Modeled Role of Heterogeneous Chemistry in Regional Sulfate Formation

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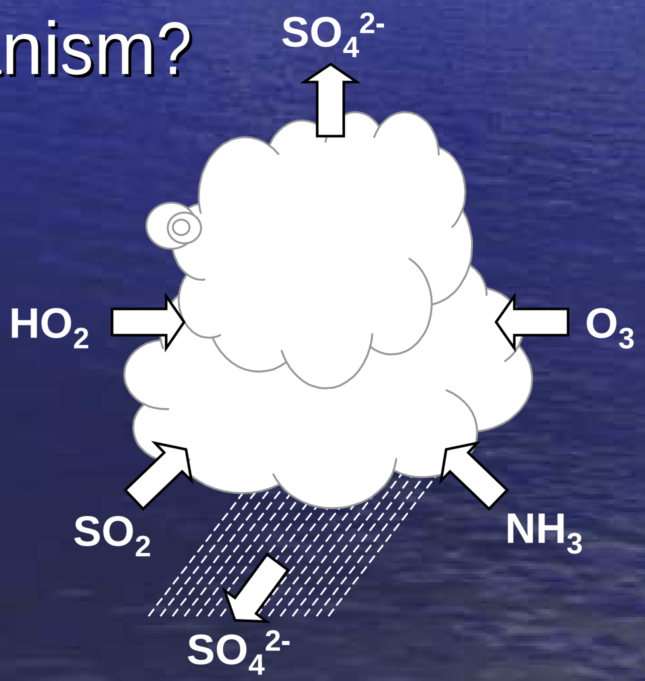
Why do we care about clouds?

- **Scientific Issue**: To what extent do modeled SO_2 – sulfate source-receptor linkages depend on the accuracy of a heterogeneous (cloud) sulfate formation mechanism?
- **Regulatory Importance**: Effectiveness of strategies for visibility improvement and $PM_{2.5}$ attainment will be affected by modeling of cloud chemistry.



Sulfate Formation from SO_2

- SO_2 reacts with OH^- in the air to form SO_4^{-2} (sulfate). The sulfate anion usually combines with H^+ or NH_4^+ in different combinations to make sulfuric acid, ammonium bisulfate or ammonium sulfate aerosol.
- SO_2 dissolves in cloud droplets, raindrops or even hydrated haze particles. SO_2 then reacts with ozone (O_3) and peroxides (HO_2) in solution to form SO_4^{-2}. Evaporation leaves behind sulfate aerosol.

Relative Contributions of Sulfate Formation Mechanisms

- The gas-phase reaction is relatively slow, but continuous, as long as sunlight is available.
- Heterogeneous sulfate formation depends on the presence of condensed water. The reaction can be very fast and efficient.

Ingredients for Modeling Heterogeneous Chemistry

- Condensed water as raindrops, cloud droplets or hygroscopic aerosols at high relative humidity.
- Air concentrations of O_3, peroxides, SO_2, and other gases & particles that influence the pH of droplet/aerosol solutions.

Modeling Condensed Water

- Clouds & precipitation are highly parameterized, even in meteorological models.
- Separate modeling of meteorology & atmospheric chemistry means that different assumptions are made, even though meteorological & chemical processes are interdependent.

A Modeling Approach: URM-1ATM

- Used by the Southern Appalachian Mountains Initiative (SAMI).
- Clouds are defined using water vapor, cloud & precipitation parameters provided by the RAMS meteorological model.

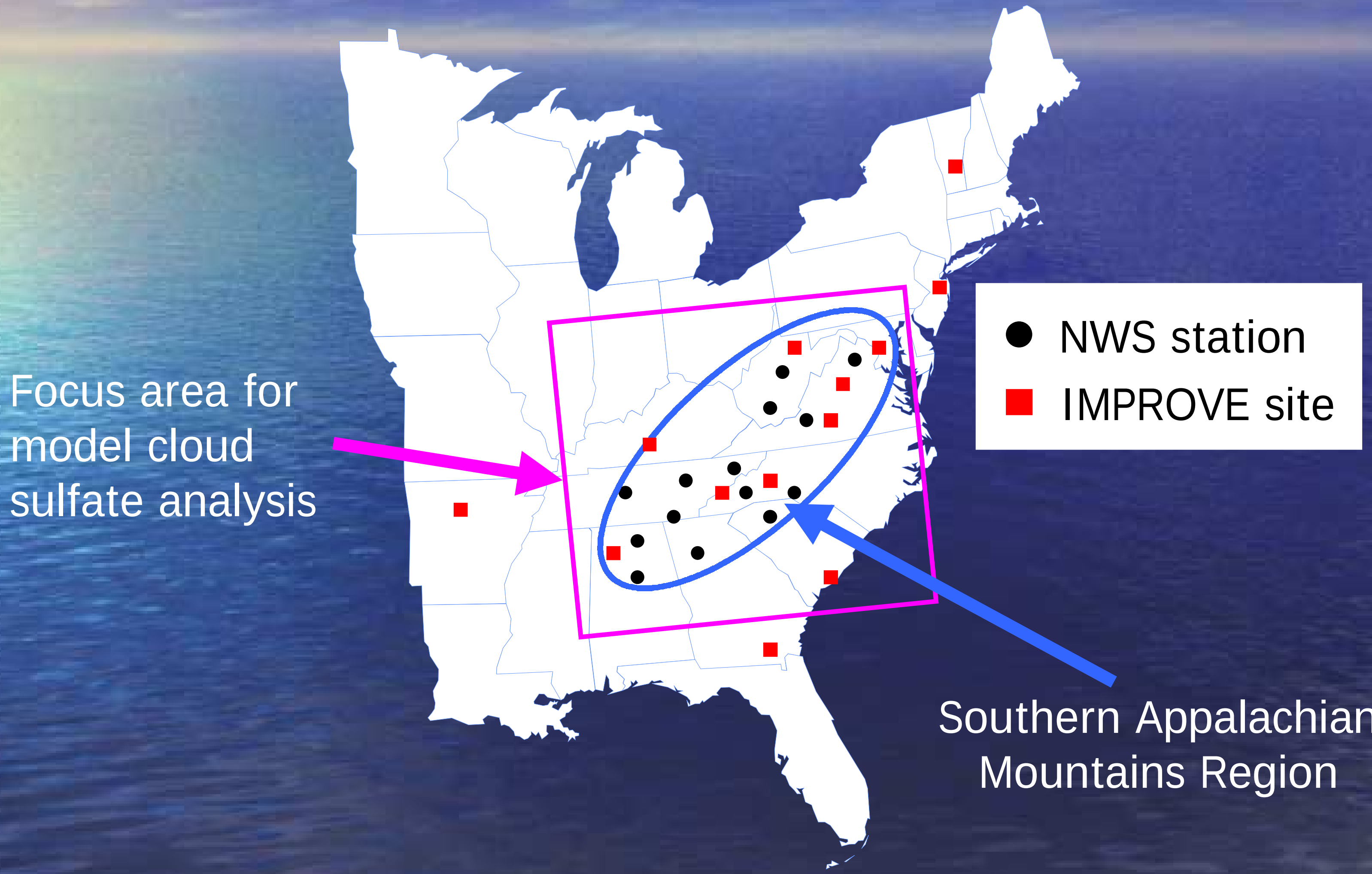
Examining Model Treatment of Clouds

- Examined how well the model simulated certain cloud characteristics.
- Examined the cloud influences on computed sulfate levels.

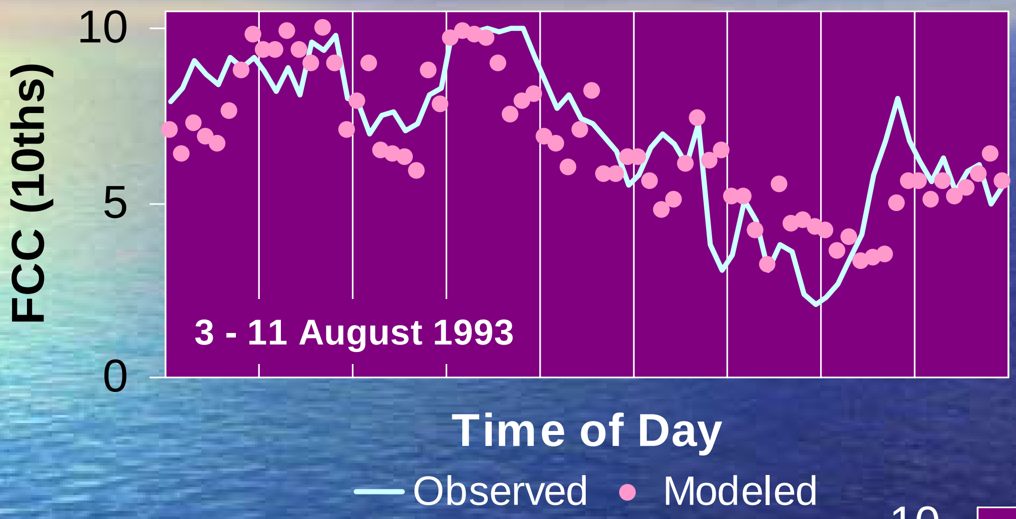
Characteristics of Periods Examined

Period	Weather	O_3 & Sulfate Levels
26 April – 3 May 1995	Light rain showers early, dry in the middle, scattered rain late	Low to high ozone Moderate sulfate
24-29 June 1992	Scattered rain throughout period, some locally heavy rain on 27 June	Low to high ozone High sulfate
3-11 August 1993	Widespread rain through 8 August, then tapering off	Low to moderate ozone Moderate to high sulfate
11-19 July 1995	Little or no rain in most areas, very hot	Moderate to high ozone Moderate to very high sulfate

Region of Analysis

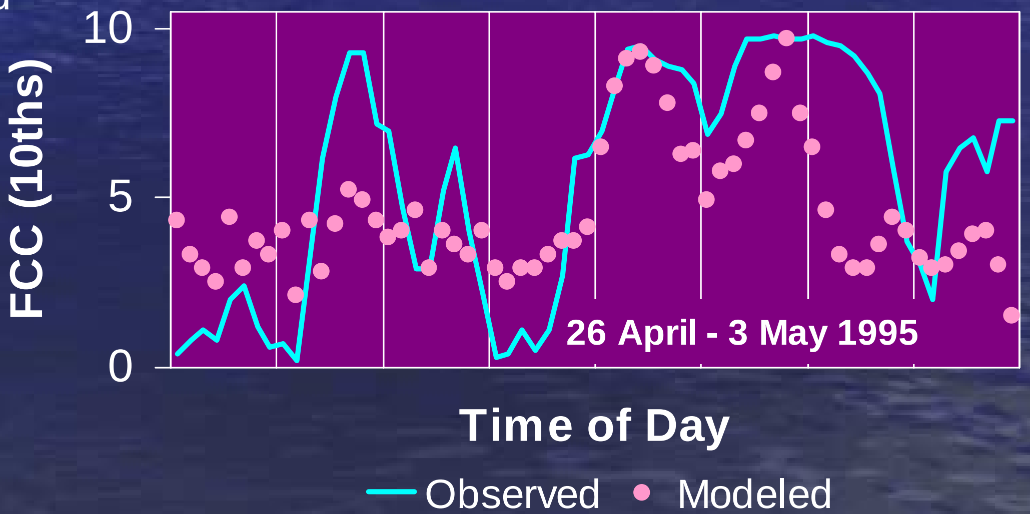


Fractional Cloud Cover (Spatial averages by hour)



Good performance

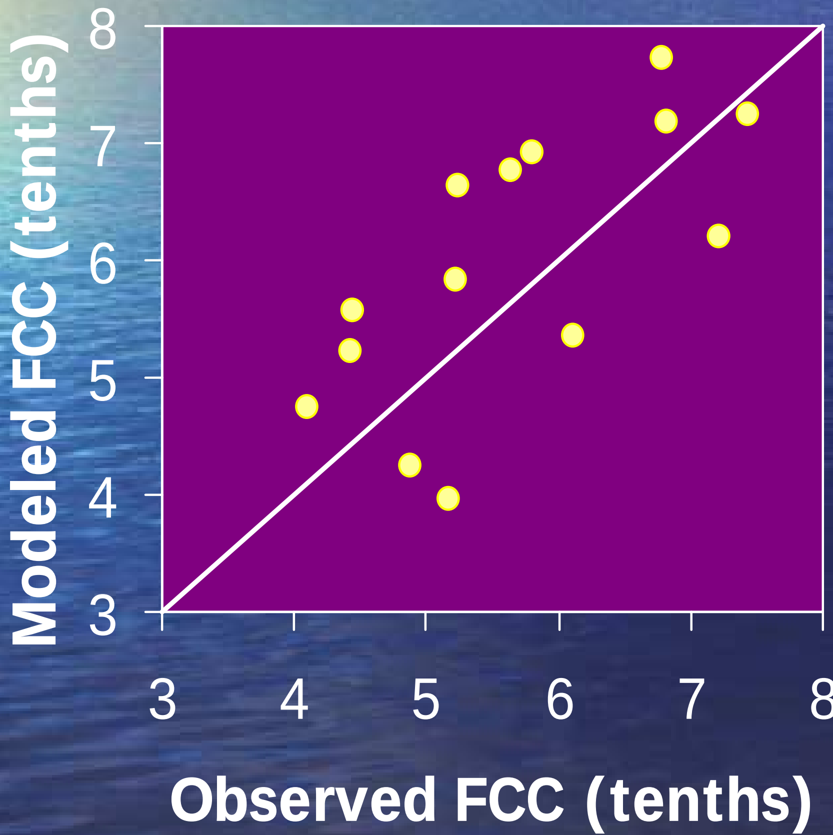
Poor performance



Fractional Cloud Cover (Temporal averages by site)

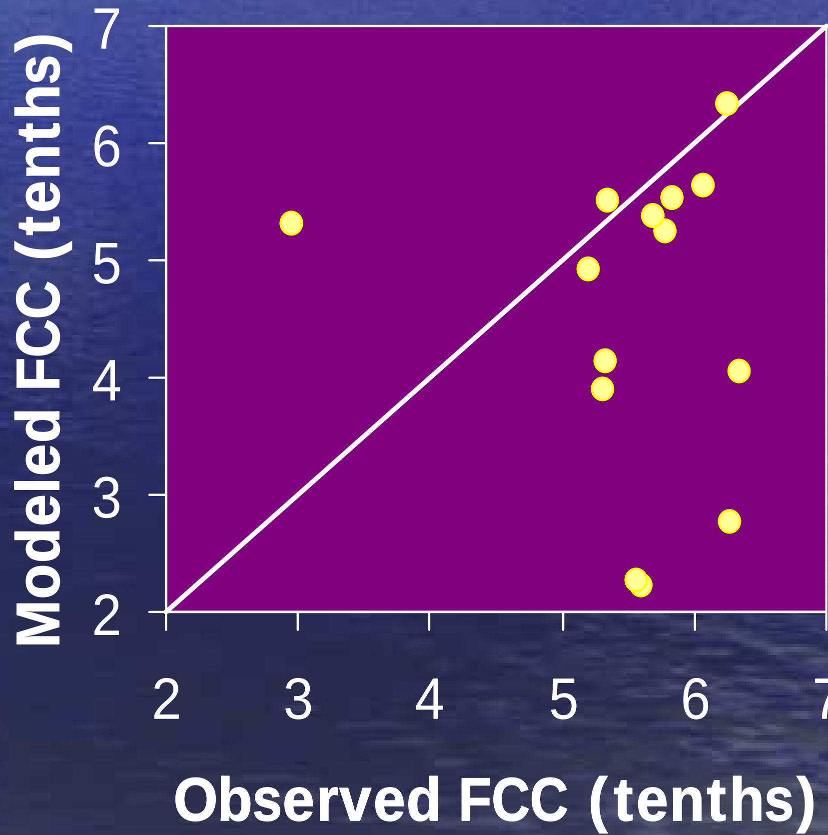
Good performance

24-29 June 1992



Poor performance

26 April - 3 May 1995



Modeling Experiment

A series of three model simulations were made for each of four episodes:

A normal simulation with all chemistry modules activated.

A simulation with the Reactive Scavenging Model (RSM), for cloud chemistry & precipitation scavenging, deactivated.

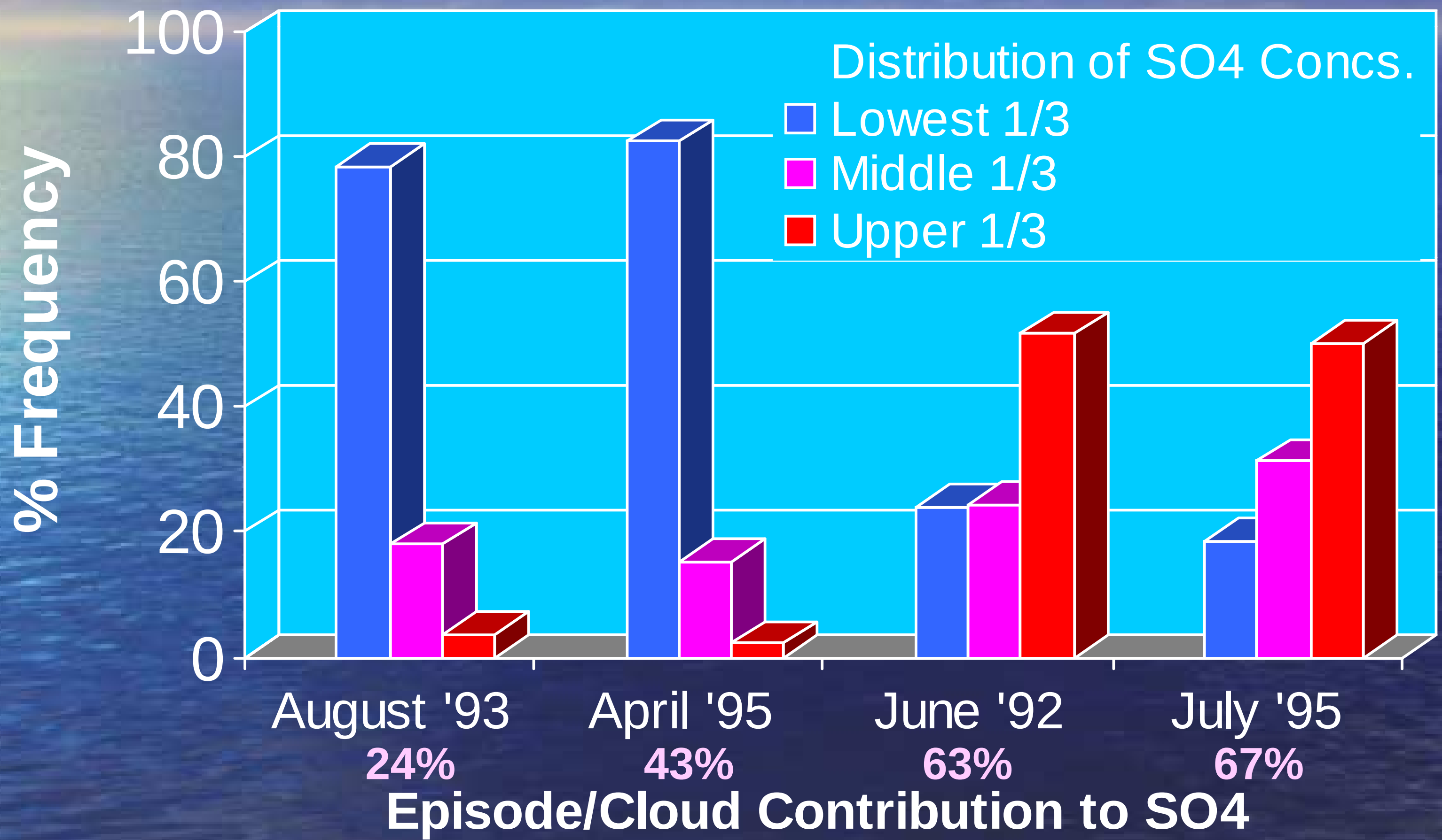
A simulation with both the RSM and the module for heterogeneous chemistry in non-precipitating clouds deactivated.

The contribution of different processes to sulfate levels was estimated by comparing results from the different simulations.

Diagnosis of Model Sulfate Formation

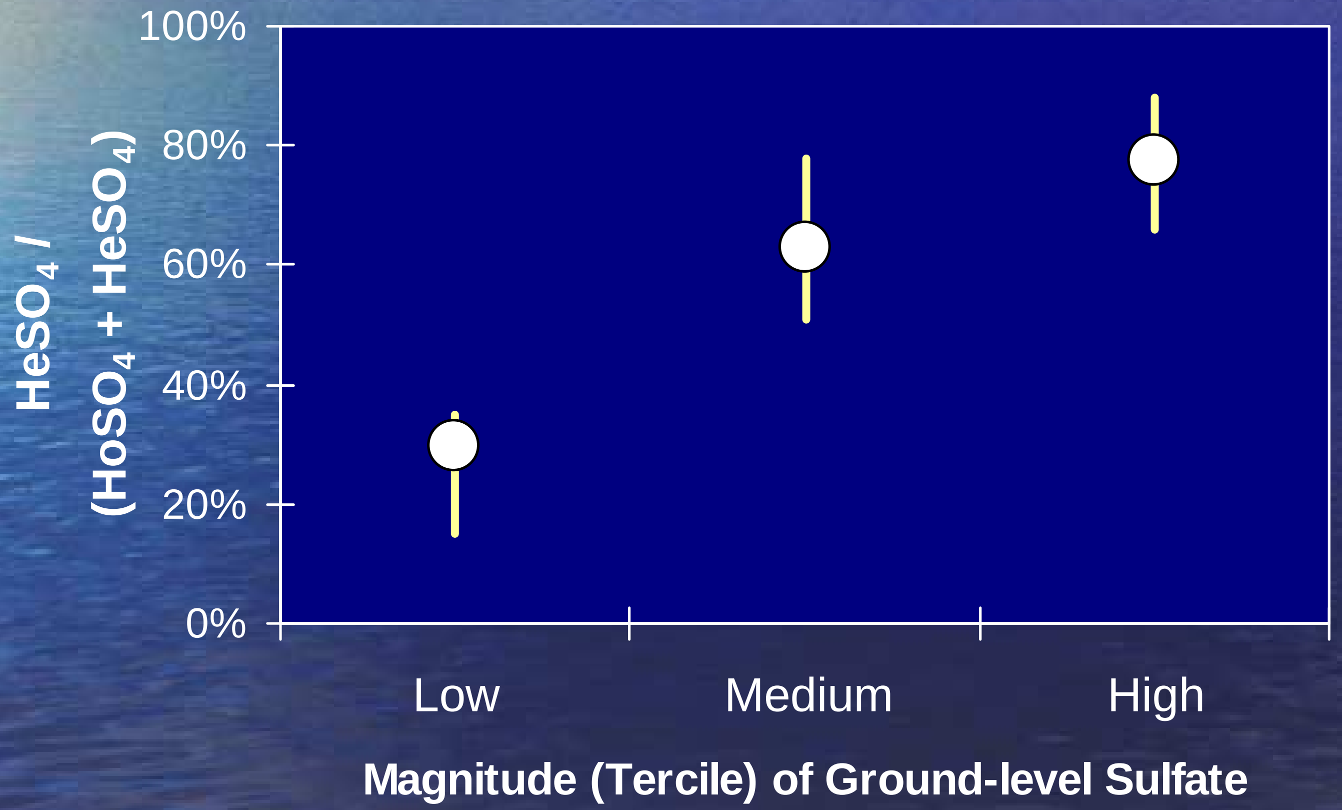
- Precipitating clouds almost always removed more sulfate from the atmosphere than they produced.
- The episode with the least cloud cover, the lowest frequency of areas having FCC>0.5, and the least precipitation produced the most sulfate aerosol through heterogeneous reactions.
- The episode with the most cloud cover and precipitation produced the least sulfate aerosol through heterogeneous reactions.

Modeled Contribution of Clouds to Sulfate Aerosol Formation

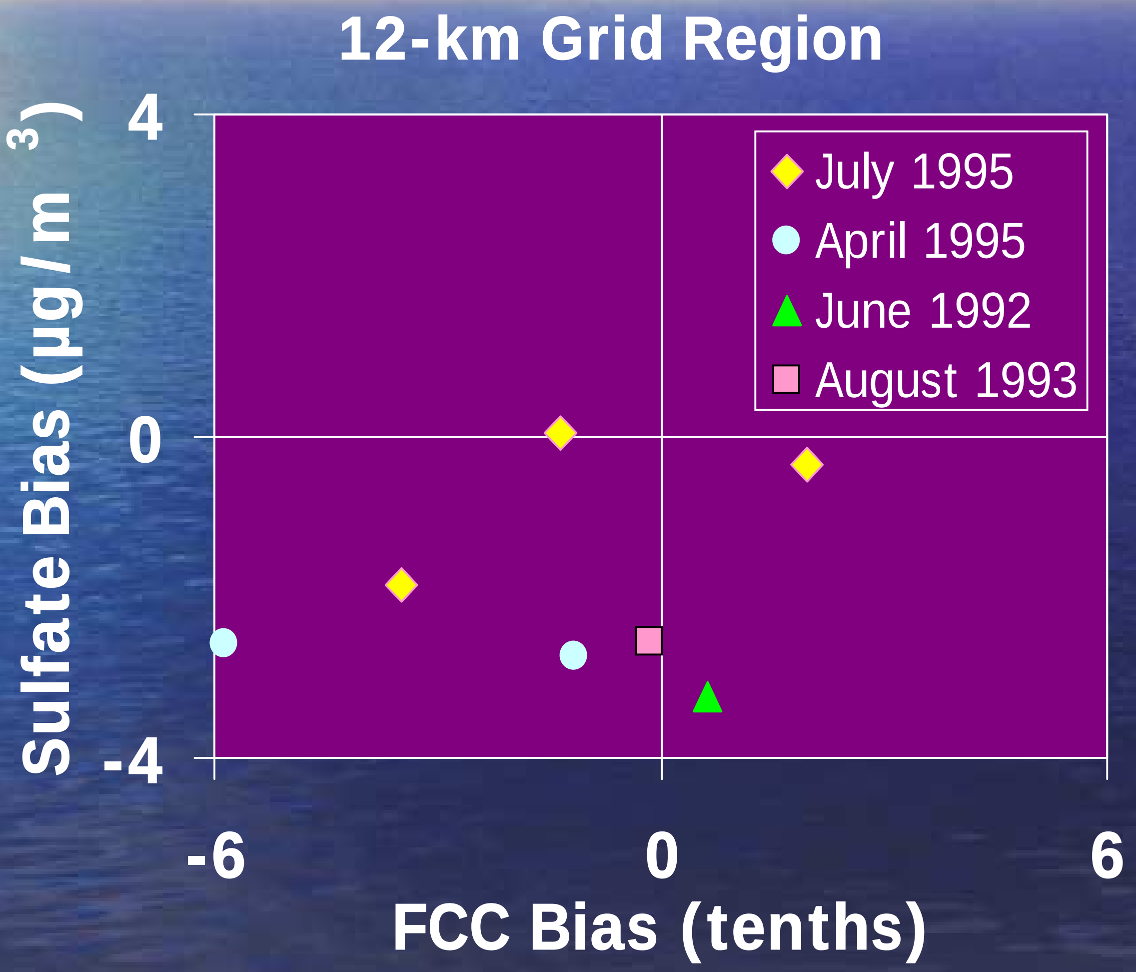


Increasing Contribution of Heterogeneous Mechanism →

Variation of Heterogeneous Sulfate Fraction with Sulfate Concentration



Model Sulfate Bias vs. Cloud Cover Biases on Dry Days



Conclusions

- Precipitating clouds act as a net sink for sulfate aerosol.
- The influence of heterogeneous (cloud) chemistry on sulfate aerosol appears greatest when photochemistry is active and cloud cover amounts are not high.
- High sulfate levels are associated with large contributions from cloud chemistry. Thus, cloud modeling is most important for poor visibility & high $PM_{2.5}$ events.
- Bias in model treatments of clouds may bias modeling of emission reduction strategies for visibility and $PM_{2.5}$.
- Limits on available data and the complexity of sulfate aerosol production make it very difficult to detect a clear cloud bias signal in model results.