Notes and Correspondence

On the Relationship between Sulfate and Cloud Droplet Number Concentrations

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Abstract

Comparisons are drawn between the aerosol cloud microphysical theory implicit in the modeling of Kaufman et al. and the cloud droplet and cloud water sulfate concentrations of Leaitch et al. for the purpose of helping to understand the effect of sulfate particles on climate through cloud modification. In terms of the range of possibilities and prospects for future climate given by Kaufman et al. for the effect of sulfur on cloud albedo, the data favor the possibility of stronger cooling. Scatter in the data makes it impossible to constrain model parameters; however, the comparisons suggest that there may not be a universal relationship, and that the uncertainties involved in trying to model this process are large.

1. Introduction

Kaufman et al. (1991) present an interesting comparison of the relative contribution to the heating and cooling of the atmosphere from CO₂ and SO₂ emitted by fossil fuel and biomass burning. Fossil fuel burning cools the earth-atmosphere system in Kaufman et al. through the effect of sulfur pollution on the cloud droplet number concentration (Nₐ) and thus cloud albedo (sometimes referred to as the Twomey effect). For the present and near future, they suggest it is more likely that cooling by this mechanism will dominate heating due to the increasing greenhouse effect of increasing CO₂, and that the trend will reverse itself sometime in the future. Wigley (1991) has shown that one must understand the effects of anthropogenic sulfate aerosols on climate to determine the course of future action on global warming.

The assessments of Kaufman et al. are derived from an analysis that strings together several relationships, including the critical but poorly understood relationship between sulfur pollution and cloud microphysics. In this paper, the theoretical approach to the effect of changing sulfate concentration on Nₐ implicit in the analysis of Kaufman et al. is compared with the observations of cloud droplets and cloud water sulfate concentrations reported by Leaitch et al. (1992) to help place our present understanding of this relationship and its role in climate in perspective. To do this, the theory used by Kaufman et al. must first be placed in terms of the measured parameters.

2. Theory

Kaufman et al. use the following equations to describe the effect of sulfur pollution on cloud droplet number concentration (Nₐ):

\[ \Delta m_d [g \text{ cm}^{-3}] = \Delta m_s (f_{sp}/f_{sw}), \]  

\[ \Delta m_s [g \text{ cm}^{-3}] = \Delta m_a f_{ac}, \]  

\[ \Delta N_a [\text{cm}^{-3}] = \Delta m_c/(1.5 V_a), \]  

\[ N_a \propto N_i^{(3/2)(k+2)}, \]

where \( \Delta m_s \) is the increase in the mass of sulfur produced by an increase in coal burning, and \( \Delta m_a, \Delta m_c, \) and \( \Delta N_a \) are the corresponding increases in aerosol mass, aerosol mass scavenged by clouds, and the concentration of cloud condensation nuclei (CCN). The constants \( f_{sp} \) and \( f_{sw} \) represent the fraction of SO₂ that is converted to sulfate aerosol and the fraction of the aerosol particle’s weight that is composed of sulfur, respectively; \( f_{ac} \) represents the fraction of the aerosol mass that is incorporated into the cloud droplets; \( V_a \) is the volume for an individual particle of mean volume radius \( r_a \); and \( k \) is the slope of the cumulative CCN supersaturation spectrum. To extract the relationship between \( N_i \) and the mass of sulfate implicit in Kaufman et al., Eq. (K8) is rewritten as

\[ f_{sw} \Delta m_e = f_{sp} \Delta m_s, \]

where the left-hand side reads as the increase in the total aerosol mass that is due to sulfur (i.e., sulfate
expressed as sulfur) and the right-hand side reads as the increase in sulfur that is converted to sulfate. Kaufman et al. assume that the fraction of an aerosol particle’s total weight that is composed of sulfur (i.e., $f_{sw}$) is equal to 0.12. Equation (1) can then be written as

$$0.12 \Delta m_a = \Delta m_{sa},$$

where $\Delta m_{sa}$ is the increase in mass of sulfur in the aerosol. This may be expressed in terms of the mass of aerosol sulfate as follows:

$$\Delta m_a = \Delta m_{SO_3}(1/0.12)(32/96) = \Delta m_{SO_3}/0.36,$$

where $\Delta m_{SO_3}$ is the increase in the mass of sulfate in the aerosol. Equation (3) simply states that 36% of the increased aerosol mass is composed of sulfate, which is reasonable [see, e.g., Heintzenberg (1989)].

Kaufman et al. employ two models in their analysis. The first is a linear model of the effect a perturbation in the loading of pollution has on $N_d$ and climate. The advantage of the linearization is that it results in the canceling of a poorly known term representing the fraction of the globe covered by pollution. To obtain the linear relationship between the increase in $N_d$ and the increase in CCN, the derivative of (K13) with respect to $N_c$ is used. This gives

$$\Delta N_d/N_{d0} = [(2/(k+2))\Delta N_c/N_{c0}],$$

and (K14), and assuming $k = 0.8$, $f_{ac} = 0.5$, and $r_m = 0.15 \mu m$ ($V = 4\pi r_m^3/3$), as in Kaufman et al., gives the following relationship defining the increase in $N_d$ due to an increase in sulfate aerosol:

$$\Delta N_d/N_{d0} = 4.65 \times 10^{13} \Delta m_{SO_3}/N_{c0}.$$

Adopting the units used by Leaitch et al. (1992) for $\Delta m_{SO_3}$ (i.e., nEq m$^{-3}$; 1 nEq m$^{-3} = 4.8 \times 10^{-14}$ g cm$^{-3}$), then Eq. (4a) becomes

$$\Delta N_d/N_{d0} = 2.23\Delta m_{SO_3}/N_{c0}.$$

The second model of Kaufman et al. (1991) is a nonlinear model describing the relationship between $N_d$ and a large change in sulfate, and it is used to discuss possible future climate scenarios. Their nonlinear model is developed from Eq. (K13) by replacing $N_c$ with $N_{c0} + \Delta N_c$ to give

$$\frac{N_{d0} + \Delta N_d}{N_{d0}} = \left(\frac{N_{c0} + \Delta N_c}{N_{c0}}\right)^{12/(k+2)}.$$

Substituting Eqs. (3), (K10), and (K11) into (5), and again setting $k = 0.8$, $f_{ac} = 0.5$, and $r_m = 0.15 \mu m$ gives

$$\frac{N_{d0} + \Delta N_d}{N_{d0}} = \left(\frac{N_{c0} + \Delta m_{SO_3}(3.14)}{N_{c0}}\right)^{0.71},$$

where $\Delta m_{SO_3}$ again has units of nEq m$^{-3}$.

The formulation of Kaufman et al. (1991) is now in a form that enables comparison with the observations of Leaitch et al. (1992).
3. Comparison with observations

Curves of $N_d$ versus sulfate concentration derived from Eqs. (4b) and (6) are plotted in Fig. 1 along with the data from Leaitch et al. (1992) for stratiform and cumuliform cloud. For plotting the relationships given by Eqs. (4b) and (6), $N_d$ of 127 cm$^{-3}$ for stratiform cloud and 277 cm$^{-3}$ for cumuliform cloud have been assumed for a baseline sulfate concentration of 4 nEq m$^{-3}$. These $N_d$ are those obtained from the relationships observed by Leaitch et al. and are not necessarily true background $N_d$ (this is an important area for investigation), but are adequate for the purpose of this comparison. A value of 300 cm$^{-3}$ for $N_{0d}$, as employed by Kaufman et al., was used. The quantity plotted on the ordinate for the model results is the sulfate scavenged by the clouds in Kaufman et al. (i.e., $f_{iw} \Delta m_{SO4}$ or $\Delta m_{SO4}/2$). This is done because the observed data points compare $N_d$ against the concentration of sulfate measured in cloud water samples, and the data therefore excludes the interstitial sulfate. The data include contributions from aqueous-phase oxidation of $S(IV)$, meaning that some or all of the data points must be shifted toward the left to obtain the effect of aerosol sulfate only on $N_d$. The oxidation of $S(IV)$ may change the sensitivity of the $N_d$ to sulfate aerosols slightly; however, the direction of such a change is unknown.

The data of Leaitch et al. (1992) in Fig. 1 exhibit considerable scatter for a number of reasons: variations in temperature, differences in the chemical composition of the CCN, oxidation of $S(IV)$, and variations in the updraft speed. It is likely that the latter contributes the most to the high scatter in the data. Although the data are separated between stratiform and cumuliform cloud, the variability in supersaturation and in particular the possibility of imbedded convection in some of the stratiform cloud cases will result in scatter within the cloud groups. Following the formulation of Twomey (1959), the updraft speed will be the dominant factor when the value of $k^2$ is higher. Thus, in clouds where the supersaturation is high enough such that the appropriate value of $k$ may be <1, the CCN should exert more control on $N_d$ (e.g., cumulus). For clouds where the supersaturation is lower (i.e., stratiform cloud), and the appropriate value of $k$ may be >2, then the updraft speed should be the more dom-

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1 Liu et al. (1993) estimate for these data the typical fraction of sulfate due to $S(IV)$ oxidation in the summer cloud water is about 40%.

2 Here, $k$ is the slope in the CCN-supersaturation spectrum. It was introduced here through Eq. (K13). The value of 0.8 for the $k$ parameter used by Kaufman et al. is applicable for CCN active at supersaturations above about 0.2%. For lower supersaturations, the nature of the size distribution of the atmospheric aerosol dictates a higher value of $k$ (Junge and McLaren 1971). A value of 2–4 for $k$ at lower SS is reasonable (e.g., Hudson 1980; Alofs and Liu 1981; Leaitch and Megaw 1982).
inant factor in determining the $N_d$. This may explain why, in the Leaitch et al. (1992) data, considerably more of the variance in $N_d$ is explained by the sulfate concentrations for cumuliform cloud ($R^2$ for a linear regression is 0.62) compared with stratiform cloud ($R^2$ for a linear regression is 0.23).

The high scatter in the data as presented makes it impossible to draw conclusions concerning the model parameters appropriate to the data of Leaitch et al. (1992). However, it is possible to reduce the effect of the scatter by segmenting the data, first by individual flight and then by season.

Only the data for which samples were collected at more than one altitude on a flight are shown in Fig. 2, thus indicating the change in $N_d$ versus the cloud water sulfate concentration within a flight. The points from each flight are connected by a line. This procedure reduces the effect of some of the more severe variations in the data due to reasons discussed above. (These data are plotted on log-log scales in order to improve the visibility of most of the data, which is at lower sulfate concentrations.) Of the 16 stratiform cloud cases included here, 14 have positive slopes and 2 have negative slopes, while for the cumuliform cloud, 5 of 6 cases have positive slopes. One of the interesting aspects of these results is the steepness of the slopes for many of the cases: of the 19 positive slopes, 9 have slopes $\geq 5.0 \times 10^6$ nEq$^{-1}$ (linear scale), which is considerably higher than the maximum value of $2.0 \times 10^6$ nEq$^{-1}$ for the slopes of the model curves shown in Fig. 2. Thus, the data suggest the possibility that in many instances the sensitivity of $N_d$ to sulfate is greater than indicated by the model for the indicated input parameters.

Five-point moving averages of the stratiform cloud data, segmented by season, are shown in Fig. 3a. The moving average for the complete cumuliform cloud dataset (Fig. 3b) could not be separated by season because of the paucity of cumuliform cloud data outside of the summer months. The use of the moving average indicates the general tendency of the data without assuming a functional form. The summer data suggest relatively sharp increases in $N_d$ for increases in sulfate at lower concentrations. The winter data suggest a much lower sensitivity of $N_d$ to sulfate at lower concentrations, and the fall result lies between the winter and summer data. The moving average of the cumuliform cloud data (Fig. 3b) also suggests the possibility of greater sensitivity at lower sulfate concentrations. Thus, the differences in sensitivity among the data that appear in Fig. 2 are also evident in the representations in Fig. 3.

It is important to emphasize that the sensitivity of $N_d$ to sulfate may be greater at lower sulfate concentrations, a possibility that is suggested from the reports of Jensen and Charlson (1984) and Leaitch et al. (1986). Although our understanding of the effect of intense pollution on cloud microphysics is by no means satisfactory, efforts should be focused on obtaining more data concerning the effect of anthropogenic sulfate, and other aerosol species, at concentrations more typical of global sulfate concentrations [i.e., $<50$ nEq m$^{-3}$, e.g., Langner and Rodhe (1991)].

The nonlinear model results of Kaufman et al. for three combinations of two model parameters ($r_m$ and $k$) are also shown in Fig. 3. In Fig. 3a for lower sulfate concentrations, the model results for the smaller $r_m$ value are closer to the moving averages of the summer and fall data, while the larger $r_m$ model result is closer to the winter data moving average. For higher sulfate concentrations, all the moving averages begin to approach the larger $r_m$. An increased value of $k$ reduces the sensitivity of $N_d$ to sulfate, and in some instances may be more appropriate. The moving average of the cumuliform cloud data (Fig. 3b) is similar to that of the stratiform cloud in terms of comparison with the model data. These comparisons should not be construed as acceptance of these values for the specified conditions. Rather, in addition to offering a perspective on the modeling results of Kaufman et al. (1991), these comparisons suggest that there are not universal values for these model parameters. There is a clear need to study the relationships among $N_d$, CCN, and sulfate in detail before parameterizations of this nature can be properly described. To help reduce the data scatter of the type discussed here, it will be necessary to accumulate case studies of similar cloud types, but with varying sulfate contents, so that further differentiation by cloud type is possible.

It is interesting that the apparent differences in sensitivity in the data for both cloud types can be explained in the model by differences in $r_m$. Whether this explanation is correct or not, the sensitivity of $N_d$ to $r_m$ is very important to the results of Kaufman et al. (1991), since a small change in $r_m$ produces a relatively much larger change in the cooling of the atmosphere, as shown in Table 6 of Kaufman et al. Following this table, the present comparisons suggest that the net effect of coal burning will be more cooling, as suggested by Kaufman et al.

The global simulations of Langner et al. (1992) indicate only that 6% of the anthropogenic sulfur is available for new aerosol particle formation, from which they questioned the assumption of Kaufman et al. (1991) that 40% of the fossil fuel SO$_2$ emissions resulted in new particles. Although this discrepancy is quite large, the Langner et al. model does not include the detailed aerosol physics or chemistry necessary to

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3 The ability of Twomey's formulation to accommodate large differences in $k$ over a wide range of CCN concentrations is another question mark. One limited comparison suggests higher values of $k$ may be more appropriate at higher CCN concentrations (Leaitch et al. 1984).
properly delineate this problem. In fact they state that “detailed calculations of aerosol dynamics are needed to establish changes in number concentration.” In terms of gas-phase oxidation, 6% of the anthropogenic sulfur could produce a very large number of sulfate particles, depending on their size. In terms of aqueous-phase oxidation, Langner et al. point out that “it can modify the size distribution of the aerosol so that additional particles may be activated at a given supersaturation.” It is quite possible that aqueous-phase oxidation will reinforce the mass distribution of the accumulation-mode particles, in effect increasing the number of these particles as the mass increases (e.g., Fitzgerald and Hoppel 1988; Hegg 1990). Leaith et al. (1986) and Leaith et al. (1992) present data demonstrating strong positive correlations between sulfate mass and the number concentrations of the accumulation-mode aerosol particles (i.e., those represented in Kaufman et al.), indicating that increases in anthropogenic sulfate result in increases in the number of aerosol particles of primary importance to both light scattering and cloud droplet nucleation. Thus, it appears that the assumption of Kaufman et al. concerning the production of new particles is reasonable, although our understanding of the mechanisms is still very weak. Certainly future gains in understanding the impact of anthropogenic sulfur on climate will require a better knowledge of aerosol particle formation.

4. Implications for climate

Kaufman et al. discuss the effects of the various combinations of the model parameters on the present climate, but develop a future scenario using their nonlinear $r_m = 0.15$-μm model (Table 7 in their paper). For comparison their Table 7 is recalculated here using the results of Leaith et al. (1992) to represent the effect of sulfate on $N_d$.

Through their Eqs. (16)–(19), Kaufman et al. use the following relationship to describe the effect of sulfur on the radiative forcing through cloud albedo

$$\left(\frac{\Delta F_0}{F_0}\right)_s = 0.33 \frac{\gamma \alpha \beta}{(1 - \alpha)} \frac{\Delta N_d}{N_{d0}}, \quad (K16)-(K19)$$

where $F_0$ is the solar constant, $\gamma$ is a factor relating cloud albedo to optical depth and is set to 0.17, $\beta$ is the cloud coverage over the area impacted by pollution and is set to 3.0, and $\alpha$ is the total albedo and is set to

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0.3. The factor $\alpha$ indicates the fraction of the globe influenced by the pollution. The observations of Leaitch et al. suggest $\Delta N_d/N_{do} = (250 - 160)/160$ (i.e., 0.56) for eastern North America, giving

$$\langle \Delta F_0/F_0 \rangle_k = 0.013 \alpha. \quad (7)$$

The values of $(\Delta F_0/F_0)/(\Delta F_0/F_0)_k$, are given in Table 1 for different $\alpha$ and $(\Delta F_0/F_0)_k$, where the latter is the forcing due to increased CO$_2$ $(\Delta F_0/F_0)_c = 0.02$ in Kaufman et al. equates to CO$_2$ doubling. The values in Table 1 here are comparable to those for the ratio of cooling to heating ($\xi$) given in Table 7 of Kaufman et al. with the exception that those given in Table 1 do not allow for increases in sulfur emissions except through $\alpha$. The results in Table 1 show that the effect of sulfur cloud albedo increases for the smaller $(\Delta F_0/F_0)_k$, is very much greater than the effect of CO$_2$ for most $\alpha$. As CO$_2$ in the atmosphere rises, a warming is eventually indicated with the cooling due to the sulfur cloud albedo effect at about 13% of the warming for an $\alpha$ of 0.2 and CO$_2$ doubled. Because no allowance for increasing sulfur emissions is included, the results in Table 1 are an underestimate of this effect relative to those in Kaufman et al. It is cautioned that the data of Leaitch et al. (1992), although collected in a variety of situations, are for only one region of the world, and the validity of the extrapolation of the results to the globe is unknown.

If emissions of sulfur rise with CO$_2$ emissions, then the cloud albedo cooling will also increase; although, because of vastly different lifetimes, the CO$_2$ increase in the atmosphere will inevitably become the dominant factor. A significant saturation effect, suggested by Kaufman et al. (1991) as a possible termination step for sulfate influence on cloud, is evident in the data for higher sulfate concentrations (Fig. 3), but is not clear at the more common concentrations $(50 < nEg m^{-3})$. If, for example, sulfate is doubled from the median concentration for the cloud water observations of Leaitch et al. (1992) of $25 \text{nEg m}^{-3}$ to $50 \text{nEg m}^{-3}$ it appears that a substantial increase in $N_d$ will still result. Thus, this limitation is still one of considerable uncertainty and requires further study.

The value of $\alpha$ is also a source of considerable uncertainty. It seems likely that $\alpha$ will increase in the future as the development of less industrialized nations progresses, however, the sphere of influence of aerosol pollution from industrialized regions is unclear. As anthropogenic particles are dispersed throughout the troposphere, their concentration is reduced, but, the effective value of $\alpha$ is increased. Savoie and Prospero (1989) suggest that the contribution of anthropogenic sources to sulfate at the surface of the North Pacific is about 20%, and from the modeling of Langner and Rodhe (1991) it appears possible that more than 50% for the Northern Hemisphere is impacted by anthropogenic sulfate. Unfortunately, an estimate of the effective value of $\alpha$ is not possible here because of the variability in sulfate around the globe. As indicated by Kaufman et al., there is a great need to include the effect of anthropogenic aerosols on clouds in global climate models.

5. Summary and conclusions

Comparison of the observations of Leaitch et al. (1992) have been made with the relationship between cloud droplet number concentration ($N_d$) and aerosol sulfate concentrations implicit in the models of Kaufman et al. (1991). Kaufman et al. used a linear model of the relationships among changes in sulfate, $N_d$, and cloud albedo to discuss the effect a perturbation in the loading of pollution has on climate via changes in $N_d$ and cloud albedo. They offer a large number of possibilities, but outline the most reasonable results based upon current knowledge. The present comparisons (Figs. 2 and 3) suggest that within this outline, stronger cooling of the atmosphere, as opposed to warming, is more likely. Kaufman et al. used a nonlinear model of the relationships among changes in sulfate, $N_d$, and cloud albedo to present some possible impacts of pollution on future climate. Comparison of the mean properties of the observations of Leaitch et al. with the nonlinear model of Kaufman et al. indicates that the observations favor more cooling due to the effect of sulfate on cloud albedo than given in Table 7 of Kaufman et al.

The degree of cooling is quite sensitive to the relationship between $N_d$ and sulfate, but there remain a number of uncertainties involved in trying to portray this process in models. Therefore, it is important that the relationships among anthropogenic sulfate, CCN (over a wide supersaturation spectrum), and $N_d$ be understood for different cloud types. Because the influence of anthropogenic sulfate on the Northern Hemisphere appears to be extensive, it is particularly important that these relationships be studied at a number of locations well distant from pollution sources.

REFERENCES


