

Comments on "A Theoretical Study of the Wet Removal of Atmospheric Pollutants. Part I: The Redistribution of Aerosol Particles Captured Through Nucleation and Impaction Scavenging by Growing Cloud Drops," and "Part II: The Uptake and Redistribution of $(\text{NH}_4)_2\text{SO}_4$ Particles and SO_2 Gas Simultaneously Scavenged by Growing Cloud Drops"

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1. Introduction

A detailed model of the evolution of the cloud droplet spectrum and the uptake and redistribution of aerosol particles and SO_2 has been described by Flossman et al. (1985, 1987; hereafter referred to as papers I and II, respectively). The model is formulated to include the processes of particle and droplet growth by condensation, collision-coalescence, drop breakup, capture of unactivated particles by droplets via impaction, scavenging and reaction of SO_2 , and entrainment of ambient air into the rising parcel of air. We commend the authors for their comprehensive treatment of the subject, and hope to see additional refinement and applications of the model. In this context, we would like to offer some observations and comments on the formulation of the physical and chemical processes in the model, the inputs to the model, and the results of the model simulations included in papers I and II. Before beginning, we would like to thank the authors for including the large number of plots of the various distribution functions in their publications, which provide the reader with the raw information needed to understand their results.

The authors conclude in paper I that "the mass mixing ratio of the captured aerosol in the cloud water is larger inside small drops, implying that smaller drops are more contaminated than larger ones." This conclusion provided the initial impetus for our writing this comment, as it contradicts both the predictions of simple models of the condensational growth of cloud droplets (Howell 1949; Jensen and Charlson 1984) and the results of our limited number of measurements of the size-dependence of solute concentrations in strato-

cumulus cloud droplets (Noone et al. 1988; Ogren et al. 1989). It is important to focus on the size dependence of droplet composition because of its importance to gas solubilities as well as reaction chemistry and rates.

2. Model formulation

The model is formulated within a one-dimensional, rising parcel of air. For the results presented in papers I and II, this rising air parcel is continuously and uniformly diluted by the entrainment of subsaturated air. While other types of entrainment have been suggested (e. g., Telford and Chai 1980; Baker et al. 1984) and could productively be studied with the current model, the authors state that their intention is to link their scavenging model to a detailed convective cloud model. Without detracting from this ambitious goal, we would like to point out that the results obtained with the model are sensitive to the way in which entrainment is modeled (Hill and Choulaton 1986).

The condensational growth of aerosol particles and cloud droplets are modeled using the same differential equation, but for bookkeeping purposes the two populations are kept separate. Separate "activation" terms are included in the equations for the time rate of change of the various distribution functions, for the purpose of moving material between the two populations as particles become activated or droplets evaporate. Apparently, an aerosol particle is transferred to the cloud droplet population as soon as the supersaturation rises above the particle's critical supersaturation, and the activated particle is assumed to achieve its critical size instantaneously. This is physically unrealistic, as an ammonium sulfate particle with a dry radius of $0.5 \mu\text{m}$ requires of order 150 seconds (at 1% supersaturation, 20°C) to grow from its equilibrium radius of $2.1 \mu\text{m}$ at 99% relative humidity to its critical radius of $15 \mu\text{m}$ (Pruppacher and Klett 1978, Fig. 13-2). We note here that the evaporation of a cloud droplet appears to be treated differently, as the transition from drop to par-

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icle occurs when the droplet has shrunk to its critical size.

The formulation of the chemical aspects of the model is oversimplified in a number of ways, which makes it difficult to apply the results to real clouds. The rate of uptake of SO_2 is assumed to be equal to the rate of production of S(VI) in the droplets, i. e., the mass distribution function of S(IV) in the droplets, $g_{G4d}(m)$, does not change with time. This approach ignores the fact that the production of S(VI) decreases the pH of the droplets, thereby decreasing the concentration of S(IV) in the droplets.

The authors acknowledge two additional limitations in the chemical formulation of the model that may severely limit its applicability to real clouds. First, all of the cloud condensation nuclei (CCN) are assumed to have the same chemical composition. It is now well established (e. g., Whitby 1978) that the composition of aerosol particles varies systematically with the size of the particle, that submicrometer particles tend to be associated with the products of gas-to-particle conversion (and thereby usually acidic), and that the composition of supermicrometer particles is often dominated by mechanically generated substances such as soil dust and sea-salt (both of which tend to be alkaline). As a result, some droplets may be much more alkaline than others, and thereby have much higher concentrations of S(IV) and production rates of S(VI).

Second, the current formulation assumes that the rate constant for the assumed first-order oxidation of S(IV) is independent of pH. The authors justify this assumption on the grounds that the pH-dependencies of the H_2O_2 and O_3 reactions with S(IV) cancel each other. This assumption, combined with the assumption of constant CCN-composition, severely limits the ability of the model to provide insight into the chemical factors controlling the incorporation and oxidation of SO_2 in cloud droplets. We hope that future versions of the model will allow for different CCN compositions and explicitly include different SO_2 oxidation reactions, so that the size-dependence of droplet chemistry can be studied and so that the sensitivity of model results to variations in chemical inputs is evident.

3. Model inputs

The dry aerosol size distributions used for the model simulations in paper I are very unrealistic, as was implicitly acknowledged by the authors in paper II by their choice of a far different distribution. The continental aerosol distribution used in paper I (case 3) has a total number concentration of 1000 cm^{-3} and a mass concentration of $233 \mu\text{g m}^{-3}$. In paper II, these values were changed to 590 cm^{-3} and $28 \mu\text{g m}^{-3}$. Even the distribution used in paper II seems unrealistic, as it has a much lower number concentration, relative to its mass concentration, than would be expected based on

typically measured size distributions. This is illustrated in Fig. 1, which compares the volume size distribution used in paper II to the average urban size distribution reported by Whitby (1978). In addition to the difference between the shapes of the distributions, the distribution used in paper II has a volume-mean particle radius that is a factor of two larger than the mode containing most of the CCN in Whitby's distribution (0.17 vs $0.08 \mu\text{m}$). Given the dependence on the dry aerosol size distribution of both the evolution of the droplet size distribution and the scavenging efficiency of aerosol particles, it would be very useful if the authors were to present a sensitivity study of their results to the input aerosol size distribution.

After having studied in paper I the effects of changing the fraction of soluble material ϵ in the aerosol particles, this value is set to 0.1 in paper II. A value of 0.5 or higher would be more realistic, especially for the smaller particles (Winkler 1974). Given the sensitivity reported in paper I of the time required to produce precipitation-sized droplets to the value of ϵ , a larger value of ϵ might be preferable in future studies.

The authors find that essentially all of the mass of aerosol particles is incorporated into the cloud droplets. This is not surprising for a cloud with an initial updraft velocity of 1 m s^{-1} , but it would be of interest to see the sensitivity of the mass scavenging efficiency to lower values of the updraft velocity.

4. Model results

To begin with, the ordinate axes of Figs. 3f and 4f in paper I appear to be mislabeled. The variable plotted is a dimensionless mass mixing ratio, while the indicated units are for a dimensionless distribution function. The numerical values plotted also seem to be in error, as they would indicate that the droplets have higher mass mixing ratios than at the point of activation, i. e., that the droplets are not yet activated. This

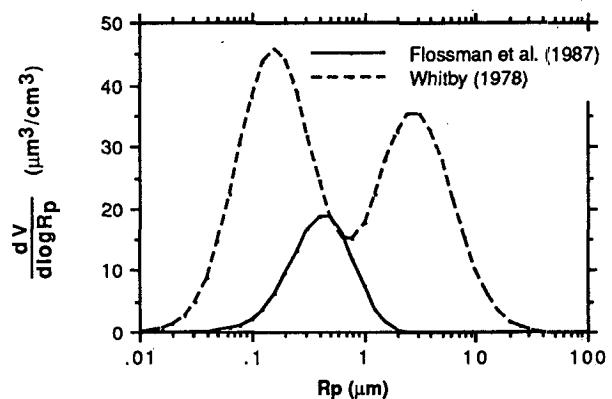


FIG. 1. Comparison of average urban size distribution (Whitby 1978) with assumed distribution of Flossman et al. (1987).

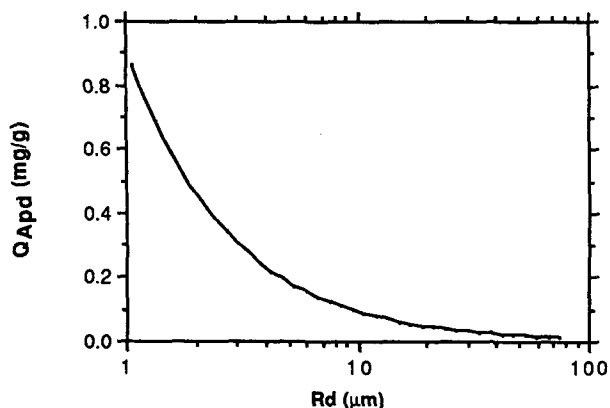


FIG. 2. Mass mixing ratio of ammonium sulfate in cloud droplets at the point of activation.

can be seen in Fig. 2, which shows the mass mixing ratio of ammonium sulfate in cloud droplets when the droplets have grown to their critical size. This is an upper limit to the mass mixing ratios in activated droplets, as additional growth of the droplets only serves to dilute them. After 200 seconds of growth, the results in Fig. 3f of paper I indicate that a 2 μm radius droplet would have an ammonium sulfate mass mixing ratio of ca. 0.007. From Fig. 2, we see that at the point of activation, a 2 μm radius droplet has an ammonium sulfate mass mixing ratio of 0.0005. We conclude that a computational error exists, and are uncertain as to what the effects of this error are on the conclusions reached by the authors. We note, however, that there is very little liquid water (Fig. 3b) or sulfate mass (Fig. 3c) associated with droplets below 3 μm radius after 200 seconds, indicating that the small droplets with the erroneously high mass mixing ratios are not associated with CCN that were scavenged at cloud base. Closer examination of Fig. 3f reveals a small bump at 10 μm radius (200 s), which is associated with the main mass of liquid water and sulfate. In the radius interval of 5–10 μm , the mass mixing ratio is seen to increase with droplet size, in agreement with our measurements and simple models of condensational growth. Presumably, this tendency is present at later times as well, but the choice of ordinate scales makes it impossible to see.

5. Conclusions

Flossman et al. make very sweeping conclusions about the uptake and redistribution of aerosol particles and SO_2 by cloud droplets, but it should be stressed even more than they do that the results are applicable only to the limited set of input conditions studied, and are only as realistic as the model formulation. Without an evaluation of the sensitivity of the results to variations of the input parameters and model formulation, it is impossible to extend the results to other situations. Before increasing the complexity of the model, we would urge the authors to evaluate model sensitivity and changes in controlling factors to variations in input conditions and model formulation.

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