Cloud Reflectivity and Autoconversion Rate: Sensitivity to Organic Compounds for Different Aerosol Types

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A number of aerosol particles released by human activities has the potential to cool the climate system by modifying the cloud radiative properties via the cloud formation process. Although the aerosols are mostly composed of inorganic species, measurements show organic compounds (OC) could also contribute to cloud condensation nuclei concentration and this depends on aerosol type. Our approach involves estimations of the cloud properties and autoconversion rate taking into account measured aerosol number size distributions and current observations of chemical composition for three types of aerosols: marine, rural, urban. We provide a measure of the ability of organics to change these parameters by calculating relative differences in cloud albedo and autoconversion rate when OC is included with respect to the case when only inorganic aerosol species are considered. The presence of organic compounds may enhance the cloud reflectivity by 1-5% and autoconversion rate changes with 2 orders of magnitude when we move from marine to polluted urban case, with respect to the base-case cloud droplet number.

Keywords: aerosol physical and chemical properties, organic aerosol, cloud albedo, autoconversion rate

Atmospheric aerosol is a complex mixture of tiny liquid or solid particles of varying chemical nature, composition and size. The size of particles composing atmospheric aerosol (expressed as radius or diameter in spherical approximation) ranges over more than four orders of magnitude, from a few nm to around 100 μm. Aerosols originate from a wide variety of natural and anthropogenic (man-made) processes either through direct injection of particles in the atmosphere, mostly by dispersion processes resulting in so-called *primary aerosols* or through transformation of inorganic and organic gaseous precursors resulting into so-called *secondary aerosols*.

Once formed in the atmosphere, aerosols play an important role in atmospheric chemistry having effects on human and animal health and welfare, and influencing climate. The climatic effect of aerosols arises from the fact that they affect the heat balance of the Earth, both *directly* by reflecting and absorbing radiation, and *indirectly* by acting as cloud condensation nuclei (CCN). The indirect aerosol effect is normally splited into two components corresponding to (1) the radiative effect due to modification of the radiative properties of clouds (*cloud albedo effect* [1]) and (2) the effects of aerosols upon the lifetime of clouds by suppressing the rainfall and, therefore, increasing the cloud lifetime (*cloud lifetime effect* [2,3]). The third climatic effect of aerosols is linked to the presence of absorbing species in aerosol particles; these species absorb radiation and the resulting radiative heating in elevated layers can perturb the temperature profile, which can lead to evaporation of low-level clouds (*semi-direct effect* [11, 12]).

The second indirect effect has been observed both over ocean areas in ship tracks [4] and over land [5]. *In situ* experiments have documented how man-made aerosol emissions influence the albedo of warm clouds [6] and precipitation [7]. Andreae *et al.* [8] also reported *in situ* measurements comprising quantitative information on aerosols, cloud droplet size distribution, and precipitation under a wide spectrum of conditions, from very clean air masses through smoky air masses, to the extreme of pyro-clouds (*i.e.* clouds that form in the smoke plume over an active fire). Both biogenic and pyrogenic particles consist predominantly of organic material (about 80% [9]), of which about 60% is water-soluble [10]. The rest of the mass contains mainly soluble inorganic salts (NH_4^+, K^+, SO_4^{2-}, and NO_3^-). Due to the spatial and temporal variability of anthropogenic aerosols [13,14], the radiative perturbation (forcing) has strong regional character [15], so that also the climate response to the aerosol forcing is regionally heterogeneous [16]. The climatic effect of aerosols is in the direction of cooling (under most circumstances) and is of a magnitude comparable to that of the greenhouse gas warming [17]. When aerosol particles contain absorbing material, total forcing can become positive giving a warming effect [18]. The resulting total radiative forcing (well-mixed greenhouse gases, solar activity, ozone, direct aerosol effects and Twomey effect) has a 75–97% probability of being positive [19] and it has been shown (e.g.[20, 21]) that numerical simulations of global climate are sensitive to small changes to cloud optical properties. The cooling from both indirect effects has been estimated by climate models to be from –1 to –4.4 W m^{-2} in the global mean (e.g. [22]), but this estimate is still very uncertain. For the second indirect aerosol effect alone, Rotstayn [23] gives a global-mean value of –0.28 W m^{-2} pointing out on its poor understanding.

With respect to the chemical composition, atmospheric aerosol contains typical hygroscopic species, e.g. NaCl, $(NH_4)_2SO_4$, H_2SO_4, NH_4NO_3, partially soluble species as $CaSO_4$, and hydrophobic carbonaceous particles, with or without the presence of organic surfactants [24].

While a large body of data exists on chemical composition of the inorganic fraction of aerosol, the present knowledge on the organic fraction and its behaviour in

atmosphere is rather incomplete [25,26]. The organic carbon component of atmospheric aerosols is present in both fine and coarse ranges and comprises hundreds if not thousands of individual compounds. Specific classes of organic compounds identified have included aliphatic and aromatic HCs, PAHs, aliphatic and aromatic aldehydes and ketones, phenols, quinones, polyols, phthalic acid esters, sulfur heterocyclics, aryl and alkyl halides, chlorophenols, and alkylating agents. A very detailed characterization of the organic composition of aerosols is presented in studies of Decesari *et al.* [27], and Tagliavini et al. [28]. Organic compounds (OC) are significant components of PM2.5 aerosols (aerosols with diameter below 2.5 μm) collected in western U.S. cities such as Los Angeles (20 to 45%), Phoenix ($\approx$ 34%) and Denver ($\approx$ 34%) [24]. The carbonaceous aerosol shows a relative enrichment in OC during summer periods in different environments. This result suggests that in summer there is an increased formation of secondary OC, because of more favourable conditions for gas/particle conversions of VOCs as a result of photochemical activity [29].

Recently, some progress has been made in assessments of the radiative effects of various aerosol components such as sulphate, organics, black carbon, sea-salt, and crustal species [31,32,33,34]. Penner *et al.* [35] suggested a research strategy which encompasses surface-based observations of aerosol chemical and physical properties. Uncertainty in the estimations can be attributed to the complex issues regarding the treatment of aerosols and clouds in the models and reflects the poor state of knowledge regarding the sources, properties of atmospheric aerosols and their interaction with clouds.

With respect to the OC aerosol climate effects, Novakov and Penner [36] have found that OC account for a major part of both total number concentration and the cloud condensation nuclei fraction. Saxena *et al.* [37] have shown that organics can alter the hygroscopic behaviour of atmospheric particles, affecting the ability of mixed aerosols to act as cloud condensation nuclei. Shulman et al. [38] have shown that slightly soluble OC affect cloud droplet growth by two mechanisms: gradual dissolution in the growing droplets which affect the critical size, and lowering of surface tension which decreases critical supersaturation. Zappoli *et al.* [39] investigated the

composition of fine aerosol at three different sites in Europe (polluted, rural and background) and found the soluble fraction of organic component of ranges from 20% to 50% aerosol, and over 70% of the organic compounds in the fine aerosol at all sites is of polar nature. Considering the insoluble fraction of organic component, it is worthy to mention that much less research has been performed, but to this insoluble fraction, 25% can be attributed the humic-like substances [40] and plant debris [41]. Among other possible contributors, bioaerosols (e.g. [42,43]) or polymers [44] might be of interest.

As organic component is chemically very complex, in Global Chemistry Climate Models there is a strong need of simplified representation of the volatility, solubility, hygroscopicity, chemical reactivity and the physical and optical properties of OC. Practically, the net effect of a complex mixture of OC is described by only a limited number of representative compounds or mixtures. Up to now, there are only few studies reporting information concerning both inorganic and organic aerosol chemical composition which can be directly used by cloud models (e.g. [39,45,46]). However, it is extremely difficult to estimate the magnitude of organic species effects on the radiation budget without climate model simulations.

Knowing that the large variability of measured CCN [47] might be partially explained by the OC in percentages reported by Mircea *et al* [48], namely as increases in CCN concentrations of up to 13% in the marine case, up to 97% in the rural case, and up to 110% in the urban case, it is reasonable to search for the influence of organic aerosol species on the cloud parameters and the autoconversion rate, counting for the aerosol indirect effect. In the present paper, starting from a lognormal size distribution and a specific chemical composition for three types of aerosols, we calculated the cloud radiative properties and the autoconversion rate. The aim here is to investigate the effects of OC on the cloud optical depth and albedo and on the autoconversion rate through implications of the increased droplet concentration. Section 2 presents the model description and the parameterizations used, while the results and discussions are presented in section 3 of this work.

Model description
Aerosol indirect effect is broadly defined as the overall process by which aerosols perturb the Earth-atmosphere radiation balance by modulation of cloud albedo and cloud
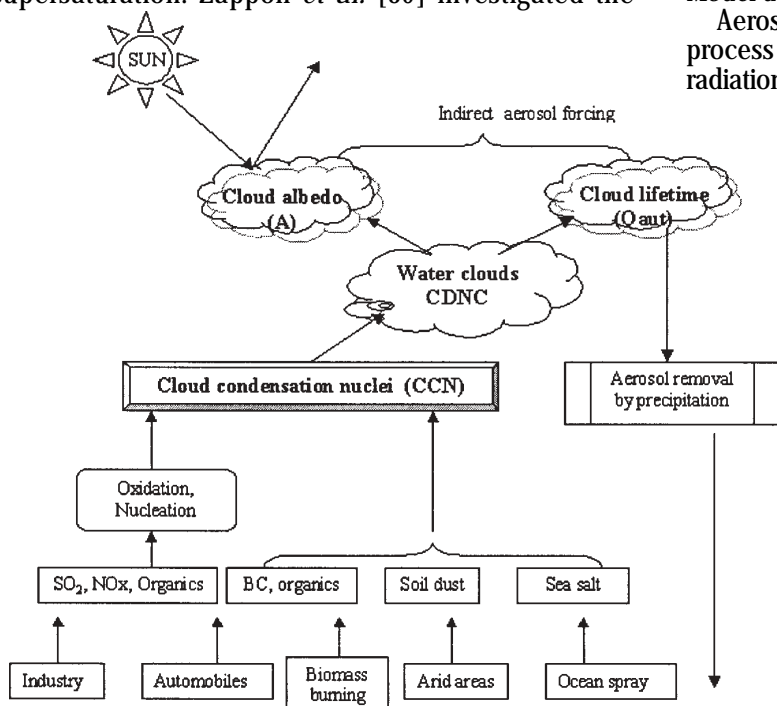

Fig 1. Flow chart showing the aerosol emissions or production in the atmosphere and the linkage processes associated with the indirect forcing (changes in cloud albedo and lifetime); CDNC is cloud droplet number concentration; Qaut is autoconversion rate

Table 1

PARAMETERS OF THE SIZE DISTRIBUTIONS[a], SURFACE AREA CONCENTRATION (A) AND
VOLUME CONCENTRATION (V) OF ALL AEROSOL TYPES

		N (cm^{-3})	D (μm)	Log σ	A (μm^2·cm^{-3})	V (μm^3·cm^{-3})
Marine aerosol	Mode I (nucleation)	133.0	0.008	0.657	0.06	0.25·10^{-3}
	Mode II (accumulation)	66.6	0.266	0.210	16.17	800.39·10^{-3}
	Mode III (coarse)	3.1	0.580	0.396	4.48	641.38·10^{-3}
Rural aerosol	Mode I (nucleation)	6 650.0	0.015	0.225	5.20	14.76·10^{-3}
	Mode II (accumulation)	147.0	0.054	0.557	2.50	48.96·10^{-3}
	Mode III (coarse)	1 990.0	0.084	0.266	50.82	849.12·10^{-3}
Urban aerosol	Mode I (nucleation)	99 300.0	0.013	0.245	59.45	149.65·10^{-3}
	Mode II (accumulation)	1 110.0	0.014	0.666	1.66	11.74·10^{-3}
	Mode III (coarse)	36 400.0	0.049	0.337	344.58	3 740.00·10^{-3}

[a]From [51].

Table 2

CHEMICAL COMPOSITION (%) FOR THE THREE AEROSOL TYPES IN TABLE 1[b]

Aerosol type	(NH$_4$)$_2$SO$_4$	NH$_4$NO$_3$	NaCl	Fulvic acid	Dicarboxylic acids	Insoluble
Marine	41	0	21	3	7	28
Rural	26	24	0	6	14	30
Urban	22	29	0	6	14	29

[b]From [48].

amount [49]. For liquid water clouds, it can be viewed as a series of processes linking various intermediate variables such as aerosol mass, cloud condensation nuclei (CCN) concentration, water phase partitioning, cloud optical depth, etc., which connect emissions of aerosols (or their precursors) to the top of the atmosphere radiative forcing due to clouds. The flow chart in figure 1 presents aspects directly relevant to quantification of the indirect radiative forcing by aerosols. For a complete view of aerosols effect on climate, the direct and semi-direct aerosol forcing have to be added.

The present study focuses on the computation of parameters involved from number concentration of aerosol particles to cloud albedo and autoconversion rate counting for indirect aerosol effect in a sensitivity test on effect of presence of organic species inside the aerosol particles (see the next section).

Aerosols and cloud condensation nuclei

The aerosol distribution in atmosphere is well described by a multimodal log-normal function dN/dlogD [50] comprising nucleation mode (diameter D being between 1 and 100 nm), accumulation mode (0.1-1μm), both counting for fine mode, and the coarse mode (>1mm). In our calculations we used for all aerosol types a three-modal log-normal function:

$$\frac{dN}{d \log D} = \sum_{i=1}^{3} \frac{N_i}{\sqrt{2\pi} \log \sigma_i} \exp\left(-\frac{\left[\log(D/\overline{D}_i)\right]^2}{2(\log \sigma_i)^2}\right) \qquad (1)$$

where N_i, $\overline{D}_i$ and σ_i are the total number concentration, geometric mean diameter of dry particle, and geometric standard deviation of aerosol mode *i*, respectively. Table 1 summarizes some properties of the atmospheric aerosol size distributions measured by Jaenicke [51] and calculated in this study.

Recent extensions of the fundamental theory (Köhler theory) about cloud droplet formation have shown that water-soluble gases, substances of slight solubility, surfactants, and condensation kinetics can, in combination, significantly alter droplet populations and sizes (e. g. [52,53]). The combination of measurements of aerosol particle dry size distributions, chemical composition and the hygroscopic properties enables us to predict the CCN concentration of the atmospheric aerosol particles. CCN concentrations were obtained using the CCN-supersaturation relationships [48] for the two different chemical compositions of the aerosol: (a) the inorganic case

(denoted hereafter as -OC) and consisting of 50% soluble inorganic and 50% insoluble material and (b) the inorganic+organic case (denoted hereafter as +OC), being a mixture of 50% soluble inorganic, 30% insoluble material and 20% water-soluble organic species (WSOC). The dicarboxylic acids and the fulvic acids have been counted for the organic compounds, in the percentages shown in Table 2, according to the recent results on WSOC in different areas of Europe of[54,39,55,56].

Effect of CDNC changes on cloud radiative properties and autoconversion rate
a. CDNC calculations

The first indirect aerosol effect enters into the model through the effect of variations of cloud droplet number concentration (CDNC) on the droplet effective radius (r_{eff}) in liquid water clouds, and hence on their shortwave radiative properties. The CDNC is calculated starting from the previous CCN taking into account that any activated particle has to continuously grow throughout the duration of cloud formation. Experimental evidence indicates under certain circumstances growth kinetics may retard the growth of CCN sufficiently to limit the number of activated droplets formed. The studies of Nenes et al. [57] and of Ramanathan et al. [58] show, for low concentrations of particles, kinetic effects that influence droplet number concentration are negligible, regardless the particles diameter. Kinetic limitations on droplet formation are important for an aerosol with a mode number concentration higher than 1000 cm^{-3} when the deactivation and evaporation mechanisms are much more prominent. Larger mode radius tends to accentuate kinetic effects. In this respect, we considered a droplet number concentration by reducing CCN with a percent of 20% for urban and rural aerosol, and we kept cloud droplet number to be the same as the number of cloud condensation nuclei for marine aerosol, as its number concentration is too low for kinetic effects to be important.

b. Effective radius, optical depth and cloud albedo

In global climate models (GCMs), cloud radiative properties are expressed using a parameter called effective radius r_{eff}. The effective radius, liquid water content (LWC) in a cloud and the cloud droplet number concentration (CDNC) are related through a parameterisation as "1/3" power law of the ratio between LWC and CDNC [59,60]:

$$r_{eff} = \left(\frac{3}{4\pi\rho} \cdot \frac{LWC}{CDNC} \right)^{1/3} \qquad (2)$$

where ρ is the water density. If is of interest to include the influence that an increasing number of cloud droplet has on the shape of cloud droplet spectrum (dispersion effect), the above r_{eff} has to be multiplied by a factor of which dependence of the characteristics of droplet spectrum has been derived by Liu and Daum [61].

Extinction of the radiation by a cloud of geometrical thickness (H) is described using cloud optical depth (τ):

$$\tau = \frac{3}{2} \frac{LWC \cdot H}{r_{eff} \cdot \rho} \qquad (3)$$

The two-stream approximation of a non-absorbing, horizontally homogeneous cloud [62] gives the cloud reflectance R (albedo):

$$R = \frac{\tau}{6.7 + \tau} \qquad (4)$$

c. Autoconversion rate

The second indirect effect enters into the model through the parameterization of autoconversion (coalescence of cloud droplets to form small raindrops) because the rainfall is initiated by the autoconversion process. The autoconversion rate (Qaut) describes how rapidly the cloud water converts into rainwater and it depends largely on the available LWC and droplet concentration. Most existing GCM simulations have used the threshold-based autoconversion scheme, whereby autoconversion is initiated when the volume-mean cloud droplet radius is above a given threshold. We calculated Qaut using the newest introduced threshold-based autoconversion scheme of Liu et al. [63] without considering the dispersion effect:

$$Q_{aut} = k \times CDNC^{-1} LWC^3 \left\{ 1 - \exp\left[-\left(1.03 \times 10^{16} CDNC^{-3/2} LWC^2 \right)^2 \right] \right\} \qquad (5)$$

where k is a constant related to the particles' collection.

The critical radius (r_c) can be also predicted from the liquid water content and droplet concentration following Liu et al [64]:

$$r_c = 5.6084 \times 10^2 \left\{ \left[\exp\left(\frac{3 \times 10^{-17} CDNC}{LWC} \right) - 1 \right] \frac{1}{LWC} \right\}^{1/6} \approx 0.99 CDNC^{1/6} LWC^{-1/3}$$

$$(6)$$

Results and Discussion

A comparative view of the aerosol number size distributions for all aerosol types is presented in figure 2. As we move from clean marine areas to polluted continental areas, the number concentration increases with about 3 orders of magnitude. Surface area concentration A and volume concentration V values for each mode (table 1) indicate that the second mode (accumulation) is predominant for marine aerosol, while for rural aerosol the third mode (coarse) is most important. The processes which aerosol particles are produced explain this behaviour.

The accumulation mode is generally produced by the *coagulation* of smaller particles, mainly previously produced by *gas-to-particle conversion* in the nucleation mode, and by the *heterogeneous condensation* of gas vapour onto existing aerosol particles (sulfates, nitrates, organic mater from biogenic volatile organic compounds). The coarse mode corresponds to the aerosols directly injected into the atmosphere as particles from the surface of the earth as emissions from soil and industrial dust, sea
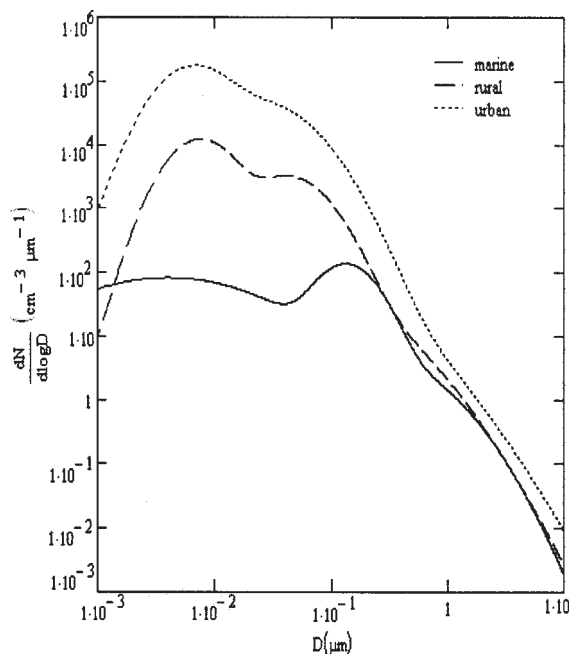

Fig. 2. Aerosol number size distribution for marine, rural and urban aerosol

salt and biological debris. For urban aerosol, the coarse mode is predominant, but the nucleation mode also has a significant contribution to the total aerosol, indicating that anthropogenic sources as fossil fuel burning (generating, for instance, black carbon) plays an important role.

While the inorganic compounds ((NH_4)$_2$$SO_4$, NH_4NO_3) comprise a large part of fine range, and the insoluble fraction lies mainly in the coarse part, the organics are present over the entire size spectrum (table 1 and 2).

The concentration of available CCNs depends on the aerosol size distribution, their chemical composition and the cloud supersaturation S. We have calculated (according to aerosol size distribution parameters in Table 1 and the chemical composition in percentages presented in table 2) a significant increase in CDNCs in the presence of organic compounds when water vapour supersaturation needed for activation of aerosol particles lies between 0 and 1%.

The estimated increase in CDNC by our model calculation ranges from up to 11% for marine to 94% for rural and to 107% for urban aerosols, relative to the case when aerosol particles are composed only of inorganic species.

As a dataset on observed CCN and CDNC was not available for the size distributions considered by us, we compared our results with reports from field campaigns. Roberts *et al.* [9] has shown that the CCN properties of both pyrogenic and biogenic aerosols can be explained on the basis of their size-dependent chemical composition, which is characterized by a mixture of soluble inorganic and partially soluble organic constituents. During Smoke, Aerosols, Clouds, Rainfall, and Climate (SMOCC) campaign, Andreae et al. [8] found out that about 40 to 60% of available aerosol particles are able to nucleate cloud droplets at S=1% in the freshly polluted boundary layer, whereas the larger particles in aged smoke and in the clean planetary boundary layer have a distinctly higher efficiency (60 to 80%). Our results fit well in this range (table 3).

We found a CCN enhancement of about 2 when organics are taken into account, a result which is also consistent with the results of Dusek *et al.* [65] that pollution outbreaks enhance the CCN concentrations at supersaturation near 0.2% by a factor of 3 (aged pollution) to 5 (recent pollution) compared to the clean marine background concentrations.
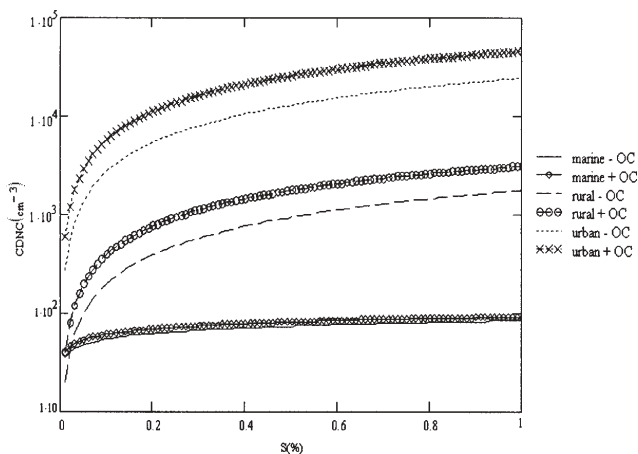
Fig. 3. CDNC concentration as a function of supersaturation, calculated for marine (diamonds), rural (circles), and urban (crosses) aerosols. Simple lines consider the inorganic case and lines with symbols consider the presence of organic species
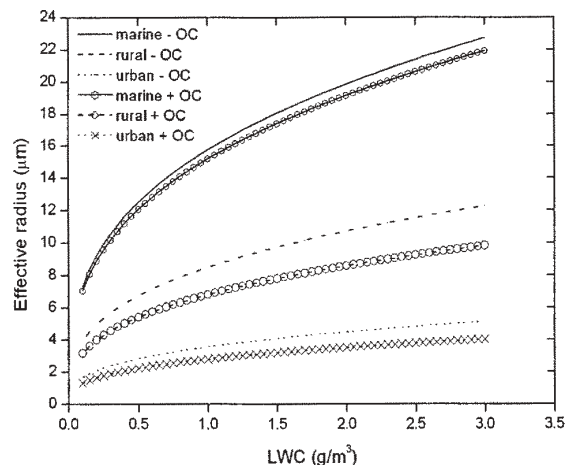

Fig. 4. Comparison of the calculated effective radius (diamonds-marine, circles-rural, crosses-urban) in both cases: –OC and +OC

Table 3
AEROSOL (Na, IN cm⁻³) AND CCN CONCENTRATIONS (iIN cm⁻³) AT A SUPERSATURATION
OF 1% FOR THE THREE AEROSOL TYPES FOR THE ORGANIC CASE (+OC)
COMPARATIVE WITH MEASUREMENTS IN SMOCC CAMPAIGN

Aerosol	Present study		SMOCC	
type	Na	CCN	Na	CCN
Marine	202	91	100-350	320
Rural/smoky clouds	8787	3797	2000-8000	1000-4000
Urban/pyro-clous	136810	56330	20×10^4 - 44×10^4	10×10^4 - 23×10^4

Table 4 lists the CDNC values calculated by using total aerosol number concentrations listed in table 1 and the aerosol concentration-cloud droplet concentrations relationships reported by Gultepe and Isaac [66] for five field measurements. Results from SMOCC campaign [8] are also indicated.

Table 4
CLOUD DROPLET CONCENTRATION INFERRED FROM FIELD
MEASUREMENTS [66, 8] AND CALCULATED IN PRESENT STUDY[c]

Field project		marine	rural	urban
Syracuse		148	481	723
EMEFS I		89	697	1140
EMEFS II		39	563	945
NARE		99	376	577
RACE		103	357	542
		600	2200	2400
SMOCC		(marine clouds)	(smoky clouds)	(pyro-clouds)
Present	-OC	61	388	5319
study	+OC	68	753	11017

[c]The Syracuse project was performed in New York State during 1984. The Eulerian Model Evaluation Field Study was conducted in southern Ontario during 1988 (EMEFS I) and 1990 (EMEFS II). The North Atlantic Regional Experiment (NARE) was conducted in Nova Scotia during 1993. The Radiation, Aerosol, and Cloud Experiment (RACE) took place over the Bay of Fundy and central Ontario during 1995. SMOCC was conducted in Amazon in 2002.

A comparison of our CDNC concentrations with that inferred from [66] shows a good agreement only for marine case; a slightly overestimation is seen in our results for rural case, with a higher aerosol number; for urban case our model overestimates by an order of magnitude even the prediction using EMEFS I relationship and the measurements in highly polluted case of pyro-clouds in SMOCC. Many studies revealed discrepancies between predicted and measured CCN or CDNC and always the predicted values appear to be larger than those measured. Up to now there is no general consensus regarding the
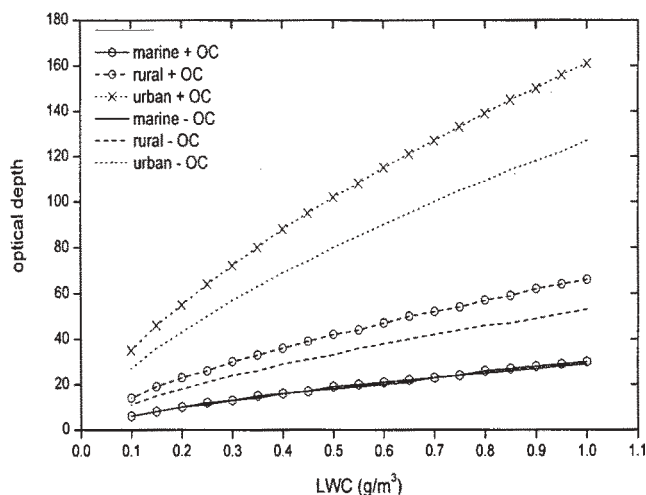

Fig. 5. OC effect on cloud optical depth for a cloud of 100 m thickness, over continental (rural and urban) and marine areas

causes of these discrepancies due to the complex issues regarding the treatment of aerosols and clouds. Snider *et al.* [67] suggested that these discrepancies could be in part because of theoretical reasons, but due to multiple and poorly characterized experimental errors, as well.

As typical supersaturations measured in *stratus* clouds (most important in the indirect effect of aerosols as they cover large areas) are generally estimated to lay below 0.5% [68,69], we further used in computations of cloud parameters the droplet number concentration values for a supersaturation of 0.2%.

An investigation of the OC presence on effective cloud droplet radius revealed a decrease of r_{eff} when OC is present (with respect to the case when only the inorganic aerosol compounds are considered, "-OC" as base-case). This behaviour varies with aerosol type, the decrease being of up to 4% in the marine case, up to 20% in the rural case, and up to 22% in the urban case. In the Earth's atmosphere a large variety of droplet sizes can be found depending
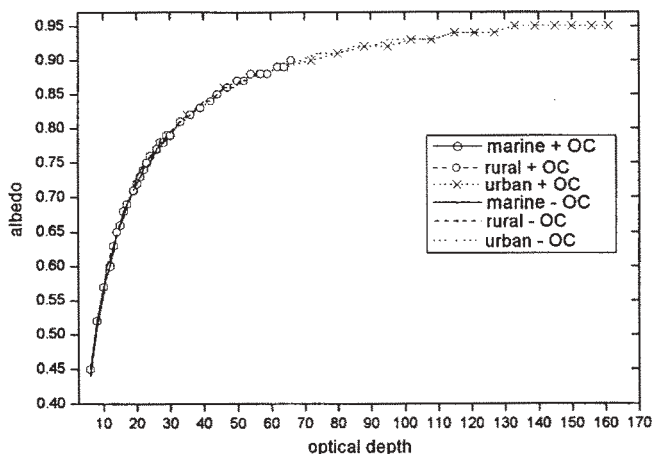
Fig. 6. OC effect on cloud optical depth for a cloud of 100 m thickness, over continental (rural and urban) and marine areas

Fig. 7. OC effect on the autoconversion rate over continental (rural and urban) and marine areas

very much on the type of cloud they are embedded in. Stephens [59] quotes radii ranging from 2.25 for stratus clouds to 7.5 for stratocumulus. Han et al. [70] derived radii for water clouds from satellite measurements between 6 and 15 μm. As an example of absolute values we calculated, the effective radius decreases from 10.55 μm (-OC) to 10.17 μm (+OC) for marine clouds (fig. 4), from 5.69 μm to 4.56 mm for rural case, and from 2.38 μm to 1.87 μm for urban case, respectively, for a LWC of 0.3 g m⁻³; thus there is a good agreement with measurements. The absolute very low values in urban +OC case are due to the very large number of cloud droplets that our model provide.

Boundary layer clouds are typically 100-500 m thick, with most in the range 200-400 m ([71]). For a thin marine cloud (below 100 m and higher droplet radius) and a low LWC, the optical depth is low. As we move from clean marine conditions to the polluted urban areas, the cloud becomes optically denser. We explored the dependence of OC presence on cloud optical depth and albedo as LWC ranges between 0.1 to 1 g m⁻³ (the most measured values in the atmosphere). While the changes in optical depth for a marine cloud is insignificant, τ increases for instance by a factor of 1.2 for rural and of 1.3 for urban case at the same liquid water content of 0.3 g m⁻³ (fig. 5).

The curves for cloud reflectivity variation in figure 6 are not visually distinguishable between the two considered cases (-OC and +OC) as the calculated differences are very small for the entire range of optical depths. Nevertheless, Figure 6 shows the increase of cloud albedo as cloud optical depth covers all calculated values for clouds over marine, rural and urban regions. As the pollution level increases, the clouds became optically deeper and more reflective. This shows the cooling effect of more polluted clouds. Optical depth values ranging from about 30 to about 70 (corresponding to clouds over rural areas) represent a transition area from smaller optical depths of clean marine clouds to that of highly polluted urban regions. The OC presence leads to an increase in cloud albedo from 1% (marine case) to 5% (urban case). This means that the effect of OC presence is more pronounced as the cloud droplet number concentration (determined by the aerosol number concentration) has higher values. Therefore, the Twomey effect (first indirect aerosol effect) we expect to be more prominent in OC presence, following the tendency of cloud albedo. The reflectance of the underlying surface may also play a role when trying to quantify the first indirect aerosol effect.

In a research to estimate the effect of anthropogenic pollution on cloud albedo, Menon *et al.* [72] have calcu-
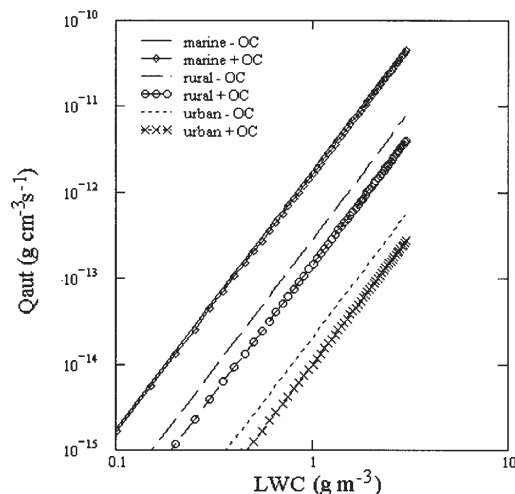
lated cloud albedo from in-situ measurements and inferred it from the Advanced Very High Resolution Radiometer data. For example, for an optical depth of 13 in the continental case they found an in-situ albedo of 63% and an AVHRR albedo of 57%; for an optical depth of 10 in the marine case they reported in-situ albedo of 57% and AVHRR albedo of 56%.

A comparison of our calculated cloud albedo with these shows a good agreement. The differences might be explained by the larger values we found in cloud droplet number for the same LWC.

Our model also shows that addition of cloud droplets due to the OC presence in air enhances cloud lifetime by delaying the onset of precipitation. Our calculations indicate that the autoconversion rate depends strongly upon the cloud droplet concentration (fig. 7) such that for an increase with three orders of magnitude in CDNC (moving from marine to urban areas), Q_{aut} is diminished by 2 orders of magnitude.

We found that the doubling of CDNC concentrations due to organic compound presence leads to a reduction in autoconversion rate of about 2 (rural and urban case).

This agrees with findings of detailed observational research of Wood [73] on examining drizzle in stratiform boundary layer clouds that states a doubling of droplet number determines a reduction in autoconversion rate between 2 and 4.

The relative change in the droplet critical radius is up to 2% for marine case, up to 12% for rural case and up to 13% for urban case.

The reduction of cloud droplet size by a larger number of aerosols is associated with an inhibition of the onset of precipitation up to heights of ≈ 6.5 km above cloud base in smoky-clouds [8], compared to <3 km in smoke-free clouds [74]. This increases the transport of water and smoke to upper levels, allows invigoration of the updrafts, causing intense thunderstorms, large hail, and greater likelihood for overshooting cloud tops into the stratosphere, as Andreae et al.[8] pointed out. There, detrained pollutants and water vapour would have profound radiative impacts on the climate system.

In the context of global warming, future cloud properties are likely to change due to the warmer and moister conditions, and possibly due to increased aerosol particle emissions from both primary (e.g. wind generated seaspray) and secondary aerosols (from biogenically and anthropogenically influenced gas-to-particle conversion processes). Current legislation over Europe will probably

result in lower emissions of aerosols and aerosol precursor ([75] and references therein). The relative role of nitrates, sulfate, and organic aerosols may therefore change in the future. An essential step is also the effort to reduce uncertainties in assesments of aerosol radiative effects in the atmosphere.

Conclusions

Understanding how pollution aerosols are incorporated into clouds and affect their properties is necessary before we can correctly assess anthropogenic influences on clouds and climate. We show the importance of inclusion in modelling of cloud properties of the aerosol chemical composition for three major aerosol types: marine, rural and urban. Cloud condensation nuclei and cloud droplet number at low supersaturation are increased strongly by pollution. This leads to a significant effect on cloud reflectivity and autoconversion rate. The organic compounds presence leads to an increase in cloud albedo from 1% (marine case) to 5% (urban case). Our calculations indicate that the autoconversion rate depends strongly upon the cloud droplet concentration such that for an increase with 3 orders of magnitude in cloud droplet number concentration (moving from marine to urban areas) Q_{aut} is reduced by 2 orders of magnitude. We provide a measure of the ability of organics to change the cloud radiative properties and the autoconversion rate. This study emphasizes the need for an integrated approach chemistry-physics in modelling the indirect effect of aerosols due to its implications for the global change.

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