Implications of Sulfate Aerosols on Clouds, Precipitation and Hydrological Cycle

Source:

- ✓ Sulfate aerosols are produced by chemical reactions in the atmosphere from gaseous precursors (with the exception of sea salt sulfate and gypsum dust particles). The two main sulfate precursors are sulfur dioxide (SO2) from anthropogenic sources and volcanoes, and dimethyl sulfide (DMS) from biogenic sources, especially marine plankton.

- Industrial: 65–92.4 (Tg aerosol year^{-1})
  Ocean: 10.7–23.7 (Tg aerosol year^{-1})
  Aircraft: 0.04 (Tg aerosol year^{-1})
  Biomass burning: 2.0–3.0 (Tg aerosol year^{-1})
- The major anthropogenic sulfur source is SO_2 emissions from the burning of sulfur-containing fuels, mainly coal. Metal smelting and other industrial processes also release significant quantities of SO_2.
  =>Sulfate emissions from biomass/biofuel are typically smaller than that from fossil fuel sources.

- Sea salt, mineral dust and soot particles are clearly primary particles, whereas organic particles from the oxidation of volatile organic compounds (VOC) and sulfates from the oxidation of SO_2 or other sulfur-containing gases are clearly secondary.
- The secondary aerosol species (e.g., sulfates, secondary organics) are not directly emitted, but are formed in the atmosphere from gaseous precursors.

- Evaporating clouds also release sulfate particles that are somewhat larger than non-cloud processed aerosol because of the additional material deposited onto them in clouds
- The droplet that forms is large enough for coalescence to start immediately even before the droplet reaches its critical size based on the Köhler equation. This can occur if the nuclei are completely soluble (e.g., sea-salt particles) or are mixed particles with a soluble coating [e.g., mineral dust with a coating of sulfate, *Levin et al.*, 1996] or are very large and wettable.

  (the form of the gases dimethylsulfide (**DMS**) and methane sulfonic acid (**MSA**))
- The most important natural sources of DMS and SO2 are the marine biosphere and exhalation from volcanoes, respectively.
- The greatest perturbation to DMS flux is simulated at high latitudes in both hemispheres, with little change predicted in the tropics and sub-tropics. The largest change in annual integrated flux is simulated in the Southern Hemisphere between 50S and 60S.

Size Distribution
Measurements show two modal diameters for sulfates, with typical diameters of approximately 0.3 and 0.7 μm. These are associated with two different dominant chemical mechanisms governing sulfate formation – gas-to-particle conversion and homogeneous and heterogeneous condensation reactions.

Existing mechanisms of sulfate aerosol-cloud-precipitation relations:

Category	Mechanism		Details	Spatial and temporal scales
Radiative Effects	Sulfates in the atmosphere	Negative TOA Forcing	Scattering is the dominant effect upon SW forcing at TOA.	Regional scale Hours to days
		Surface Cooling in the SW	Less solar radiation reaches the ground, thus reducing the available energy for sensible and latent heat fluxes, which drives the boundary layer growth and cloud formation.	
	Sulfates-cloud Radiation Effects [indirect effect]		Sulfates acts as CCN, changing cloud properties (e.g., coverage, lifetime, height) and consequently have cloud radiation effects.	Regional and Global
Dynamic Effects	Invigorate convection		Smaller cloud droplets freeze at lower temperature. Upon cloud droplet freezing latent heat is released at higher altitude, which can invigorate convection within the cloud.	Individual cloud systems and precipitation events
	Reduced surface latent heat		Latent heat associated with evaportranspiration provides moisture for the atmosphere, and also affects the atmospheric temperature profile (e.g., level of free convection), thus reduction of latent heat due to surface cooling can **decrease** atmospheric humidity and influence the boundary layer convection.	
Microphysical Effects [Sulfates as CCN/IN]	Sulfates as CCN		Sulfates are soluble species - provide a surface on which water condense thereby making them into a CCN. Smaller cloud droplets freeze at lower temperature.	Interaction between individual aerosol particles and cloud droplets happen on scale of micro-meters. Time Scales: Order of seconds
	Sulfates(H_2SO_4) as IN		Sulfuric acid droplets can serve as IN centers to form ice crystals.	

Microphysical effects (sulfate as CCN)

- Over the oceans, organic sulfur from the ocean (in the form of the gases dimethylsulfide (DMS) and methane sulfonic acid (MSA)) provides a source of CCN, with the DMS and MSA being converted to sulfate in the atmosphere
- It has been estimated that ~80% of sulfate mass globally is formed in the aqueous phase, and the remainder from the gas phase. As expected from the Köhler curves, larger sulfate particles serve more efficiently as CCN
- The production of sulfates (and maybe other soluble materials), followed by the release of these particles when the droplets evaporate, is an important mechanism for increasing the efficiency of CCN.
- The CCN are a subset of the total aerosols present in the atmosphere. Most of the pollution aerosols above a certain size threshold are effective CCN (e.g. sulfate, nitrates and certain organics).
- Dust particles coated with soluble material (sulfate and sea salt) have been measured as ice residuals further indicating their role in cloud and ice formation in the atmosphere.
- A substantial source of very small seasalt particles could be of importance to the marine CCN budget even if they are below the critical diameter for droplet activation at the low supersaturations in marine stratus clouds, because they can serve as nuclei for the growth of sulfate particles from the oxidation of dimethyl sulfide, DMS which is produced from ocean biota [*Charlson et al.*, 1987]. Direct production of sulfate particles by homogeneous nucleation is thought to be only rarely possible in the clean marine atmosphere [*Pirjola et al.*, 2000].
- On the other hand, larger seasalt particles also serve as a sink for gaseous H_2SO_4 molecules, thereby reducing the amount of sulfate available for the formation of accumulation mode particles [*Gong and Barrie*, 2003].
- In summary, seasalt particles are only a minor fraction of the CCN population under most situations, except for the winter Southern Ocean, North Atlantic and North Pacific. There is evidence for the existence of fine and ultrafine seasalt particles, but their abundance and their direct or indirect role as CCN source remains unclear. More detailed studies on the size distribution, composition, and production rates of the submicron marine aerosol will be required to resolve these issues.

Transport

- When emitted into the atmosphere, sulfur species undergo transport and chemical reactions to form compounds that condense on aerosol surfaces or nucleate.
  - ✓ Wet deposition removes gases and particles in the atmosphere and deposits them on the Earth's surface by means of precipitation.
  - ✓ With dry deposition, particles and gases reach land and water surfaces without precipitation.
  - ✓ All the processes controlling dispersion, residence time in the atmosphere, aerosol load and composition vary with weather and climate.
- The percentage of SO_2 transformed into sulfate, according to simulations with global chemistry models, falls between 51 and 56% (four models) with one outlier calculating an efficiency of 83% (due to low dry deposition flux of sulfur dioxide). This transformation rate depends on **transport, sink processes and chemical transformation.**
- Secondary particle formation from gas-phase sulfuric acid dominates the nucleation mode and contributes significantly to the particle number concentrations although contribution to total aerosol mass is small.
- Thus, the maxima of the nucleation mode number concentration can be found in the upper tropical troposphere and in the remote regions of the Antarctic. The soluble Aitken mode numbers are dominated by particles growing from the nucleation in the Aitken size range. Accumulation mode soluble numbers are highest in the lower troposphere between 30 S and 60 N close to the sources from biomass burning and fossil fuel use. Increased levels can also be found in the upper troposphere, attributable to convective detrainment of particles and their precursors and evaporation of cloud droplets and ice crystals.

- *Graf et al.* [1997] have shown that the efficiency by which sulfur precursors are transformed to sulfate depends on the source type. However, it depends additionally on the location and the season of the release.
- Southeast China emitted 11.6% of the global anthropogenic sulfur emissions and contributed 9% to the global sulfate burden in their simulations

Estimate of aerosol effects on climate
- Sulfates tend to produce cooler and drier climates.
- Forcing efficiency values for sulfate aerosols range from -125 to $-460 \mathrm{Wg}^{-1}$ (The direct forcing values range from -0.29 to -0.82 W m^{-2} for sulfate column burdens of 1.14 to 3.3 mg m^{-2}, with lower burdens producing lower forcing values in general.).
- When anthropogenic sulfur emissions were doubled, the aerosol burden contributed by China increased by a factor of 2.2. Their simulations show a gas-phase oxidation rate from south-east-Asian emissions above average. Sulfate formed via this pathway is less susceptible to wet scavenging and thus contributes more efficiently to the atmospheric sulfate load than sulfate formed in clouds, which is already incorporated in cloud droplets and thus is more likely to undergo wet removal.

-Thermodynamical effects
- There have been several studies that have attempted to quantify precipitation changes for the Asian monsoon from increased sulfates.
  - ✓ A slight weakening (related to land-sea contrasts) for the Indian summer monsoon was found if sulfate aerosols were included (first indirect effect only).
  - ✓ Based on observational data, Xu linked the southward shift of the Chinese monsoon to the direct radiative effects of sulfate aerosols over China.
  - ✓ Observational evidence from the Indian Ocean Experiment (INDOEX) field study by Ramanathan et al. indicate a regional scale warming of approximately 1K in the lower atmosphere over the tropical Indian Ocean and land surface cooling of approximately 0.5 to 1 K. These changes and redistribution of heat within the boundary layer were thought to have a strong impact on tropical circulation and interhemispheric precipitation patterns, and they were related to the presence of absorbing aerosols over the Indian subcontinent.
- Another study found that the trends in summer precipitation over China—North China droughts, South China floods—considered to be the largest observed in several decades, were related to the increased aerosol emissions observed over East Asia in recent years. These trends were attributed to changes in vertical temperature profiles, stability, and vertical velocity fields from absorbing aerosols, which were thought to increase/decrease cloud cover and precipitation in the south/north of China.

-Indirect Effects
- Rotstayn & Penner estimate climate sensitivity parameters for both the first and second indirect effect (from sulfates only) to be 0.78 and 0.7 K m^2 W^{-1}.
  - ✓ These are comparable to the climate sensitivity parameters derived for the direct sulfate and $2 \times CO_2$ forcings of 0.69 and 1.01 K m^2 W^{-1} from the same model, and therefore these indirect effects are quite critical for climate change studies.
  - ✓ In addition to these radiative and hydrological effects, the indirect aerosol forcing was also thought to substantially alter low-latitude circulation and rainfall based on results from Rotstayn & Lohmann, who used a mixed-layer ocean model coupled to an atmospheric model. They found that the near-global quasi-hemispheric pattern of contrasting SST (sea surface temperature) anomalies associated with trends in the drying conditions found in the Sahel may have some contribution from the indirect effect, although they only include sulfate aerosols in their analysis.

- Average values of the indirect effect in W m^{-2} estimated by different models for the listed aerosol species and for all aerosols, given as the difference between simulations with present-day aerosols and that with preindustrial aerosols.

    ✓ **Sulfate**
    Ghan et al.: −1.7 to −3.2
    Jones et al.: −0.5 to −1.5
    Rotstayn: −2.1
    Kiehl et al.: −0.4 to −1.78
    Williams et al.: −1.37
    Chuang et al.: −0.30
    Lohmann et al: −0.4
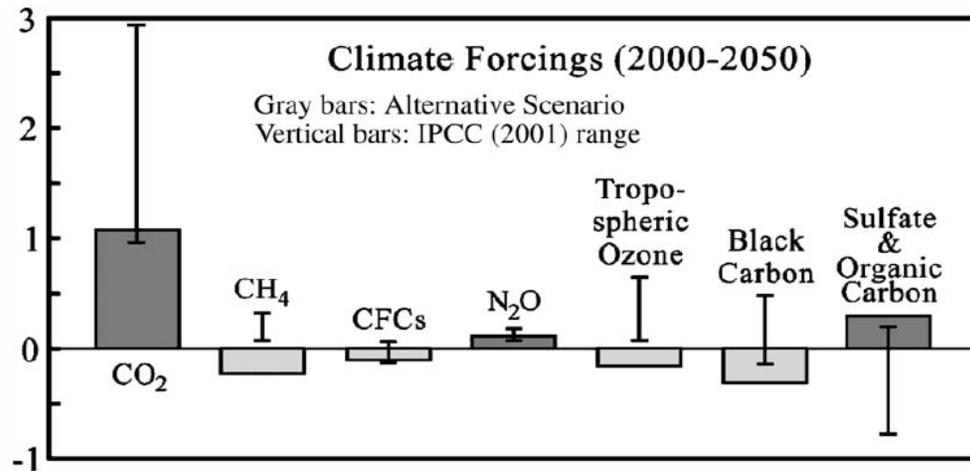   Menon (This work): −1.78

Figure 4 Climate forcings for 2000–2050 based on the "alternative scenario" of Hansen & Sato (107) and from the IPCC scenario (1). [Reprinted with permission of Hansen & Sato (107).]