CLOUD DROPLET NUCLEATION AND ITS CONNECTION TO AEROSOL PROPERTIES

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Abstract - Anthropogenic aerosols influence the earth's radiation balance and climate directly, by scattering shortwave (solar) radiation in cloud-free conditions and indirectly, by increasing concentrations of cloud droplets thereby enhancing cloud shortwave reflectivity. These effects are thought to be significant in the context of changes in the earth radiation budget over the industrial period, exerting a radiative forcing that is of comparable magnitude to that of increased concentrations of greenhouse gases over this period but opposite in sign. However the magnitudes of both the direct and indirect aerosol effects are quite uncertain. Much of the uncertainty of the indirect effect arises from incomplete ability to describe changes in cloud properties arising from anthropogenic aerosols. This paper examines recent studies pertaining to the influence of anthropogenic aerosols on loading and properties of aerosols affecting their cloud nucleating properties and indicative of substantial anthropogenic influence on aerosol and cloud properties over the North Atlantic.

Keywords - Climate, aerosols, clouds, radiation

INTRODUCTION

In recent years awareness has increased of the possible climatic influence of anthropogenic aerosols though modification of the shortwave (solar) radiation budget. Two key mechanisms have been described. The first, the so called "direct effect", consists of enhancement of scattering of radiation by aerosols in clear (cloud-free) air; a portion of the scattered radiation is scattered in the upward direction, leaving the planet and thereby decreasing the radiant energy absorbed by earth-atmosphere system and exerting a cooling influence on the climate (Charlson *et al.*, 1991, 1992). The second mechanism, the so-called "indirect effect", arises from an increase in the concentration of cloud droplets resulting from enhanced concentrations of aerosol particles that serve as nuclei upon which water vapor condenses to form cloud droplets (Cloud Condensation Nuclei, CCN). The increase in cloud droplet number concentration is postulated to increase multiple scattering within clouds, thereby increasing cloud-top albedo, a phenomenon originally suggested by Twomey (1971*a*; Twomey *et al.*, 1984; Platnick and Twomey, 1994). The increase in cloud droplet concentration may also inhibit precipitation development, enhancing cloud lifetime and resulting in an increase in planetary shortwave albedo (Albrecht, 1989) and possibly also in the atmospheric absorption of longwave (thermal infrared) radiation by the resultant increased atmospheric loading of liquid water and water vapor.

Estimates of the global and annual average magnitude of possible anthropogenic perturbation of the shortwave radiation budget through these mechanisms are of comparable magnitude to the perturbation in the longwave radiation budget of the troposphere due to increased concentrations of infrared active ("greenhouse") gases over the industrial period (IPCC, 1996 and earlier publications in this series; Charlson *et al*., 1992; Jones *et al*., 1994) but opposite in sign. It must be stressed, however, that these estimates are quite uncertain; indeed the uncertainty in the perturbation of the radiation budget by anthropogenic aerosols is now thought to be the greatest source of uncertainty in secular "forcing" of climate change over the industrial period. This uncertainty in turn greatly restricts the confidence that can be placed in empirical inference of climate change over this period and its qualitative and quantitative attribution to changes in radiative forcing.

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Much of the uncertainty in estimates of both the direct and indirect aerosol forcing arises from the present lack of ability to describe the processes governing the loading and geographical and vertical distribution of anthropogenic aerosols. This uncertainty is attributable in large part to uncertainties in the understanding of the cloud droplet nucleating properties of aerosols that govern not only the indirect effect but also the removal of aerosol particles from the atmosphere in precipitation. These uncertainties are manifest on local scales, which are suitable for study, for example, by aircraft measurements, and *a fortiori* in extrapolation to subhemispheric scales pertinent to the transport of these aerosols within their atmospheric residence times.

This paper gives an overview of the processes governing aerosol influences on climate, with particular focus on the relation between aerosol microphysical properties and the number concentration of cloud droplets. Attention is then directed toward recent studies examining this process with the aim of identifying approaches to decreasing the uncertainties in estimating the magnitude of aerosol forcing of climate on local to global scales. For recent reviews of the direct and indirect effects see Schwartz and Slingo (1996) and Schwartz (1996), respectively.

DEPENDENCE OF INDIRECT FORCING ON CLOUD DROPLET CONCENTRATION

The theoretical basis for a dependence of cloud albedo on cloud droplet number density, and in turn on the number density of the aerosol particles on which cloud droplets form, was given by Twomey (1974, 1977*a,b*), who noted the relation between cloud albedo and optical depth and in turn cloud microphysical properties. This relation is exemplified in Figure 1, for which the cloud-top reflectance (albedo) $R_{\rm CT}$ of a nonabsorbing, horizontally homogeneous cloud was evaluated by an analytical expression for given by Bohren (1987) under assumption that liquid water path is constant with changing cloud droplet number concentration, $N_{\rm cd}$. The influence of absorbing material in aerosol particles on the albedo enhancement due to increasing droplet concentrations was examined by Twomey *et al*. (1984) who found that except for clouds having very high albedo ($R_{\rm CT} \gtrsim 0.8$), the albedo enhancement dominates over the albedo decrease due to absorbing material for reasonable assumptions of the magnitude of the absorption.

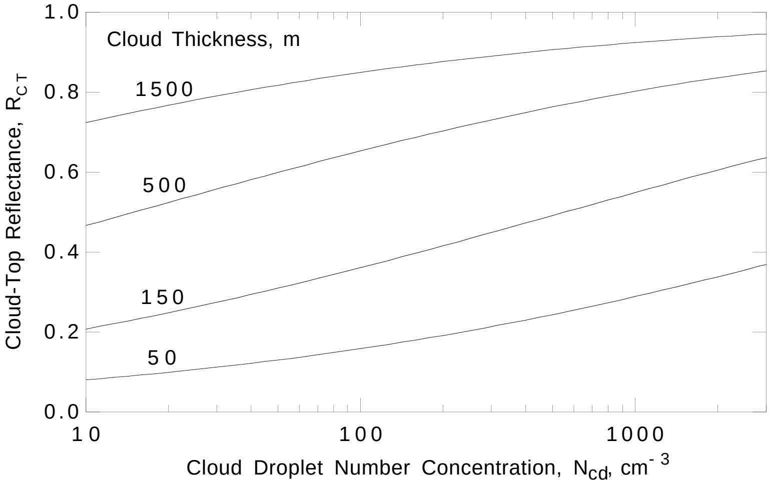


Figure 1. Dependence of cloud-top albedo on cloud droplet number concentration $N_{\rm cd}$ for liquid water volume fraction L = 0.3 cm^3 m^{-3} and indicated values of cloud thickness. From Schwartz and Slingo (1996).

Examination of the sensitivity of cloud-top albedo to change in cloud droplet concentration yields, within the same assumptions,

$$\Delta R_{\rm CT}\big|_{L,z_{\rm C}} = \frac{1}{3}\left[R_{\rm CT}(1-R_{\rm CT})\right]\Delta \ln N_{\rm cd} \; . \qquad (1)$$

The quantity $R_{\rm CT}(1-R_{\rm CT})$ exhibits maximum value of $\frac{1}{4}$ when cloud-top albedo $R_{\rm CT} = \frac{1}{2}$, for which $\Delta R_{\rm CT}$ assumes a maximum value $\Delta R_{\rm CT}^{\rm max} = \frac{1}{12}\Delta \ln N_{\rm cd}$. As shown in Figure 2, $dR_{\rm CT} / d \ln N_{\rm cd}$ varies only slowly with $R_{\rm CT}$ for intermediate values of $R_{\rm CT}$, 0.3 to 0.7, characteristic of the prevalent and climatically important marine stratus clouds.

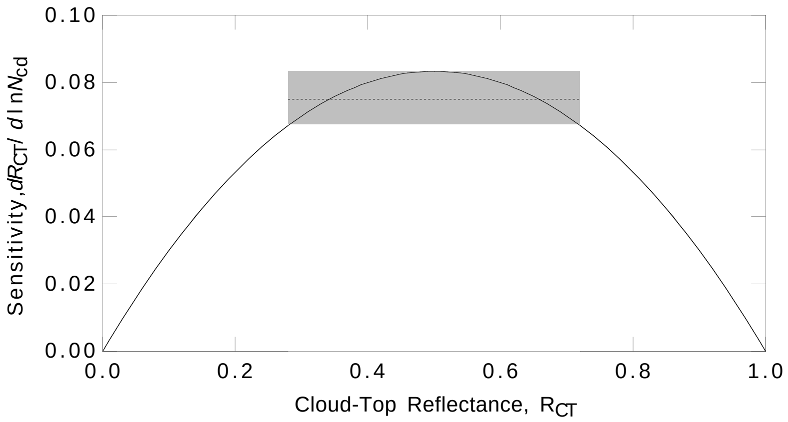


Figure 2. Dependence of sensitivity of cloud-top albedo R_{CT} to a logarithmic change in concentration of cloud droplet number concentration N_{cd}, as a function of R_{CT}. The shaded band indicates the region, $0.28 \lesssim R_{\mathrm{CT}} \lesssim 0.72$, for which the approximation $dR_{\mathrm{CT}} / d\ln N_{\mathrm{cd}} \approx 0.075$ holds within 10%. Modified from Charlson *et al.* (1992).

To gain a sense of the magnitude of albedo change and forcing that would be associated with a possible anthropogenic perturbation in N_{cd}, we note that a 30% relative increase in N_{cd} corresponds to an increase in absolute cloud-top albedo by about 2%. This high sensitivity to N_{cd}, together with the large amount of shortwave power reflected by clouds, is the basis of global estimates of the indirect aerosol forcing effect. Charlson *et al.* (1992; *cf.* also Kaufman *et al.*, 1991) estimated the global mean forcing due to anthropogenic aerosols in this way based on the fractional global coverage by marine stratus clouds. For a given cloud-top albedo perturbation the corresponding perturbation in top-of-atmosphere (TOA) albedo was taken as

$$\Delta R_{\mathrm{TOA}} = T^2 \Delta R_{\mathrm{CT}} \tag{2}$$

where T is the fraction of incident shortwave radiation transmitted by the atmosphere above the cloud layer. To obtain the change in global- or hemispheric-mean albedo due only to the change in albedo of marine stratus clouds $\Delta R_{\mathrm{TOA}}^{\mathrm{mst}}$, the albedo change given by (2) must be decreased further by the fractional coverage by marine stratus clouds, A_{mst}, yielding

$$\overline{\Delta R_{\mathrm{TOA}}} = A_{\mathrm{mst}} \Delta R_{\mathrm{TOA}}^{\mathrm{mst}} . \tag{3}$$

The corresponding perturbation in global- or hemispheric-mean shortwave forcing was estimated as

$$\overline{\Delta F_{\mathrm{C}}} = -\overline{F}\,\overline{\Delta R_{\mathrm{TOA}}} = -(F_{\mathrm{T}} / 4)\overline{\Delta R_{\mathrm{TOA}}} , \tag{4}$$

where $\overline{F}$ is the global- or hemispheric-mean top-of-atmosphere shortwave radiation evaluated as $\overline{F} = F_{\mathrm{T}} / 4$, where F_{T} is the solar constant. The negative sign denotes a cooling tendency. The forcing depends linearly on the perturbation in cloud-top albedo and thus exhibits a logarithmic dependence on N_{cd} given by (1).

$$\overline{\Delta F_{\mathrm{C}}} \approx -0.075(F_{\mathrm{T}} / 4) A_{\mathrm{mst}} T^2 \Delta \ln N . \tag{5}$$

Figure 3 shows the dependence of global- or hemispheric-mean radiative forcing on a change in N_{cd} and indicates a sensitivity comparable to that estimated above. For an assumed 30% increase in hemispheric-mean N_{cd}, the hemispheric-mean forcing evaluated by this approach is -1.1 W m^{-2}; it must be emphasized, however, that the premise of the estimate (30% hemispheric enhancement in cloud droplet number concentrations) remains at present little more than an educated guess. It is clear, nonetheless, that even modest increases in the concentrations of cloud droplets by anthropogenic aerosols can lead to shortwave radiative forcing of climate that is substantial in the context of longwave forcing by anthropogenic greenhouse gases, about +2.5 W m^{-2} at present, global and annual average. As shown below (see also Schwartz and Slingo, 1996) the anthropogenic perturbation on aerosol mass loadings and resultant concentrations of CCN and cloud droplets can be *several fold*, at least on scales of 1000 km or more.

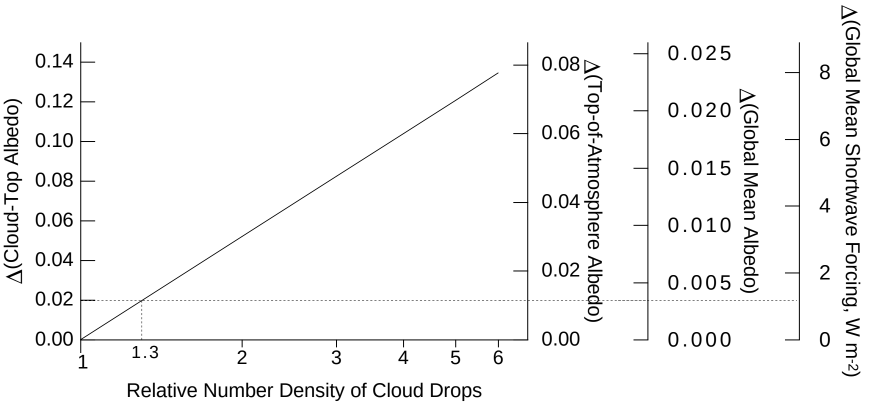


Figure 3. Calculated perturbation in cloud-top albedo (left ordinate), top-of-atmosphere albedo above marine stratus, global-mean albedo, and global-mean cloud radiative forcing (right ordinates) resulting from a uniform increase in cloud droplet number concentration N_{cd} by the factor indicated in the abscissa. The global-mean calculations were made with the assumption (Charlson *et al*., 1987) that the perturbation affects only non-overlapped marine stratus and stratocumulus clouds having a fractional area of 30%; the fractional atmospheric transmittance of shortwave radiation above the cloud layer was taken as 76%. The dotted line indicates the perturbations resulting from a 30% increase in N_{cd}. Modified from Charlson *et al*. (1992).

Much work remains to be done before knowledge of the magnitude of the indirect forcing by anthropogenic aerosols, as well as that of the direct forcing, can be refined to an uncertainty comparable to that associated with anthropogenic greenhouse gases (Penner *et al*., 1994). Key sources of uncertainty arise from the mass loading and geographical and vertical distribution of anthropogenic aerosols, and the microphysical properties of the aerosols governing their cloud nucleating properties and their atmospheric residence times. As noted above, changes in cloud microphysical properties can further influence cloud short- and longwave radiative properties through changing the persistence of clouds against precipitation. However no estimates of the global forcing resulting from changes in cloud persistence appear yet to have been given.

RELATION BETWEEN AEROSOL PROPERTIES AND CLOUD DROPLET CONCENTRATIONS

Cloud droplets form on existing aerosol particles by the process of heterogeneous nucleation. Soluble material (mainly inorganic salts) provides a favorable site for nucleation by reducing the vapor pressure of the water relative to that of the pure solvent at the same particle radius that assists in overcoming the free energy barrier to cloud droplet activation. This process, initially described by Köhler, is treated in detail for example by Pruppacher and Klett (1980) and is not reviewed here; attention is called also to a recent paper (Reiss and Koper, 1995) which gives a rigorous thermodynamic treatment of the phenomenon. The thrust of such analyses is the concept of a "critical" set of values of drop radius and supersaturation, such that if the supersaturation exceeds the critical value for sufficiently long for the drop to grow to the critical radius, the droplet continues to accrete water and becomes a cloud droplet.

In the ambient atmosphere the environmental supersaturation is governed by the interplay of the updraft velocity, which may be thought of as "generating" supersaturation, and condensation of water vapor on aerosol particles and growing cloud droplets, which provide a "sink" for supersaturation. This basic interplay has served as the basis for analytic and numerical examination of the dependence of cloud droplet concentration on the concentration and microphysical properties of aerosol particles and on such macrophysical environmental factors as relative humidity, lapse rate, vertical velocity, and turbulence (*e.g*., Roesner *et al*., 1990; Kaufman and Tanré, 1994; Gillani et al., 1995; Leaitch et al., 1996). For given macrophysical properties the maximum environmental supersaturation decreases with increasing concentration of aerosol particles because of the greater surface area and sink rate for supersaturation afforded by the greater particle surface area. Nonetheless the supersaturation spectrum, the dependence of number density of aerosol particles activated to cloud droplets as a function of applied supersaturation is a key property necessary to describe cloud activation and the number density of cloud drops formed, and the dependence of this quantity on aerosol properties.

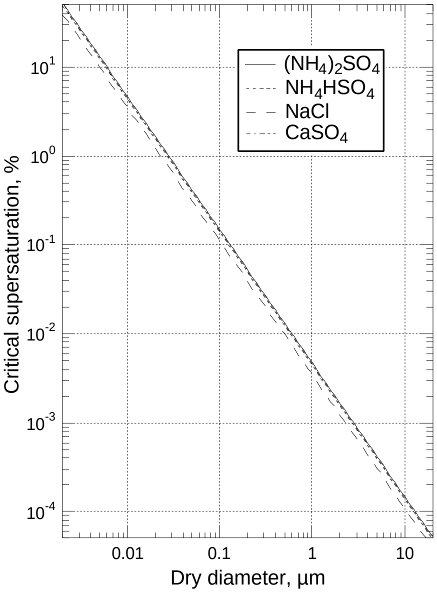


Figure 4. Dependence of critical supersaturation on dry diameter of aerosol particle serving as cloud condensation nucleus. Particle is assumed to consist entirely of salt indicated.

For a single particle the dependence of critical supersaturation, S_c -1 (where S is the saturation ratio), on dry particle radius r_0 can be evaluated from the Köhler equation under assumption that the particle consists of a single solute of molecular weight M_s, van't Hoff factor i, and density ρ_s (cf. Pruppacher and Klett, 1980, p. 141 *ff.*; also Junge and McLaren, 1971) as

$$S_c - 1 = \left(\frac{32}{27}\right)^{1/2} \left(\frac{M_w}{\rho_w}\right) \left(\frac{M_s}{i\rho_s}\right)^{1/2} \left(\frac{\sigma}{R_g T}\right)^{3/2} r_0^{-3/2} \qquad (6)$$

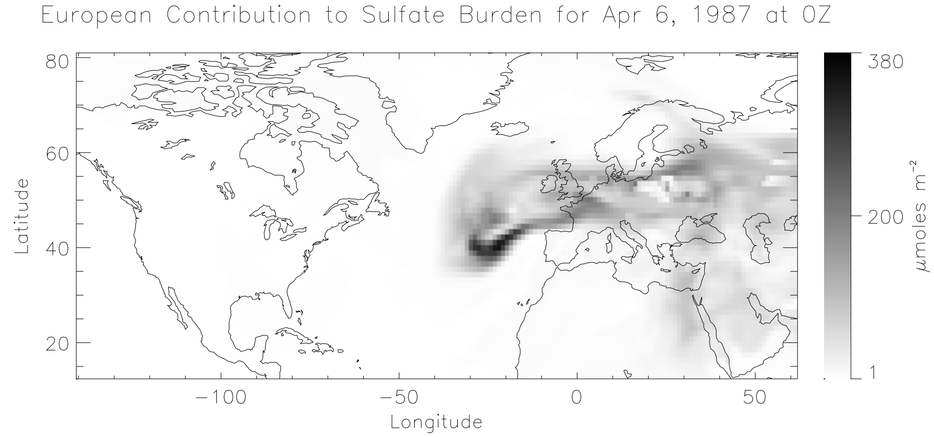
where σ is the surface tension and the remaining symbols have their customary meaning (the subscript w refers to water) and in any event are defined in Pruppacher and Klett. If for an ambient aerosol the number distribution of particles as a function of dry radius is known and the composition is known or assumed, equation (6) may be used to infer the supersaturation spectrum. This dependence is shown in Figure 4, which indicates a strong dependence on particle dry diameter and a weak dependence (especially in a log-log plot) on particle composition. Equation (6) and Figure 4 provide the link between aerosol size distribution (number concentration of particles versus diameter) and supersaturation spectrum (number concentration of CCN versus supersaturation).

ANTHROPOGENIC INFLUENCE ON NORTH ATLANTIC AEROSOL

The North Atlantic provides a valuable testbed for studies of the influence of anthropogenic continental emissions on aerosol loadings and properties and on clouds because of the high spatial and temporal contrast between situations where the aerosol is predominantly anthropogenic transported from the adjacent continents versus situations of relatively pristine marine aerosol. Previous studies documenting the anthropogenic influence on the North Atlantic aerosol and its variability include Schwartz (1988) Hoppel *et al*. (1990), Arimoto *et al*. (1992), and Van Dingenen *et al*. (1995). Calculations of concentrations of aerosol sulfate with an Eulerian model (Benkovitz *et al.*, 1994) indicate that much of the loading of this material over the North Atlantic results from transport of industrially emitted material from the continents. These calculations also indicate substantial spatial and temporal variability of loading of this material resulting from synoptic-scale variability in transport winds and precipitation. Figure 5 shows an example of the calculated distribution of column burden of sulfate from European anthropogenic sources over the European continent and the North Atlantic at 00 UTC on April 6, 1987. The preceding days had been characterized by a strong low pressure system that was responsible for circulating sulfate from Northern European sources well out into the North Atlantic. European emissions were the dominant source of sulfate in the indicated region during this time period.

Substantial spatial and temporal variability in aerosol loadings and properties is evidenced in measurements from the ASTEX-MAGE project conducted in the vicinity of the Madeira-Azores-Canaries Islands during June 1992. Figure 6 shows a time series of sulfate concentrations at Santa Maria Island, Azores, with high excursions associated with trajectories from the British Isles and northern continental Europe (Harrison *et al.*, 1996; Huebert *et al.*, 1996*a*). Numerous measurements of aerosol loadings and size distributions taken during this project are consistent with that interpretation (Jensen *et al*., 1996; Russell *et al*., 1996).

Figure 5. Column burden of sulfate aerosol derived from European sources for April 6, 1987 at 00 UTC. Sulfate concentrations were calculated with an Eulerian chemical transport and transformation model that is driven by observation-derived meteorology, specifically the 6-hour forecast fields calculated by the European Center for Medium Range Weather Forecasts (ECMWF). Emissions include anthropogenic and natural SO_2, non-seasalt sulfate, and reduced sulfur gases (mainly dimethylsulfide, DMS). Chemical transformation includes clear-air and in-cloud oxidation of SO_2 and clear-air oxidation of DMS. Material is removed by wet and dry deposition. The model extends from -140° to +62.5° longitude (west of North America, across North America, the North Atlantic, and Europe, to the Urals) and has 1.125° resolution. There are 15 levels in the vertical extending from the surface to about 100 hPa (the model uses ECMWF "eta" coordinates to conserve mass). Column burdens depicted here are evaluated as the vertical integral of concentration. The model is fully described in Benkovitz *et al*. (1994), which presents results for a one-month simulation during fall 1986, comparisons with observations, and various statistics characterizing the model output. Figure provided by C. Benkovitz.



Examples of differences in aerosol and cloud microphysical properties in maritime and continental air are shown in Figure 7, which presents two sets of vertical profiles obtained at ~1000 km separation on 16 June 1992. The concentration of accumulation mode particles (0.1 - 3 μm diameter) is greater in continental air by a factor of *ca*. 30, ~1500 cm^{-3} *vs*. ~50 cm^{-3} and the cloud droplet concentration by a factor of *ca*. 5, 250 cm^{-3} *vs*. 50 cm^{-3}. Although increase in cloud droplet content may be attributable in part to increased liquid water content, it is clear from the decrease in cloud drop effective radius that the increase in drop concentration is due mainly to the increased concentration of aerosol particles serving as cloud drop nuclei. It may be observed from Figure 3 that such a fivefold enhancement in cloud droplet concentration gives rise to a local increase in TOA albedo of ~7%, corresponding, for solar irradiance of 1000 W m-2, to an instantaneous shortwave forcing of -70 W m^{-2}. Indeed the AVHRR visible satellite image obtained at the time of the measurements shows marked increase in cloud reflectivity in the continental air *vs*. the maritime air (Albrecht *et al*., 1995).

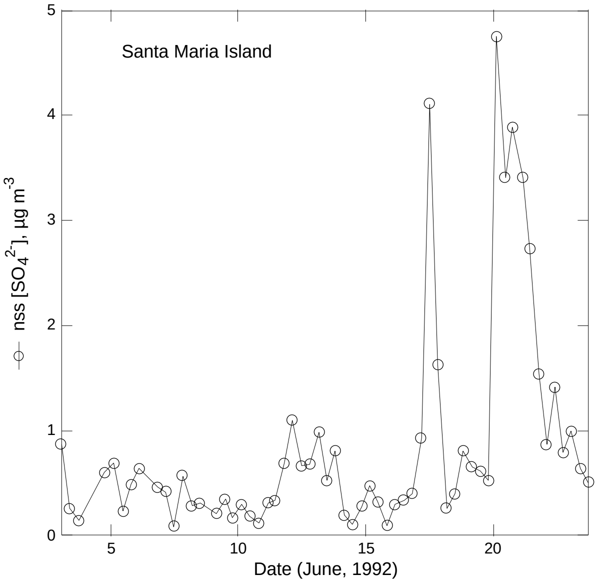


Figure 6. Time series (8-hour samples) of non seasalt sulfate concentration measured during the ASTEX-MAGE project at Santa Maria Island, Azores (Harrison *et al*., 1996).

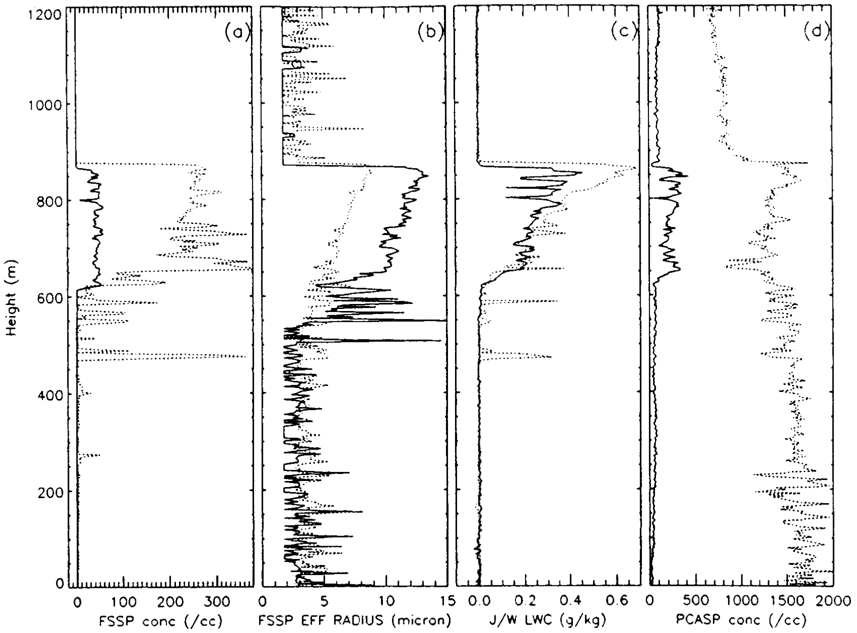


Figure 7. Vertical profiles of aerosol and cloud microphysical properties over the North Atlantic in the vicinity of the Madeira Islands on June 16, 1992, obtained with the UK Meteorological Research Flight C-130 aircraft during the ASTEX-MAGE project. Solid lines represent measurements in a maritime air mass; dotted lines, continental air. a) Cloud droplet concentration; b) Cloud droplet effective radius; c) Liquid water content; d) Concentration of aerosol particles in diameter range 0.1-3.0 µm (increase indicated in cloud is instrument artifact). From Albrecht *et al.* (1995).

Measurements of the size distribution of aerosol chemical composition are notoriously difficult because of the small amount of mass contained in particles of diameter below ~ 0.5 µm, and because of the difficulty in physically separating this material. Consequently volatility measurements have long been used as a surrogate to determine the relative role of seasalt (which is non volatile) *vs.* sulfate salts, which are volatile. Such an approach, introduced by Twomey (1971*b*), has indicated that volatile sulfate salts are the dominant source of CCN in both marine and continental air, a result which has been found to hold in the ASTEX-MAGE project by Hudson and Da (1996). Likewise in the same project Clarke *et al.* (1996) showed that the great majority of aerosol volume in the diameter range 0.15-0.6 µm is volatilized at temperatures below 300°C, albeit with a small residual nonvolatile core, indicative of an internally mixed aerosol consisting mainly of sulfate salts.

Also in the ASTEX-MAGE project Huebert *et al.* (1996) presented measurements of the mixing ratio of aerosol substances size-resolved over the diameter range 0.1 - 10 µm. Representative composition spectra for "clean marine air masses" and "heavily polluted continental air masses" are shown in Figure 8. In both cases the chemical amount mixing ratio of the aerosol is dominated by Na and Cl, but this material, undoubtedly seasalt, is confined mainly to the large end of the size range. Ammonium and sulfate (in a near 1-to-1 ratio indicative of ammonium bisulfate) is present mainly in the accumulation mode, 0.1 to 1 µm diameter. Figure 9*a* shows the particle number concentrations for NaCl and NH_4HSO_4 evaluated under the assumption that the ionic species are present in particles of those compositions. It is clear that advected continental air contains substantially more ammonium bisulfate particles in the accumulation mode than does the marine air. Despite the low molar mixing ratios for NH_4^+ and SO_4^{2-} at the low end of the diameter range, the particle number concentrations continue to increase strongly with decreasing diameter in this region. This suggests that substantial numbers of particles are present at sizes below the range for which the chemical measurements are made, a situation that presents a very demanding challenge to measurements or, more practically, requires inferences on composition to be made by alternative means, such as volatility as noted above. As noted, measurements of the volatility of particles and CCN in this project are entirely consistent with the dominant species in this range being volatile sulfate salts, but as noted by Novakov and Penner (1993), the possible role of organics needs to be considered as well.

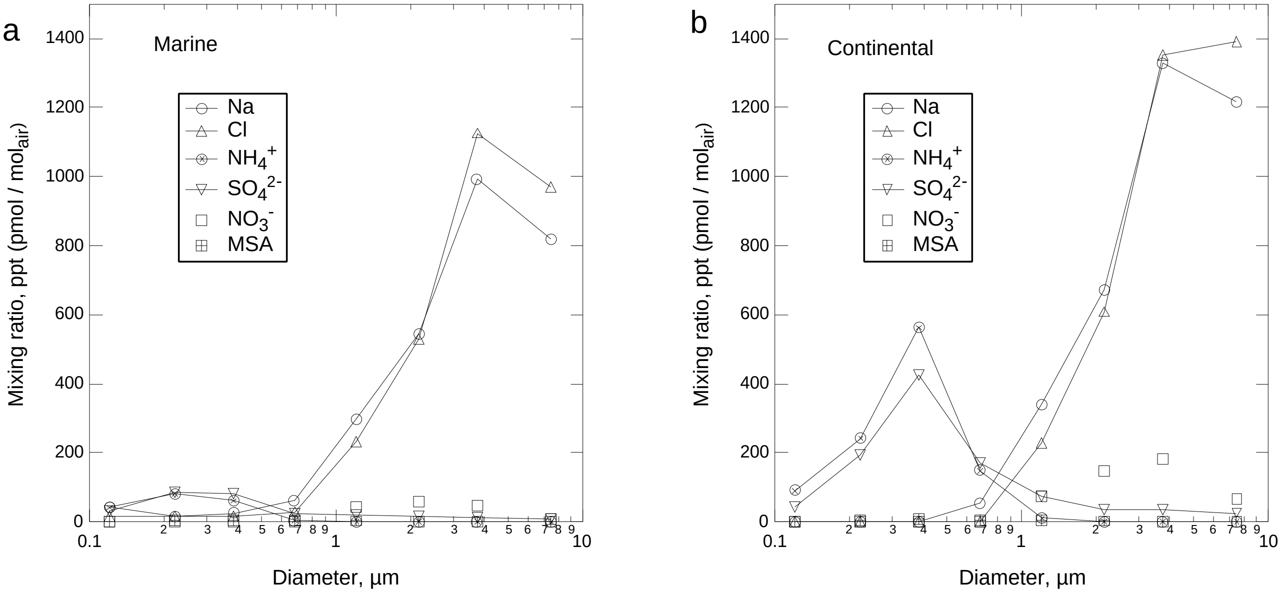


Figure 8. Chemical composition spectra of aerosols during ASTEX-MAGE. *a*) Size distribution of major ionic species representative of "clean marine air masses"; *b*) "heavily polluted continental air masses". Data of Huebert *et al* (1996*b*).

Figure 9*b* shows the supersaturation spectra calculated, by Eq (6), for the particle number distributions given in Figure 9*a*. The continental air contains much greater concentrations of CCN than does the marine air, by a factor of 2 to 6, depending on maximum supersaturation encountered. Despite the much greater mass loading of NaCl vs. NH_4HSO_4, NH_4HSO_4 dominates the CCN for both air mass types in the supersaturation range 0.01 to 0.1%, important for marine stratus clouds. Also shown for comparison are CCN spectra for continental and marine air measured from the UK Meteorological Flight C-130 during the ASTEX project . In the limited range of overlap the agreement is quite good, both in

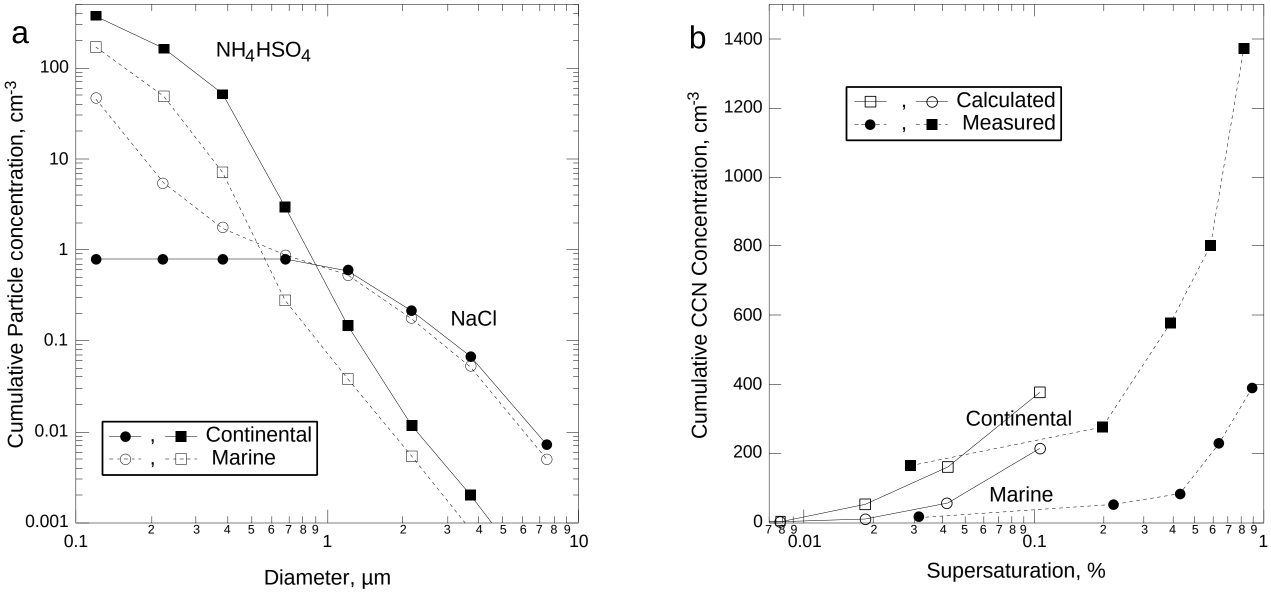


Figure 9. *a*) Cumulative particle number spectra (i.e., number of particles of diameter greater than value given by abscissa) for inorganic salts evaluated from measurements of Huebert *et al*. (1996*b*) shown in Figure 8 under assumption that Na and Cl in the several size ranges are present as NaCl particles and likewise that NH_4^+ and SO_4^{2-} are present as NH_4HSO_4 particles. *b*) Calculated supersaturation spectra. corresponding to these size distributions (open symbols) and supersaturation spectra representative of continental and marine air measured on the UK Meteorological Flight C-130 during the ASTEX project (filled symbols) as reported by Albrecht *et al*. (1995).

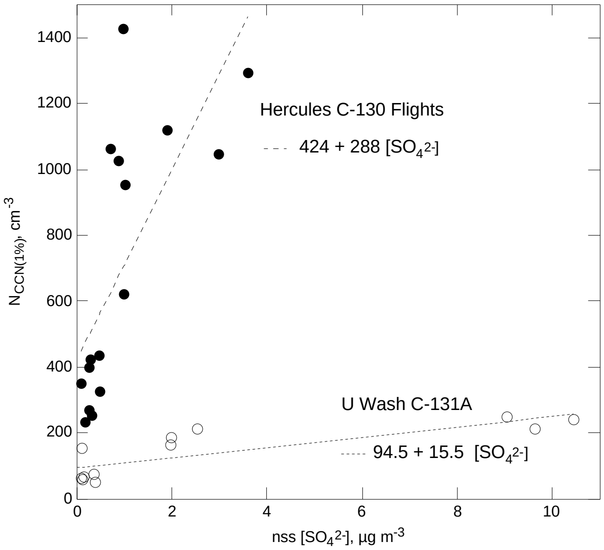


Figure 10. Scatter plots of aircraft measurements of CCN concentration (1% supersaturation) *vs*. non-seasalt sulfate measured during the ASTEX-MAGE campaign in June 1992. Data from the UK Meteorological Flight C-130 (Harrison *et al*., 1996) and from the University of Washington C-131A (Hegg *et al*., 1993).

absolute numbers and in dependence on supersaturation.

A persistent issue in assessing the impact of anthropogenic aerosols on marine stratus clouds is the relation between CCN concentration and non-seasalt sulfate, the presumed major contributor to anthropogenic CCN. Figure 10 shows the dependence of CCN concentration on non-seasalt sulfate concentration measured in the ASTEX-MAGE project on two different aircraft, the UK Meteorological Flight C-130 and the University of Washington C-131A. In both data sets a rather robust relation is indicated. However the slopes of the relations are substantially different, a situation that must be resolved.

CONCLUSIONS

The magnitude of the hypothesized indirect aerosol forcing of climate by enhancing cloud albedo rests to great extent on the assumed widespread influence of anthropogenic aerosols in the marine atmosphere. Recent measurements in the North Atlantic provide convincing evidence of marked enhancement (several fold) of aerosol sulfate, aerosol number, CCN, and cloud droplet concentrations, at least at distances of a few thousand kilometers from the source of the aerosol material, albeit with considerable short range spatial and temporal variability due mainly to variability in transport meteorology. The magnitude of the enhancement in cloud droplet concentrations and inferred cloud albedo suggests substantial radiative forcing by the indirect (cloud brightening) mechanism.

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