The influence of the organic aerosol component on CCN supersaturation spectra for different aerosol types

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ABSTRACT

This paper describes the effect of the presence of water-soluble organic compounds (WSOC) in aerosol particles on the aerosol critical supersaturation as defined by the Köhler theory and on cloud condensation nuclei (CCN) number concentration. Taking into account both the soluble mass increase and the surface tension depression due to WSOC, we calculated a substantial decrease of the aerosol critical supersaturation, which results in a large increase in CCN number concentration. CCN supersaturation spectra were computed for three different aerosol types: marine, rural and urban. The increase of CCN number concentration in the presence of WSOC (with respect to the case when only the inorganic aerosol compounds are considered) varies with aerosol type, with an increase up to 13% in the marine case, up to 97% in the rural case, and up to 110% in the urban case, for the supersaturation range typical of atmospheric conditions.

1. Introduction

Aerosol particles influence the radiation budget of the Earth by directly scattering and absorbing the incoming solar radiation (direct effect), but also by altering the structure and radiative properties of clouds (indirect effect). The indirect effect of aerosols on climate is, in particular, far from being quantified accurately because of the complex chain of chemical and microphysical processes that relate the aerosol with the cloud optical properties and lifetime through the cloud condensation nuclei (CCN) and cloud droplet number concentration (IPCC, 1996).

The importance of the relationship between aerosol and CCN concentration in assessing the impact of aerosol particles on the change of the cloud albedo has been evidenced in several studies (Hegg et al., 1991; Jones et al. 1994; Boucher and Lohmann, 1995), and is also supported by observations of Hindman and Bodowski (1994), Han et al. (1994), Boers et al. (1994), Hindman et al. (1995). Unfortunately, the large variety of existing aerosol populations and atmospheric conditions do not allow theoretical or experimental derivation of an universal expression for computing CCN concentration. However, several empirical relationships are found in the literature in which the CCN concentration is related to the environmental supersaturation (CCN supersaturation spectrum).

Twomey and Wojciechowski (1969), Hobbs et al. (1985) and Hoppel et al. (1990) have obtained various parameterisations for the CCN supersaturation spectrum by fitting measurements made in different parts of the world.

On the other hand, Junge and McLaren (1971),

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Fitzgerald (1973), Jiusto and Lala (1981) and Herbert (1986) have derived CCN–supersaturation relationships theoretically using the Köhler theory and different aerosol size spectra.

The potential importance of organic compounds in influencing the CCN properties has recently been proposed, since organic compounds represent an important part of the aerosol water-soluble fraction (Saxena and Hildemann, 1996) and can also influence cloud droplet surface tension (Shulman et al., 1996; Facchini et al., 1999a).

In this paper, we have studied the influence of the aerosol water-soluble organic compounds (WSOC) on aerosol activation and CCN number concentration, and also derived new CCN–supersaturation relationships for three aerosol types: marine, rural and urban using a detailed microphysical treatment of the aerosol activation. Our parameterisations include the recent findings on surface tension of cloud droplets (Facchini et al., 1999a; 2000) and chemical composition of aerosol WSOC (Facchini et al., 1999b; Zappoli et al., 1999; Decesari et al., 2000; Putaud et al., 2000).

2. Influence of the aerosol organic compounds on critical supersaturation

Köhler theory describes the equilibrium growth of aerosol particles as a function of their size, chemical composition and physical and chemical properties of the cloud droplet solutions for different relative humidities. The Köhler equation was initially formulated for a soluble inorganic salt particle and is composed of two terms: the *Kelvin term* which accounts for the increase of the water vapour pressure due to the curvature of the droplet surface and the *Raoult term* which considers the lowering of the equilibrium vapor pressure with increasing solute concentration.

Different forms of Köhler equation (Reiss, 1950; Doyle, 1961; Pruppacher and Klett, 1997; Young and Warren, 1992; Konopka, 1996; Shulman et al., 1996; Wexler and Ge, 1998; Laaksonen et al., 1998) were developed to take into account the complex chemical composition of aerosol particles, the dissolution of gases into the droplets and the physical and chemical properties of the droplet solutions.

In order to take into account the presence of water-soluble organic compounds (WSOC) in the aerosol, we use in this paper a modified form of the Köhler equation:

$$s \cong 1 + \frac{2\sigma_s M_w}{RT\rho_w r} - \frac{3M_w \phi_s}{4\pi\rho_s(r^3 - r_N^3)}$$
$$\times \left(\sum_{i_{inorg}} \frac{v_i m_i}{M_i} + \sum_{j_{org}} \frac{v_j m_j}{M_j} \right) \qquad (1)$$

where s is the saturation ratio, M_w and ρ_w are molecular mass and density of water, σ_s is the droplet solution surface tension, ρ_s is the droplet solution density, R is the gas constant, T is the temperature, r is the droplet radius, r_N is the radius of the insoluble aerosol residue, ϕ_s is the osmotic coefficient of the aqueous solution, and v_i, m_i, M_i and v_j, m_j, M_j are the number of dissociated ions, soluble mass and molecular mass, respectively, of the inorganic and organic components of aerosol particles.

Equation (1) contains a modified Raoult term which describes the additive effect of the solutes, inorganic and organic, during droplet growth. The fact that vapour pressure is depressed proportionally to the amount of dissolved material is the only support for this assumption. This treatment was proposed by Shulman et al. (1996) for two non-volatile components, one organic and the other inorganic. In eq. (1), the additive effect was extended to a multicomponent solution droplet which contains an insoluble core. The Raoult term of eq. (1) was derived using other two assumptions: (i) the water activity of the solution droplets is not affected by the presence of the insoluble core; and (ii) the droplet volume is approximated by the sum of the volume of water and that of the insoluble core (Pruppacher and Klett, 1997).

The aerosol WSOC influence the saturation ratios calculated in eq. (1) in two ways: directly by increasing the soluble mass (Raoult term) and indirectly by decreasing the cloud droplet surface tension (Kelvin term).

The lowering of surface tension and its influence on equilibrium supersaturation were studied in the laboratory using standard compounds by Shulman et al. (1996). In fact, several organic compounds present in atmospheric aerosol exhibit surface active properties (Facchini et al., 2000). There are many surface tension laboratory measurements for different combinations of organic and inorganic compounds in aqueous solution

available in literature, but none of them is fully representative of the complex chemical composition of atmospheric aerosol and, consequently, cannot accurately describe the surface tension of real cloud droplets.

The difficulty in constructing a synthetic (standard) model of atmospheric aerosol for the study of surface tension changes was overcome by Facchini et al. (1999a) who measured the surface tension of atmospheric fog droplet samples. In order to recreate the surface tension behaviour due to variation of WSOC concentration in a growing droplet, the collected fog water samples were vacuum evaporated by factors of 10 to 100. As a result of this study, Facchini et al. (1999a) found the following relationship for the cloud droplet surface tension variation as a function of dissolved organic carbon concentration:

$$\sigma_s = 72.8 - 0.018\,7T\ln(1 + 628.14c) \tag{2}$$

where T is the temperature (in K) and c is the concentration of soluble carbon in $mol\,l^{-1}$. To investigate the influence of organic compounds on the equilibrium growth of cloud droplets, we have compared the Köhler curves obtained with eq. (1) for different chemical compositions and surface tensions.

Two different chemical compositions of the aerosol were used: (a) the *classical inorganic case* (CIC) and (b) the *inorganic + organic case* (IOC). The CIC aerosol model contains only inorganic compounds, the case usually considered in most cloud studies, and the IOC aerosol model includes the recent results on water-soluble organic aerosol composition (Facchini et al., 1999b; Zappoli et al., 1999; Decesari et al., 2000) and surface tension (Facchini et al., 1999a; 2000). Both CIC and IOC aerosol are composed of 50% (by mass) of soluble inorganic matter (composition given below). The remaining 50% is considered to be insoluble material (with a density of $2.5\,g\,cm^{-3}$) for the CIC aerosol and 30% insoluble and 20% WSOC for the IOC aerosol. The organic species, according to Facchini et al. (1999b) and Zappoli et al. (1999), were characterised as: 14% by mass of low-molecular weight substances (MA, parameterised as a dicarboxylic acid having $M = 100$ and $v = 3$) and 6% of macromolecule (MMC, parameterised as a fulvic acid having $M = 732$ and $v = 5$). The soluble inorganic part of the aerosol is considered to be composed by $(NH_4)_2SO_4$ (26%) and

NH_4NO_3 (24%). These data are representative of the composition of a rural aerosol (Zappoli et al., 1999), as explained in the next paragraph.

The molecular composition of inorganic salts was derived from the AIM model III (Carslaw et al., 1995; Clegg et al., 1998a, b), using measured aerosol ionic composition as input data.

All calculations presented in this paper were made at $T = 278.15\,K$ and assuming that $\Phi_s \approx 1$ and $\rho_s = \rho_w$ (ideal solution).

Figure 1 shows, for three different aerosol dry sizes, the equilibrium saturation as a function of equilibrium size for the two chemical compositions considered (CIC and IOC). The dotted lines correspond to the CIC aerosol with surface tension equal to that of pure water, the dashed lines represent IOC aerosol, also with constant surface tension, and the solid lines represent the IOC aerosol with variable surface tension, as from eq. (2). The surface tension was considered to be equal to that of pure water for the CIC aerosol, since inorganic salts do not have surface-active properties in the range of concentration of atmospheric interest (Pruppacher and Klett, 1997).

Comparing the three families of curves for the three aerosol sizes considered, a decrease of the critical supersaturation can be observed (maximum of the Köhler curve) due to the additional organic soluble mass (dotted vs. dashed lines) and
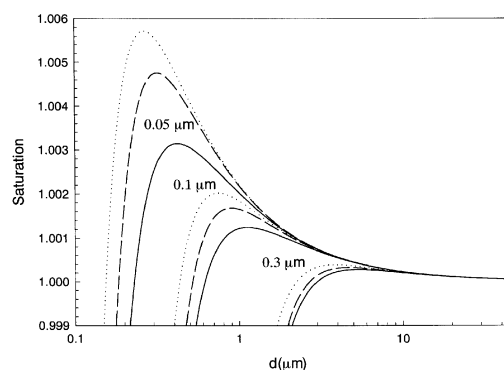

Fig. 1. Köhler curves for three aerosol sizes: 0.05, 0.1 and 0.3 μm diameter. The dotted lines correspond to the *classical inorganic case* (CIC), the dashed lines represent the *inorganic + organic case* (IOC) with constant surface tension (equal to that of pure water) and the solid lines represent the *inorganic + organic case* (IOC) with variable surface tension given by eq. (2).

a further decrease due to surface tension changes (dashed vs. solid lines).

3. Influence of the water-soluble organic compounds on the supersaturation spectrum of CCN for a given aerosol population

According to the Köhler theory, an aerosol particle is said to be activated and can serve as CCN if the atmospheric saturation is greater than the critical saturation. Knowing the critical supersaturation and size for each aerosol particle, the cumulative number concentration of CCN for a given aerosol distribution can be computed as:

$$CCN(S) = \int_{D_S}^{\infty} n(D) \, dD \tag{3}$$

where $n(D)$ is the number distribution of the aerosol population and D_S is the critical (or activation) diameter of the aerosol particles for the air mass supersaturation S.

Since the log-normal distribution provides a good fit for the atmospheric aerosol distribution and is regularly used in atmospheric applications, the number distribution of the aerosol population in eq. (3) is considered to be a sum of m superimposed log-normal functions:

$$n[\log(D)] = \sum_{i=1}^{m} \frac{N_i}{\sqrt{2\pi} \log \sigma_i}$$

$$\times \exp\left(-\frac{(\log D - \log \bar{D})^2}{2 \log^2 \sigma_i}\right) \tag{4}$$

where D is dry aerosol diameter, N_i is the aerosol particle number concentration, $\bar{D}_i$ is the geometric mean diameter and σ_i is the geometric standard deviation of the ith log-normal mode.

In our simulations we use three-modal distributions for marine, rural and urban aerosol as reported by Jaenicke (1993). The multi-modal shape of the aerosol distribution can be seen in all three cases (Fig. 2), but is more pronounced in the case of marine aerosol. Table 1 lists the values for N_i, $\bar{D}_i$ and σ_i [see eq. (3)] for each mode and each aerosol type. These distributions are widely used in literature, since they are considered to be typical distributions under average atmospheric conditions for marine, rural and urban air masses.

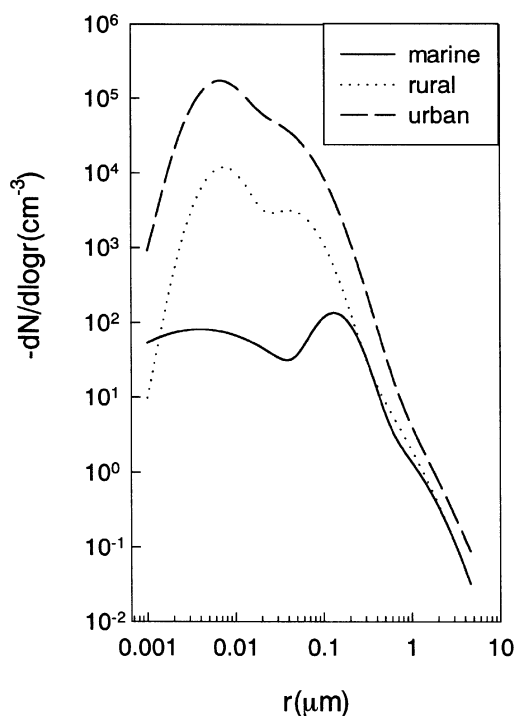The chemical composition of the different aero-

Fig. 2. Number size distribution for marine, rural and urban aerosol calculated from Jaenicke (1993).

sol types for IOC was derived as described in the previous paragraph, using experimental data reported by Putaud et al. (2000) for marine aerosol, Zappoli et al. (1999) for rural aerosol and Putaud (personal communication) for urban aerosol (Table 2). The CIC aerosol has an inorganic composition as reported in Table 2, and the rest of the mass is considered insoluble material.

Using eqs. (1)–(4) and the parameterisations reported in Tables 1 and 2, we computed supersaturation spectra of CCN. All computations were performed using 74 bins for representing the aerosol spectra and assuming an internally mixed aerosol.

Figure 3 shows the supersaturation spectra of CCN for the three aerosol types considered and the two associated chemical compositions, IOC and CIC. For the IOC aerosol, both the increase of soluble mass and the decrease of surface tension due to the presence of WSOC were taken into account. The figure shows that the multi-modal influence of aerosol is more pronounced for the marine case. As expected, the CCN concentration

Table 1. *Parameterisations for the three aerosol size distributions (Jaenicke, 1993)*

Aerosol type	Mode I			Mode II			Mode III		
	N (cm^{-3})	D (µm)	$\log \sigma$	N (cm^{-3})	D (µm)	$\log \sigma$	N (cm^{-3})	D (µm)	$\log \sigma$
Marine	133	0.008	0.657	66.6	0.266	0.210	3.1	0.05	0.396
Rural	6650	0.015	0.225	147	0.054	0.557	1990	0.084	0.266
Urban	9.93×10^4	0.013	0.245	1.11×10^4	0.014	0.666	3.64×10^4	0.58	0.337

Table 2. *Chemical composition of the three different aerosol types as a percent of the total aerosol mass*

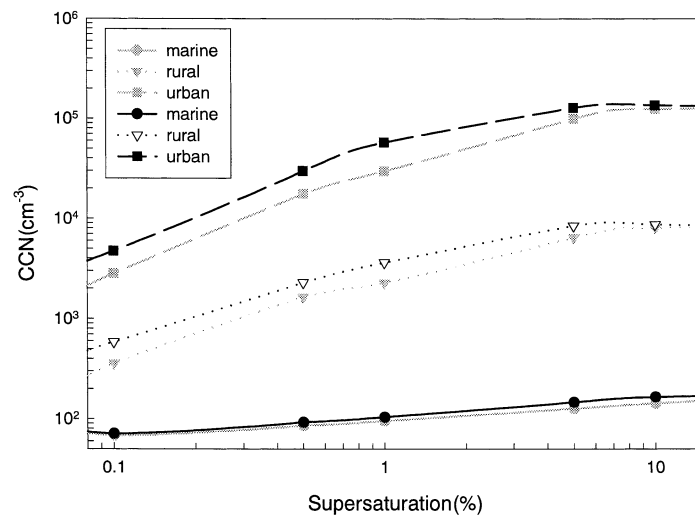| Aerosol type	$(NH_4)_2SO_4$		NH_4NO_3		NaCl		MA		MMC		INS	
	CIC	IOC	CIC	IOC	CIC	IOC	CIC	IOC	CIC	IOC	CIC	IOC
Marine	0.41	0.41	0.00	0.00	0.21	0.21	0.00	0.07	0.00	0.03	0.38	0.28
Rural	0.26	0.26	0.24	0.24	0.00	0.00	0.00	0.14	0.00	0.06	0.50	0.30
Urban	0.22	0.22	0.29	0.29	0.00	0.00	0.00	0.14	0.00	0.06	0.49	0.29

Fig. 3. CCN concentration as a function of supersaturation for three aerosol types: marine (dots), rural (triangles) and urban (squares). The black lines consider the presence of organic compounds (IOC) and their effect on surface tension, while grey lines are computed considering only the inorganic composition (CIC) and constant surface tension, equal to that of pure water.

is higher for IOC than for CIC and the difference depends on WSOC concentration, being substantially higher for urban and rural aerosol than for marine aerosol. The differences between IOC and CIC, normalised with respect to the CIC aerosol, are up to 13% in the marine case, up to 97% in the rural case, and up to 110% in the urban case, for the supersaturation range typical of atmospheric conditions. These results point out the importance of the chemical composition of the aerosol, showing that the CCN number concentration depends not only on the percentage of WSOC, but also on the inorganic composition considered. In fact, the presence of sodium chloride in the marine aerosol produces a much lower variation in CCN number concentrations for the IOC case, because the activation supersaturation is already low (Pruppacher and Klett, 1997). However, for

all three aerosol types, the differences are important in the range of supersaturations usually encountered in the atmosphere (less than 10%).

The results presented in Fig. 3 were fitted for supersaturation greater than 0.1%. The expressions obtained for the best fits of the CCN supersaturation spectra are presented in Table 3, where both CIC and IOC cases are shown. As can be seen, only in the case of the marine aerosol does the CCN supersaturation spectrum obey a power law, which is the kind of relationship widely used in current cloud models. For the rural and urban aerosol, the results differ considerably from the power law (von der Emde and Wacker, 1993) and an exponential function was instead used for the CCN supersaturation spectra for the supersaturation range of atmospheric interest.

4. Conclusions

We calculated a significant decrease of the activation supersaturation of aerosol particles taking into account the presence of aerosol WSOC (IOC), which provide 'additional' water-soluble mass and also decrease the surface tension of droplets. The CCN number concentration can increase, when both WSOC effects are considered, up to 110% for urban aerosol relative to the case in which only the inorganic aerosol composition is considered (CIC), up to 97% for rural aerosol, and up to 13% for marine aerosol.

The estimated increase in CCN number concentration predicted by our model calculations which takes into account the effect of WSOC can significantly influence the evolution of the cloud droplet size spectrum and, in turn, the rate of rain formation (Khain et al., 1999; Rosenfeld, 2000) and cloud albedo (Schwartz and Slingo, 1996).

Given the large variability of observed CCN

Table 3. *CCN–supersaturation relationships obtained for the three aerosol types for the base case (CIC), and also taking into account the effects of the organic compounds (IOC)*

Aerosol type	CIC	IOC
	CCN (cm^{-3})	CCN (cm^{-3})
Marine	$83\,S^{0.19}$	$91\,S^{0.18}$
Rural	$8610\,(1-e^{-0.29S})$	$8739\,(1-e^{-0.57S})$
Urban	$136\,339\,(1-e^{-0.25S})$	$136\,925\,(1-e^{-0.53S})$

S is expressed in %.

populations at a given supersaturation and aerosol mass concentration (Schwartz and Slingo, 1996), it is reasonable to argue whether the influence of organic aerosol species might be a cause of some of the observed wide range of CCN number concentrations. For example, at a given sulphate mass concentration, the observations of numerous authors show roughly an order of magnitude variation of CCN number concentration (Fig. 14 of Schwartz and Slingo, 1996). Our results suggest that a part of this variability could be due to the organic compounds and their influence on surface tension.

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