" correlations:
  - Model errors?

Effect		Correlation	Expected Relationship
Indirect	Diss v Skin T	−0.77	Negative
Indirect	Diss v SW	−0.82	Negative
Indirect	SW v DTR	0.50	Positive
Indirect	CLW v DTR	−0.59	Negative
Indirect	Diss v CLW	0.39	Positive
Indirect	CLW v SW	−0.28	Negative
Indirect	Diss v DTR	−0.40	Negative
Cloud lifetime	Diss v PPN	0.43	Negative
Cloud lifetime	CLW v PPN	0.18	Negative
Indirect	CLW v LW	−0.26	Positive
Indirect	Diss v LW	−0.60	Positive
Indirect	LW v DTR	0.47	Negative

Sulfur Cycle Validation

Effect		Correlation	Expected Relationship
Cloud lifetime	Diss v PPN	0.43	(Negative)
Cloud lifetime	CLW v PPN	0.18	Positive

Consider a cloud of increasing CLW

- Cloud lifetime effect

↓ Droplet size
↓ Precipitation

- "Water-cycle effect"

↑ Droplet size
↑ Precipitation

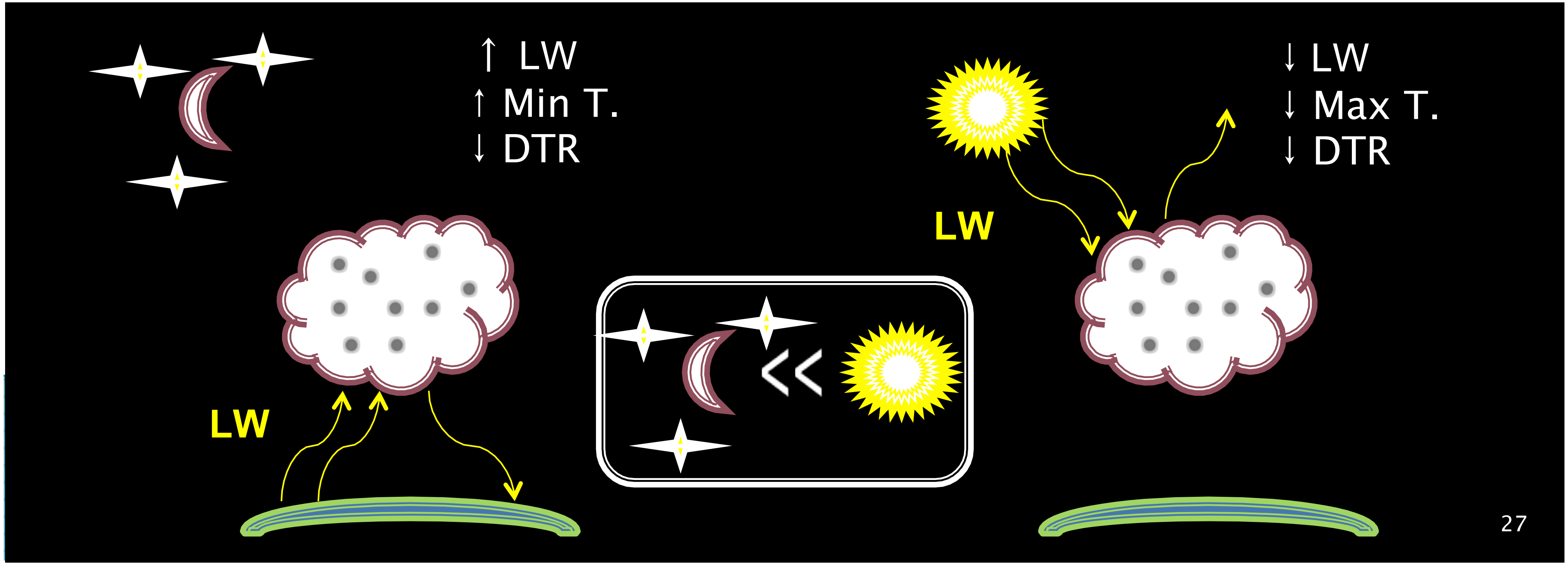
"Water-cycle effect" >> Cloud lifetime effect

Sulfur Cycle Validation

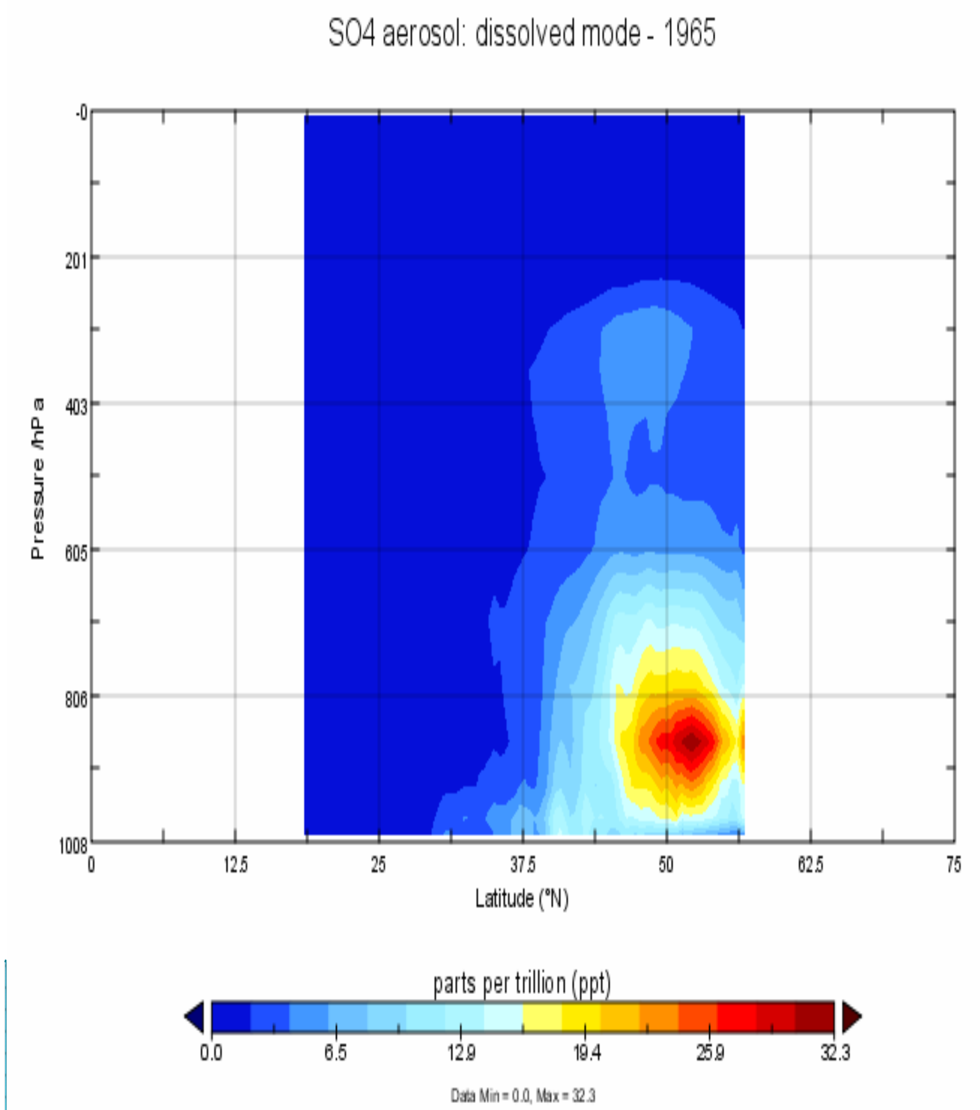
Effect		Correlation	Expected Relationship
Indirect	CLW v LW	-0.26	Negative
Indirect	Diss v LW	-0.60	Negative
Indirect	LW v DTR	0.47	Positive

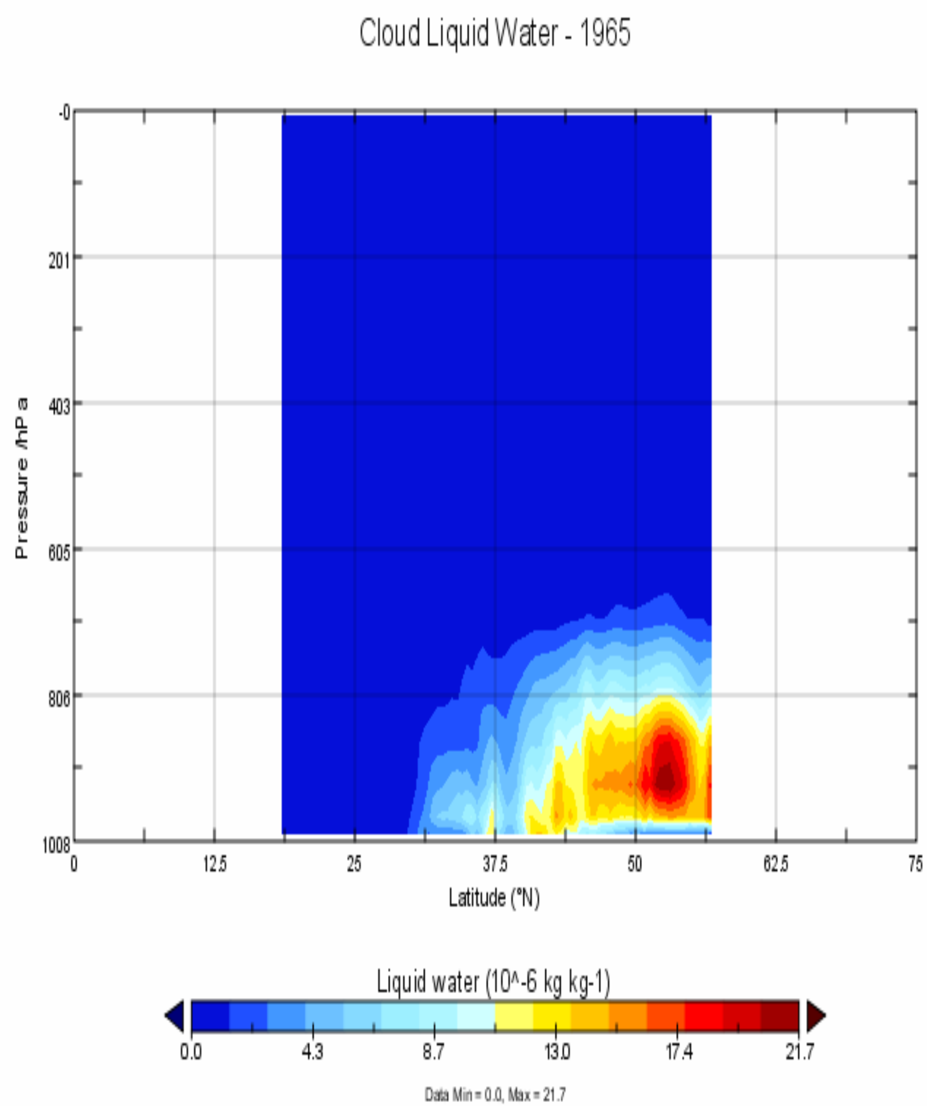
<u>Consider a cloud with dissolved aerosol</u>

Influenced by the indirect effect (↑ CLW/thickness/albedo)



Sulfur Cycle Validation





Atmospheric Sulfur Chemistry

- Atmospheric Sulfur Compounds and Sources:
  - Sulfates (SO_4^{2-}): sea spray (salts), dust (rocks)
  - Sulfur dioxide (SO_2): volcanoes, combustion
  - Hydrogen Sulfide (H_2S): bacterial reduction
  - Dimethyl Sulfide (DMS): marine phytoplankton

- SO_2 is the most abundant.

Atmospheric Sulfur Chemistry

- Aqueous oxidation Sulfur (IV) compounds:

$$\{O\} + \{S\} \rightarrow 2H^+ + SO_4^{2-} \text{ (unbalanced)}$$

  - $\{O\} = H_2O_2, HO\bullet, O_3, O_2$
  - $\{S\} = SO_2, HSO_3^-, SO_3^{2-}$

$$SO_2 + H_2O_2 \rightarrow SO_3 + H_2O \rightarrow H_2SO_4$$

$$SO_2 + O_3 \rightarrow SO_3 + O_2 \rightarrow H_2SO_4 \text{ (unbalanced)}$$

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$$

$$HSO_3^- + H_2O_2 \rightarrow HSO_4^- \text{ (unbalanced)}$$

$$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$$

Chemical Correlation

Correlations

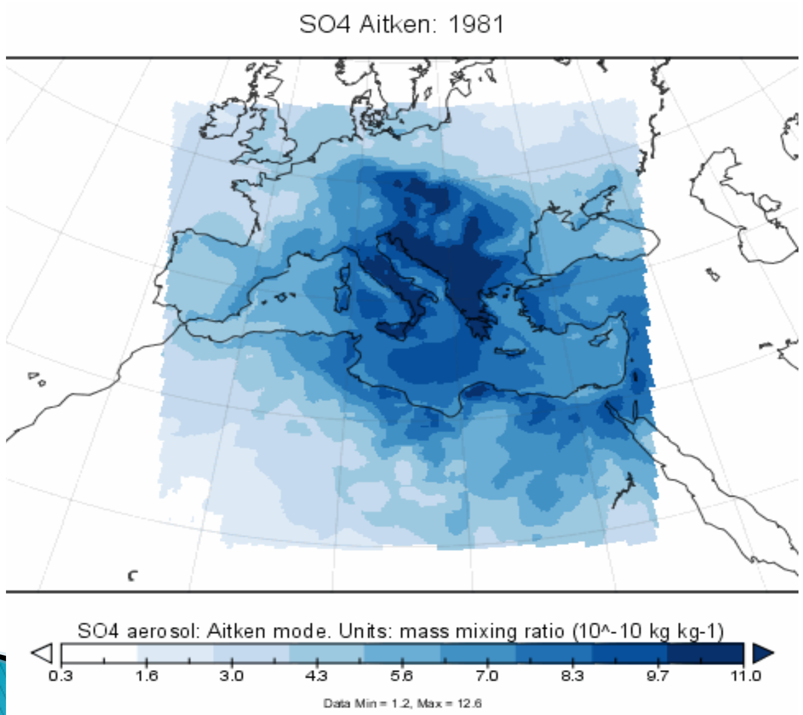
		SO2	SO4Ait	SO4Acc	SO4Dis	H2O2	DMS
SO2	Pearson Correlation	1	.144	-.105	.413*	.147	-.070
	Sig. (2-tailed)		.456	.586	.026	.445	.718
	N	29	29	29	29	29	29
SO4Ait	Pearson Correlation	.144	1	.542**	-.125	-.564**	.358
	Sig. (2-tailed)	.456		.002	.518	.001	.057
	N	29	29	29	29	29	29
SO4Acc	Pearson Correlation	-.105	.542**	1	.493**	-.521**	-.165
	Sig. (2-tailed)	.586	.002		.007	.004	.392
	N	29	29	29	29	29	29
SO4Dis	Pearson Correlation	.413*	-.125	.493**	1	-.017	-.532**
	Sig. (2-tailed)	.026	.518	.007		.930	.003
	N	29	29	29	29	29	29
H2O2	Pearson Correlation	.147	-.564**	-.521**	-.017	1	-.028
	Sig. (2-tailed)	.445	.001	.004	.930		.887
	N	29	29	29	29	29	29
DMS	Pearson Correlation	-.070	.358	-.165	-.532**	-.028	1
	Sig. (2-tailed)	.718	.057	.392	.003	.887	
	N	29	29	29	29	29	29

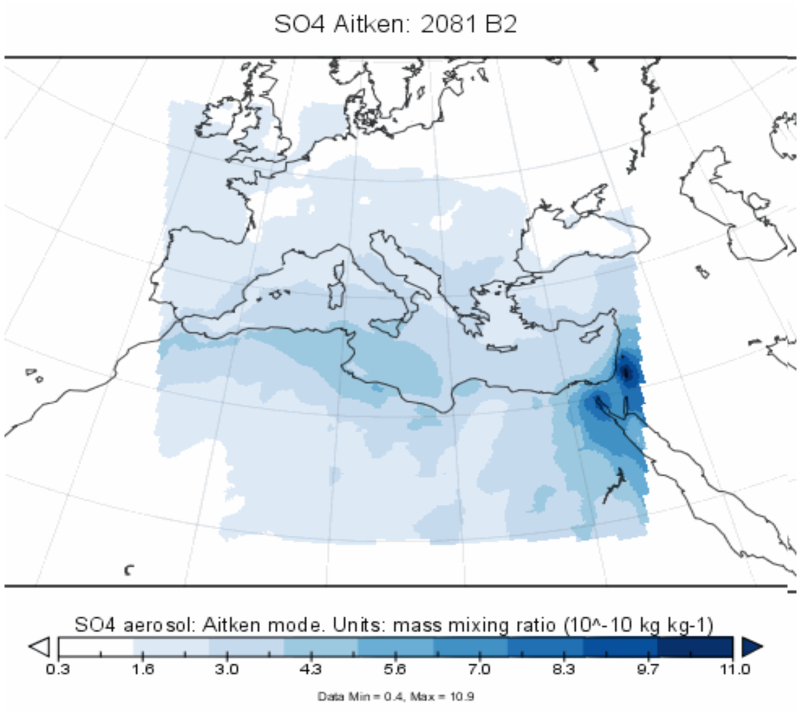
*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

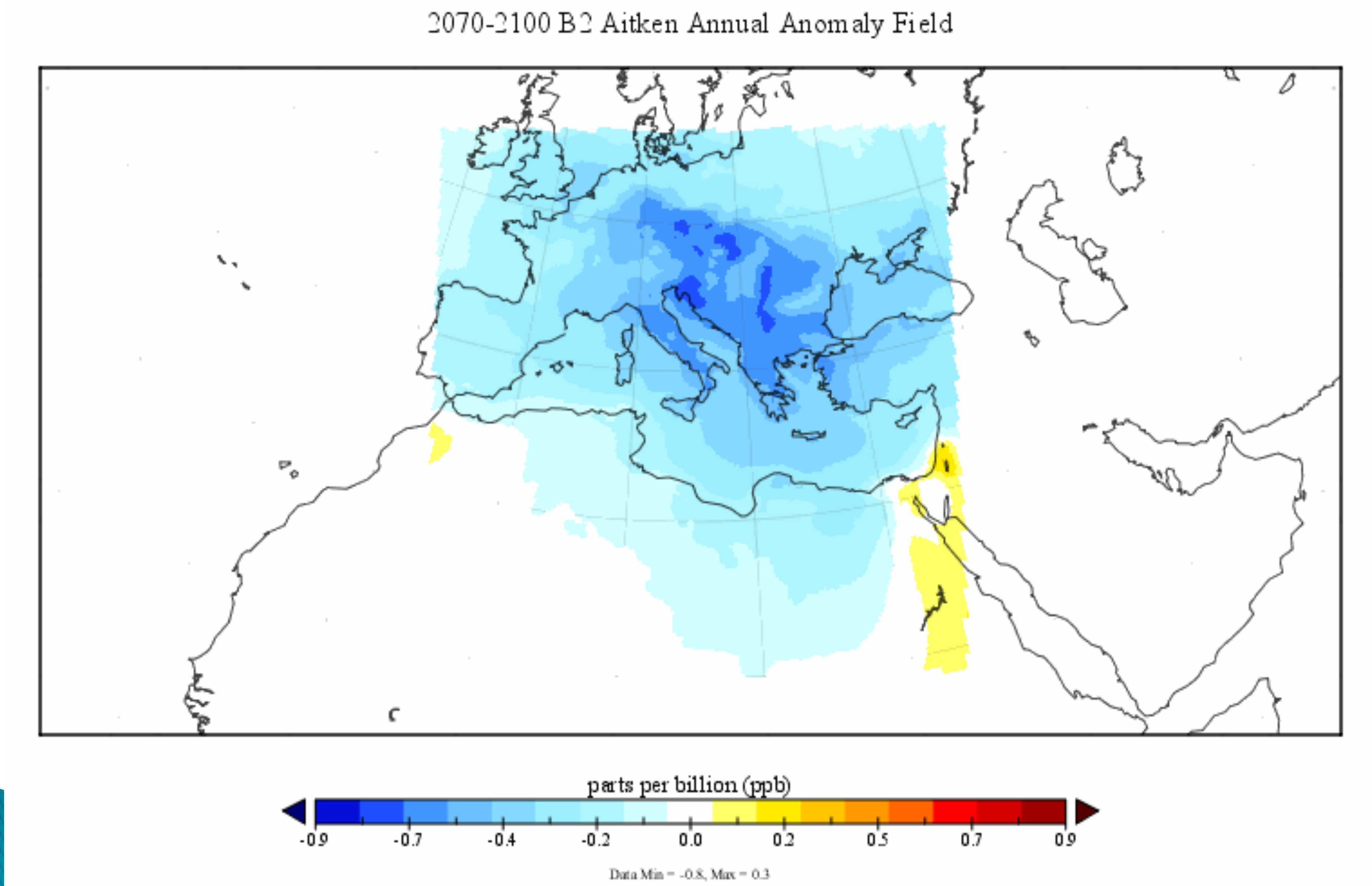
Future Scenarios

Scenario	Focus
A2	Slow technological change
B2	Sustainability: economy, society, environment
A1B	Efficient technology; Non/Fossil balance





Future Scenarios



Future Scenarios