Reexamination of the influences of carbonaceous chemicals on cloud drop activation

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Abstract

This study examines the effect of carbonaceous chemicals on cloud activation. Both black carbon(BC) and film-forming compounds(FFCs) of organics are mainly discussed. The BC heating effect has the ability of raising critical saturation ratio of a droplet and may hinder the activation of the aerosol into a cloud drop. In addition, gas phase kinetics should readjust when the heating on air. The FFCs effect may cause a significant decrease in water mass accommodation coefficient owing to their coating in droplets and then retarding the diffusional growth of droplets. The net effects of BC and FFCs could change parcel maximum supersaturation and may positively and negatively influence the cloud drop number, determined by the distribution of chemicals as well as their mass content within aerosols.

1. Introduction

Carbonaceous contents may affect the capability of cloud condensation nuclei (CCN) to activate into cloud drops in many ways. Black carbon (BC) may retard the growth of droplets by the mechanism of radiative heating (Conant et al., 2002; Nenes et al., 2002). Nonvolatile insoluble organic compounds that reside on drop surface in the form of a monolayer film may cause a significant decrease in water accommodation coefficient, thus retarding the diffusion growth of droplets (Feingold and Chuang, 2003). Soluble organic compounds decrease the water activity as well as the surface tension of droplets, both result in the enhancement of drop growth. (Facchini et al., 1999). All these mechanisms are most active during the activation stage and may thus influence the number concentration of cloud drops, as well as many microphysical and radiative processes that are strongly dependent of them. In this study we examine the first two effects, namely the BC heating effect and the condensation retardation by film-forming compounds (FFCs), using an adiabatic parcel model with detailed microphysics.

2. Method

We adopt the detailed microphysical parcel model of Chen and Lamb (1994), which applies a multi-component particle framework that categorize particles (either in cloud or aerosol phases) into many size bins according to their water and solute contents. In order to resolve the fine variations in cloud drop activation, we applied 160 solute bins with a mass ratio of 1.1 between neighboring bins. For the water component, 45 bins with a bin-sizing ratio of 2 were applied.

Under the assumption of adiabatic ascent, aerosol and cloud particles in the air parcel are allowed to evolve naturally according to explicit physics. As our goal is to understand the changes in cloud drop number concentration due to the existence of carbonaceous material in CCN, the model simulations will emphasize on the activation stage of cloud formation. So our theoretical analysis will focus on the following condensation growth equation:

$$\frac{dm}{dt}=\frac{4\pi\cdot r\cdot D_v'\cdot f_v}{R_v}\cdot\left(\frac{e_a}{T_a}-\frac{e_{sw}(T_d,r,a_w)}{T_d}\right) \qquad (1)$$

where m and r are the mass and radius of the drop, D_v' is the diffusion coefficient with correction of gas kinetic effect, f_v is the ventilation coefficient, R_v is the water vapor gas constant, T_a and T_d are the ambient and drop temperatures, e_a is the ambient vapor pressure, and $e_{sw}(T_d, r, a_w)$ is the saturation vapor pressure over the surface of the drop that has a water activity of a_w. In this equation, T_d is directed influenced by the black-carbon heating effect, and D_v' is influenced by the FFCs as discussed below.

3. Effects of BC heating

The effect of BC on cloud drop activation is treated by adding a radiative heating term in the condensation equation. We first derive the modified condensation formula and transform the effect into the Köhler equation to demonstrate the BC heating effect on a single particle. The parcel model then is used to evaluation the effects on a population of aerosols.

In equation (1) the drop temperature can be determined from the energy balance equation:

$$L\cdot\frac{dm}{dt}-4\pi\cdot r\cdot k_a'\cdot f_h\cdot(T_d-T_a)+Q=0 \qquad (2)$$

where L is the latent heat of evaporation, k_a' is the thermal conductivity of air with gas-kinetic effect correction, and f_h is the heat ventilation coefficient. The three terms represent latent heat release, heat conduction and other heat sources (Q) such as BC radiative heating. By combining (1) and (2) with some rearrangement and simplifications, the growth equation can be transformed into a form commonly seen in textbooks (cf. Pruppacher and Klett, 1997, p. 511):

$$\frac{dm}{dt}\approx\frac{4\pi\cdot r}{A_D+A_K}\cdot(S_a-S_d)\cdot(1-B) \qquad (3)$$

where

$$A_D=\frac{R_vT_a}{D_v'f_ve_{sw}(T_a,\infty,1)}, \qquad (4)$$

$$A_K=\left(\frac{L}{R_vT_a}-1\right)\frac{L}{k_a'f_hT_a}, \qquad (5)$$

S_a is the ambient saturation ratio, $S_d=S_w(T_a,r,a_w)$ is the saturation ratio of the drop with surface temperature the same as in the ambient, and

$$B=Q\cdot\frac{\left({L}/{R_vT_a}-1\right)}{(S_a-S_d)4\pi rk_a'f_hT_a} \qquad (6)$$

represents the BC heating effect.

The theoretical basis of cloud drop activation is the Köhler equation, which describes the equilibrium vapor pressure over a drop surface as influenced by the solute and curvature effects. Divide this surface vapor pressure by the saturation vapor pressure over a flat water under the same temperature one will get the S_d in (6). This Köhler theory can be written as:

$$S_d = a_w \cdot \exp\left(\frac{2\sigma}{\rho_w R_v T_a r}\right), \qquad (7)$$

where σ is the surface tension between water and air, and r_w is the water density. Heating by BC absorption will raise the drop temperature and alter S_d. By ignoring the latent heating term in 2, the temperature difference is derived as:

$$\Delta T \equiv T_d - T_a = \frac{Q}{4\pi \cdot r \cdot k'_a \cdot f_h}. \qquad (8)$$

By applying the Clausius-Clapeyon equation, the saturation ratio of heated droplet is

$$S'_d = S_d \cdot \exp\left(\frac{L}{R_v}\frac{\Delta T}{T_a(T_a + \Delta T)}\right) \approx S_d \cdot \left(1 + \frac{L}{R_v}\frac{\Delta T}{T_a^2}\right) \qquad (9)$$

The exponential term represents the BC heating effect on drop saturation ratio. Such "heated" Köhler curves are plotted in Figure 1 for CCN with dry radii of 0.1, 0.3 and 1 µm, each contains 50% BC. One can see that the critical saturation ratio is elevated significantly. This phenomenon may hinder the growth and activation of droplets as discussed in Conant et al. (2002).

The actual situation is a bit more complicated because the drop should also be heated by latent heat release during growth. One can modify (3) to get:

$$\frac{dm}{dt} = \frac{4\pi \cdot r}{A_D + A_K} \cdot (S_a - S'_d) \qquad (10)$$

where

$$S'_d = S_d \cdot \left(1 + B \cdot \frac{S_a - S_d}{S_d}\right) \qquad (11)$$

Comparing with (9), this formula shows that the BC heating effect on the capability of CCN activation into cloud drops is modulated by latent heating whenever the droplet is growing (i.e., $S_a > S_d$).

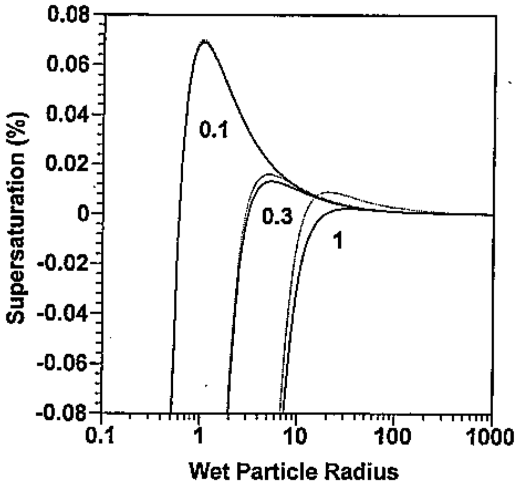

Figure 1: Effect of BC heating on the Köhler curves for particles with dry radii of 0.1, 0.3 and 1 µm. The solid lines are for unheated, and the dashed lines are for heated droplets. Particles with larger dry radius contain more BC, thus has stronger heating effect.

Nenes et al. (2002) evaluated the BC heating effect by considering four heating scenarios: no heating (NO), heat drop only (DH), externally mixed BC (EM; BC reside outside of CCN), and internally mixed BC (IM). We performed a similar test by implementing the above analysis into our model. For BC heating we adopted the radiative heating algorithm of Toon and Ackerman (1981). The initial air parcel properties are identical with those in Nenes et al. (2002) except that maritime type aerosol distribution from Whitby (1978) is used..

Figure 2 shows the evolution of cloud supersaturation in a parcel with 0.25 m/s updraft. The variation of maximum supersaturation is similar to those of Nenes et al. (i.e., DH > NO > IM > EM), but the delay of cloud formation for the EM scenario is not obvious in our simulation. The DH scenario has the highest supersaturation because BC heating hinders the growth of drop and thus increases supersaturation (hereafter called the "drop-heating effect"). Heating of BC with a thick liquid shell is stronger that that without. So the air heating in IM scenario should be stronger than in the EM scenario. Note that, the changes in maximum supersaturation become less obvious when the aerosol distribution is of continental type, because much more drops are activated to consume the excess water vapor. In the IM scenario, BC heating also raises the air temperature, which in turn reduces supersaturation (hereafter called the "air-heating effect") by increasing the saturation vapor pressure. However, drops in the EM scenario are not directly heated by BC, so they grow much faster than those in the IM scenario do. That is why the maximum supersaturation is lower in the EM scenario. So one would expect more cloud drops in the IM scenario.

The relative strength of saturation enhancement or reduction by drop-heating effect to that by air-heating effect depends on the total mass fraction of BC and their distribution among aerosols. We found that the maximum saturation ratio can be either enhanced or depressed for different BC scenarios, which means that net influence of BC heating on cloud drop number concentration can be either positive or negative, a conclusion different from that of Nenes et al. (2002).

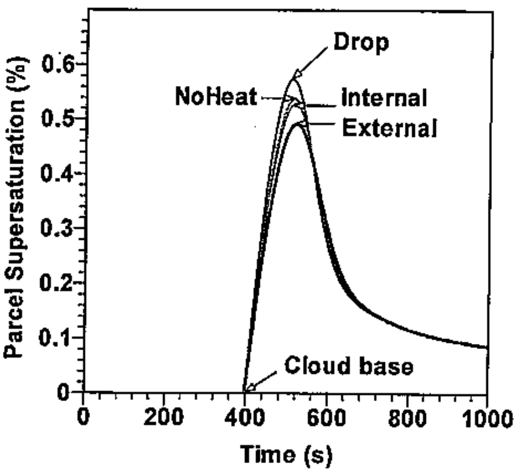

Figure 2: Development of supersaturation in air parcel for four BC heating scenarios. Marine aerosol distribution is applied and BC mass content is 50%.

4. Effect of FFCs on drop growth

Within one mean free path close to the drop surface, the transport of water vapor is considered to proceed not by diffusion but by the gas kinetic process. This "vapor jump effect" is traditionally included in the mass growth equation by using the modified diffusion coefficient D_v' in Eq. (1), which has a full form of:

$$D_v' = D_v \bigg/ \left[\frac{D_v}{\alpha r(\upsilon/4)} + \frac{r}{(r+\lambda)} \right] \tag{12}$$

where D_v is the original diffusion coefficient of water vapor, α is the mass accommodation coefficient, υ is the mean thermal velocity, and λ is the vapor jump distance (one mean free path). The FFCs retard drop growth through their influence on α. Earlier studies (e.g., Feingold and Chuang, 2002) often assume that the effect of FFC on α occur only when the surface coverage by FFC exceeds a threshold value. So the value of α is either 0.035 (for pure water) or $\sim 10^{-5}$ (for full FFC coverage). However, by reexamining the experimental data in relevant articles (e.g., Archer and La Mer, 1955; Rubel and Gentry, 1985; Seaver et al., 1992), we conclude that the effect should still exist under partial coverage. Based on molecule flux theory we developed a new, simple method to describing the relationship between α and FFC coverage.

To a first-order approximation, one may assume the FFCs affect water vapor flux only over the portion of drop surface that covered by them. Thus from the microscopic point of view, the total water vapor flux of the drop surface can be expressed as

$$\left.\frac{dm}{dt}\right|_{total} = \theta \left.\frac{dm}{dt}\right|_{\alpha_H} + (1-\theta)\left.\frac{dm}{dt}\right|_{\alpha_W} \tag{13}$$

where θ is the FFC fractional coverage, and α_H ($=10^{-5}$) and α_W ($=0.035$) are the mass accommodation coefficients over the surface with and without FFC (assuming hexadecanol in this study), respectively. By combining (12) with (13) we have

$$\frac{1}{1+1/\alpha_T \beta} = \frac{\theta}{1+1/\alpha_H \beta} + \frac{1-\theta}{1+1/\alpha_w \beta} \tag{14}$$

where

$$\beta \equiv \frac{\upsilon}{4} \frac{r^2}{D_v(r+\lambda)}. \tag{15}$$

and α_T is the overall accommodation coefficient. We found that such a relationship fits well with the experimental data of Rubel and Gentry (1984), as shown in Fig. 3. Note that some FFCs may transform into a "solid" state when the surface coverage is close to unity. So one may switch the value of α_H from 2×10^{-4} to 10^{-5} when the coverage exceeds a threshold value (0.975 in this study).

To test the effect of FFC coverage on cloud drop growth and activation, we assumed three types of FFC contents in aerosol particles. The first and second types (hereafter referred to as FFC-1 and FFC-2, respectively) follow Feingold and Chuang (2002): (1) the mass of FFC is proportional to the particle surface area; (2) the mass of FFC is proportional to the particle mass. These FFCs are presumably non-volatile, so their mass in each particle do not change with time. Then the coverage of FFC can be expressed as (Rubel and Gentry, 1984)

$$\theta = n_H \sigma_H / (4\pi r^2) \tag{16}$$

where n_H is the total number of FFC molecules, and σ_H ($=20.2$Å^2) is the effective area per hexadecanol molecule. Note that σ_H varies slightly with the total coverage, but we ignored this secondary effect here. We also would like to test the situation of gas adsorption of volatile FFC, in which case the coverage is determined solely by the gas-phase vapor pressure of FFCs. So, for the third type of FFC content (FFC-3), we assume the coverage is a fixed value.

Figure 4 shows the development of supersaturation in an ascending air parcel for three types of FFCs contents comparing with the FFC-free case (FFC-0). The setting of air parcel properties is the same as those in section 3, except that a continental aerosol type is used. The total FFC mass is 5% of the total aerosol mass for both FFC-1 and FFC-2 scenarios, in which a large portion of the aerosols are initially fully covered by FFC. In Fig. 4, we can see that all types FFC coating raised cloud supersaturation due to retardation of the condensation process. The effect of FFC on supersaturation in the FFC-2 scenario is stronger than that in the FFC-1 scenario because the larger aerosols that are more likely to be activated into cloud drops contain more FFC. In the FFC-3 scenario, particles consume water vapor faster because none of them are fully covered. Also, as the coverage decreases the maximum supersaturation becomes lower as expected. Note that the FFC effect on cloud drops weakens with time for FFC-1 and FFC-2 (but not for FFC-3) because the FFC coverage decreases as drops grow. It is noteworthy that a low amount of FFCs is enough to induce significant change of cloud properties even when the FFC surface coverage is only partial. Also, the effect is stronger for maritime aerosol situation when there are fewer drops to take up water vapor.

The effect of FFC on the maximum supersaturation certainly influences the number concentration of cloud drops. Our simulations generally show an increase in cloud drop number concentration due to the FFC effect. This result is different than those shown by Feingold and Chuang (2002). The difference stems mainly from the effectiveness of FFC under partial coverage that specified in this study.

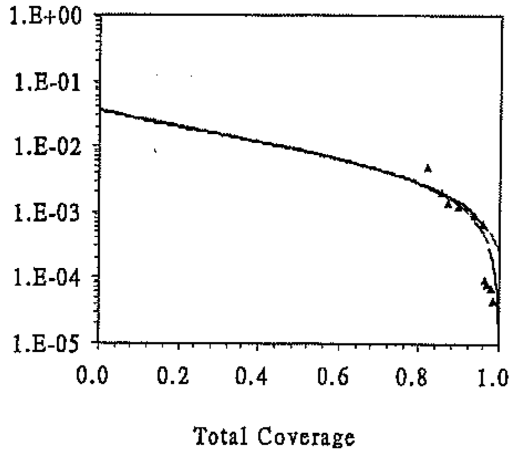

Figure 3: Overall mass accommodation coefficient as a function of FFC coverage. The upper curve is for $_H$ = 2×10^{-4} (for liquid state) and the lower curve is for $_H$ – 10^{-5} (for "solid" state). Filled triangles are the experimental data from Rubel and Gentry (1984).

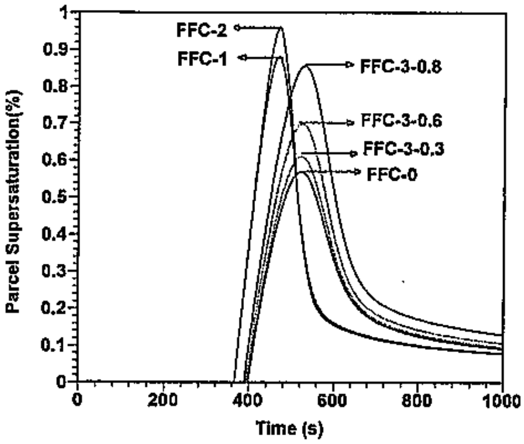

Figure 4: Supersaturation development for four types of FFC content. For FFC-3, three values of overall coverage are given for comparison. The aerosol size distribution is maritime type.

5. Conclusion

Our simple model simulations suggest that the effect of BC heating on cloud drop activation is dependent on the mass fraction of BC as well as their mixing state within aerosols. The heating on individual drops inhibits drop growth and enhance air supersaturation, but the heating on air reduces supersaturation. The net effect can be either positive or negative. So there exist great uncertainties in estimating the effect of BC on cloud drop number if the total and fractional mass of BC and their state of mixing are not clearly known.

A simple method for modeling the effect of FFCs on water accommodation coefficient suggests that FFC coating on aerosols may increase cloud supersaturation due to retardation of the condensation process. This also means more aerosols can be activated into cloud drops. The effect of FFCs on cloud drop number concentration may be greatly underestimated if one ignores the influence under partial coverage. Currently we still have very poor understanding of the possible candidate of atmospheric FFC species, as well as the species-dependent mass accommodation coefficient.

6. Reference

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