

Clouds and pollution

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Abstract: The interactions of clouds and pollution are presented. At first the different microphysical and chemical processes accumulating and modifying the pollution mass in the liquid phase are presented. Then, the processes are quantified taking as an example a medium-sized convective cloud forming in a remote marine environment. Background concentrations of particles and gases are used. With the help of this simplified scenario the processes of « venting » of pollution from the boundary layer to the free troposphere, the processes of acid deposition and the modifying, *i.e.* « processing » of atmospheric pollution by clouds are addressed. The discussion is restricted to clouds without ice phase.

INTRODUCTION

Seen from space, clouds cover at all times at least 30% of the earth. They play an important role in the radiative budget of our planet and, thus, for our climate. In the short wavelengths, clouds reflect parts of the incoming solar radiation. In the long wavelengths, they absorb terrestrial radiation and, thus, close the window of atmospheric transparency. Clouds represent an important element in the hydrological cycle too. They help to transport the evaporated waters of the oceans to the continents where the precipitation releases the water load.

Furthermore, clouds represent one important element in the self-cleansing process of the atmosphere. The vertical movement associated with clouds « vent » pollution mass produced at the earth's surface up to the free troposphere. There, the non-scavenged fraction can take part in the long range transport. The other part of the ambient trace gases and particles are taken up into the hydrometeors. Numerous chemical reactions can take place inside the liquid phase. Depending on the rate of precipitation a certain amount of the chemical species scavenged are removed from the atmosphere by wet deposition. The rest is released back into the air when the cloud evaporates modifying the chemical load of the atmosphere.

In the following, the different pathways of atmospheric pollutants entering the hydrometeors and some possible chemical reactions occurring will be discussed. Then, these different processes will be quantified taking as an example a medium-sized warm cumulus cloud developing in a remote marine environment. Aspects of venting, acid deposition and processing of chemical species will be discussed.

UPTAKE OF PARTICLES

A significant amount of the pollution mass in the atmosphere is present in the form of particles. Aerosol particles typically encountered in the atmosphere have a size range between 10^{-3} and $10\ \mu\text{m}$. Their total number concentration varies between 100 and $100\ 000\ \text{cm}^{-3}$, their mass can reach beyond $50\ \mu\text{g}/\text{m}^{-3}$. As they are normally very small their terminal velocity can

most of the times be neglected. It has been proposed to distinguish three different size ranges for the particles corresponding to different formation and destruction mechanisms:

size classes	Junge	Whitby	formation	removal
$r < 0.1 \mu\text{m}$	Aitken particles	nuclei or transient mode	condensation form the gas phase	aggregation
$0.1 \mu\text{m} < r < 1 \mu\text{m}$	large particles	accumulation mode	condensation, aggregation	washout and rainout
$r > 1 \mu\text{m}$	giant particles	coarse mode	sea spray, wind blown dust, volcanoes, plant debris,..	sedimentation

Table 1: classification of aerosol particles after Junge and Whitby and the different formation and removal processes most important for the various size classes of aerosol particle (ref. 1).

The actual distribution with size and height depends on geography and air mass. For a review see ref. 1.

These particles can enter cloud hydrometeors via 2 different mechanisms.

a) Nucleation of drops

Our atmosphere does not allow the formation of drops by agglomerating water vapour molecules (homogeneous nucleation) alone. In order to form a tiny drop of $2 \cdot 10^{-3} \mu\text{m}$, assembled of 800 molecules, would require a relative humidity of 200%. Consequently, in our atmosphere droplets form on already existing nuclei (heterogeneous nucleation). As nuclei serve certain aerosol particles present in every air mass.

Depending on their size, their chemical composition and the ambient relative humidity aerosol particles take up a certain amount of water. So even in the absence of a cloud the atmosphere is full of tiny droplets representing swollen aerosol particles. Their growth behaviour is described by the Koehler equation:

$$\frac{e_a}{e_{\text{sat},w}} = \exp\left(\frac{2M_w\sigma_{s,a}}{RT\rho_w a} - \frac{\nu\phi_s\varepsilon_v M_w \rho_s r_N^3}{M_s \rho_w (a^3 - r_N^3)}\right)$$

with e_a : actual water vapour pressure; $e_{\text{sat},w}$: saturation vapour pressure; M_w : molecular weight of water; M_s : molecular weight of salt; ν : total number of ions into which the salt dissociates; ϕ_s : osmotic coefficient of salt in solution; ε_v : volume fraction of soluble material in the aerosol nucleus; r_N : radius of dry aerosol nucleus; a : radius of humid aerosol particle; ρ_w : density of water; $\sigma_{s,a}$: surface tension.

The bigger the aerosol particle and the more soluble material it contains the more water it will take up at a given relative humidity. (For a graphical display of the curve see e.g. ref. 1) This behaviour pertains even at supersaturations. Only when a given aerosol particle has passed the maximum of its Koehler curve, we call it activated. Then, it does not require a further increase in relative humidity to grow. We, thus, call it activated and it is considered a cloud droplet.

Through this process, called nucleation scavenging, a particle can be found in every formed droplet. Non-activated particles stay between the formed droplets and can be scavenged by collision with these drops.

b) impaction scavenging

Impaction scavenging is describes by the so-called impaction scavenging efficiency E . The qualitative behaviour of E with respect to aerosol and drop radius can be found, e.g., in ref. 1 and will be discussed below.

When the particle radius is small (radius below $10^{-2} \mu\text{m}$), the efficiency of impaction is high as the particles participate in the brownian motion of the air and collide easily with the drop. E decreases as the particle size increases. Once the particles are large (radius larger $1 \mu\text{m}$), E again is large as the particle has sufficient inertia to resist the flow that wants to carry it around the drop. In between, there is a minimum called Greenfield gap, located around $0.1 \mu\text{m}$ radius. Here, only the phoretic and electric forces are active. They tend to fill this gap when the relative humidity decreases or the charges on the particle and the atmosphere increases.

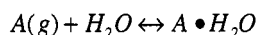
For the relative behaviour of E with drop radius we see a decrease with increasing particle radius due to the increase in flow field strength which tends to carry the particles around the drops. A minimum is located around the drop radius where the rear drop eddy forms ($200 \mu\text{m}$). As the eddy gains strength, more and more particles are captured at the rear of the drop. A maximum is located around $500 \mu\text{m}$ drop radius where the eddy sheds. Then, the efficiency decreases again.

UPTAKE OF GASES

a) Absorption equilibrium and Henry's law

Every gas $A(g)$ in the atmosphere enters to a certain degree the water phase. Given sufficient long time, in a closed system an equilibrium will be established between the gas concentration in the liquid and the gas phase.

gas	$A(g)$
liquid	$A \cdot H_2O$



The equilibrium constant is defined as K_H : Henry's law coefficient in $\text{mole l}^{-1} \text{atm}^{-1}$:

$$K_H = \frac{[A \cdot H_2O]}{p_A}$$

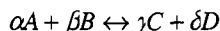
with p_A : partial pressure of A in the gas phase (atm) and $[A \cdot H_2O]$: concentration of equilibrium amount of dissolved gas A in solution (mole l^{-1}).

The Henry's law coefficient is dependent on temperature and the values K_H ($T=298 \text{ K}$) and ΔH_{298} can be taken from chemistry tables.

$$K_H(T) = K_H(T = 298) \exp \left[\frac{\Delta H_{298}}{R} \left(\frac{1}{298} - \frac{1}{T} \right) \right]$$

b) Dissociation equilibrium

Many gases dissociate in one or more stages into ions, thereby establishing equilibrium between the dissociated and undissociated species:



with the dissociation constant:

$$K = \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}$$

and

$$K(T) = K(T = 298) \exp \left[\frac{\Delta H_{298}}{R} \left(\frac{1}{298} - \frac{1}{T} \right) \right]$$

Also these values can be found in chemistry tables.

c) Mass transfer aspects of atmospheric chemistry

In the atmosphere no system is in infinite equilibrium. There are interfering processes of transport which are described by the convective diffusion equation:

$$\frac{\partial c}{\partial t} = -\vec{v} \cdot \vec{\nabla} c + D_i \nabla^2 c$$

Thus, for aqueous-phase reaction in droplets several mass transfer steps may take place:

1. *diffusion of gaseous species from the bulk gas to the surface of the droplet*
2. *transfer across the gas-liquid interface*
3. *ionization of the species, if it occurs*
4. *diffusion of the dissolved species in the aqueous phase*
5. *chemical reactions*

CHEMICAL REACTIONS

Numerous chemical reactions can go on between the various particulate and gaseous species which have been scavenged by the hydrometeors. For a review see ref. 2.

As an example of the various processes which are associated with clouds we will look at a very simple case. For this, we choose a small cumulus cloud in a remote marine environment. From the chemistry point of view we find there rather simple conditions which allow a study of the main occurring phenomena.

CHEMISTRY ASSOCIATED WITH A WARM MARINE CLOUD

The results which will be presented in this context were obtained with the dynamic framework of a two-dimensional slab-symmetric version of the three-dimensional model developed by Clark and co-workers (ref. 3-7) coupled to the *DEtailed SCAvenging Model* DESCAM as discussed in ref. 8,9. The results presented here represent a synthesis of ref. 10-13.

The cloud we will study is a moderate cumulus cloud with a cloud base around 800m and a cloud top extending up to 3km. The temperatures even at cloud top do not drop significantly below 0 °C. Thus, we can safely assume that only liquid hydrometeors were formed.

In a remote marine environment we can assume an unperturbed aerosol particle distribution which will be of oceanic origin. Thus, the small particles will preferentially consist of $(\text{NH}_4)_2\text{SO}_4$ and the larger ones of NaCl. In the model the aerosol particle distribution is prescribed as a superposition of 3 log-normal modes

$$\frac{dN}{d \ln r} = f_{APa}(\ln r) = \sum_{i=1}^3 \frac{n_i}{(2\pi)^{1/2} \log \sigma_i \ln 10} \exp\left(-\frac{[\log(r/R_i)]^2}{2(\log \sigma_i)^2}\right) \quad (1)$$

Mode <i>i</i>	n_i	R_i	$\log \sigma_i$	chemical compound
1	133	0.0039	0.657	$(\text{NH}_4)_2\text{SO}_4$
2	66.6	0.1330	0.210	$(\text{NH}_4)_2\text{SO}_4$
3	3.06	0.2900	0.396	NaCl

Table 2: Parameters for the maritime aerosol particle distribution as given in Eq. 1; n_i = total number of aerosol particles per cm^3 ; R_i = geometric mean aerosol particle radius in μm ; σ_i = standard deviation in mode i ; and chemical composition of the aerosol particle modes

This spectrum contains $170 \text{ particles cm}^{-3}$ consisting of $(\text{NH}_4)_2\text{SO}_4$ with a total mass of $5.5 \mu\text{g m}^{-3}$ and 3 particles cm^{-3} consisting of NaCl with a total mass of $24.4 \mu\text{g m}^{-3}$. Gas concentrations in the marine environment are generally low. Thus, we use concentration of SO_2 of 0.5 ppb(v), H_2O_2 of 0.5 ppb(v) and O_3 of 30ppb(v) in the boundary layer (<400m). Above the boundary layer we assumed that only O_3 was present at a concentration of 30 ppb(v); the other gas concentrations were assumed to be zero.

This allowed to study the transport of gases across the boundary layer by a medium sized convective cloud. An example for the case of SO_2 is given in Fig. 1. The shaded area gives the contours of the visible clouds. We see that one major cloud developed at around 13

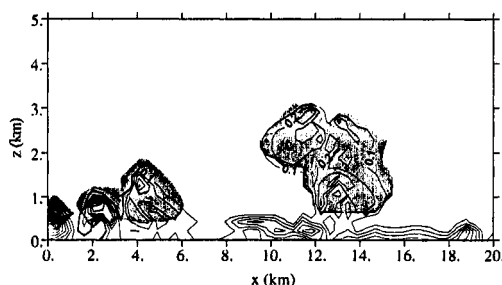


Fig. 1: SO_2 concentration fields in the air in ppb(v) after 45 min. of model time (19 min. of cloud life time). contour spacings: 0.1 ppb(v); the shaded area is the visible cloud ($q_c > 10^{-4} \text{ g/kg}$). (adapted from ref. 13)

km and 3 secondary clouds at the left corner of the domain. We chose to study only the main cloud and found that it « vented » about 60 % of the gas in its vicinity up into the free troposphere where it can participate in the long range transport. After half an hour of model time, however, only 75 % of the SO_2 transported aloft still existed in the cloudy air, the rest was scavenged into the cloud drops. This number depends of course on the type of cloud considered and on the solubility of the gas. The effect, however, is non-negligible and will allow a gas with a short life time in the boundary layer to leave its source region and to become environmentally relevant at distant locations.

In ref. 12 we further found an important up- and downward transport of aerosol particles across the mixed boundary layer (MBL) caused by the cloud. The net result of this transport emptied about 70 % of the aerosol from the MBL which is slightly higher than the

60 % previously found for gases (ref. 13). In addition, we found a downward transport of particles in all cases replenishing the MBL and, thus, preventing a complete depletion of the model MBL. We studied the mass transport and scavenging of particles by the cloud and found roughly 70 % of the particle mass vented up from the MBL entered the cloud drops due to nucleation.

Concerning these numbers a certain caution, however, is advised, as they were obtained by a 2-D model dynamics in a limited model domain. Thus, we can expect a certain dependency on the model architecture, the domain size and also the case studied. However, we are convinced that the general features will reappear as further sensitivity studies already indicate.

This is also true for the results concerning the aerosol particle concentration fields around the cloud. Here, we find evidence for an enhancement in both Aitken (Fig. 2a) particles and large and giant (Fig. 2b) particles. Our simulation confirms the measurements, *e.g.*, of Baumgardner et al. (ref. 14) who have found an increase of particles larger than 0.3 μm diameter at the outflow edges of a cloud. Our particles larger than 0.1 μm radius also increased in number concentration (Fig. 2b). This region was also associated with an increase in water vapour concentration and/or relative humidity. These particles were residues of evaporated drops or former Aitken particles that had taken up significant water vapour due to the moistening of the air by detrainment.

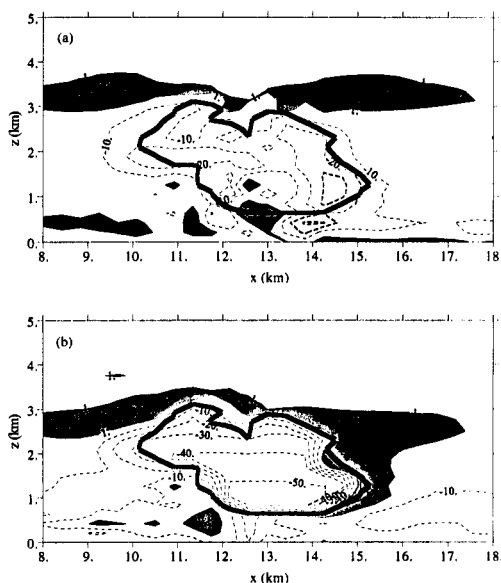


Fig. 2: Difference in (a) the number concentration of small aerosol particles (radius $< 0.1 \mu\text{m}$) in $\#/\text{cm}^3$, and (b) the number concentration of large aerosol particles (radius $> 0.1 \mu\text{m}$) in $\#/\text{cm}^3$ after 45min of model time (19 min of cloud life time) as compared to the initial state at $t=0$ min; the contour spacings are $10 \#/\text{cm}^3$, the solid line represents an increase and the dashed line represents a decrease in number concentration; the shaded area gives the region of increases larger $1 \#/\text{cm}^3$; the fat line is the contour of the visible cloud ($q_c > 0.1 \text{ g/kg}$). (adapted from Flossmann, 1998)

For the Aitken particles (Fig. 2a) we also noted an increase which is, however, decoupled from the region of enhanced relative humidity or large particle concentration. This enhancement resulted from unactivated free tropospheric aerosol which was lifted aloft by the rising cloud top.

Concerning the clouds we can, thus, note an important « venting » effect transporting gases and particles from the boundary layer to the higher atmosphere. In the free troposphere they tend to have longer lifetimes than in the boundary layer and can thus be transported to distant locations.

Clouds, however, take up also large amounts of particles and gases. These are processed in the liquid phase and will precipitate if the cloud develops rain.

The major amount of the pollution mass is incorporated into the cloud water through nucleation of aerosol particles (85 % - 95 %). Impaction scavenging of particles inside clouds is negligible due to the small mass left interstitially between the cloud drops. However, it becomes dominant below cloud base. Of the particulate pollution mass in the rain water 20 % - 40 % are scavenged below cloud due to impaction. Fig. 3 gives an example of the evolution of the rain fall rate at the surface and the deposition rate of the two incorporated particulate species $(\text{NH}_4)_2\text{SO}_4$ and NaCl. We see that roughly the double of NaCl is deposited as compared to $(\text{NH}_4)_2\text{SO}_4$. This is caused by the distribution of the particulate mass in the initial marine aerosol particle spectrum.

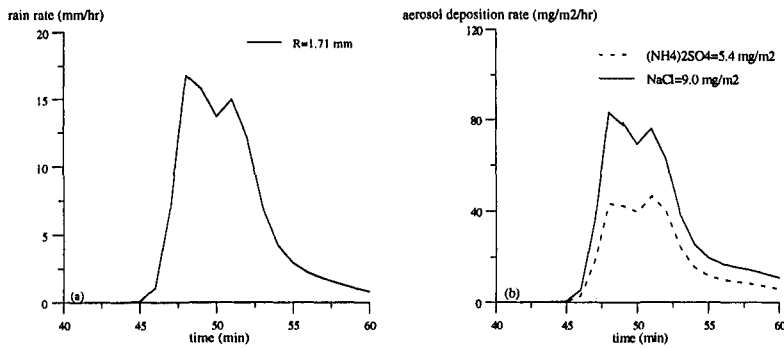


Fig. 3: Time evolution of (a) the rain rate in mm/hr, (b) the wet deposition rate of $(\text{NH}_4)_2\text{SO}_4$ and NaCl in $\text{mg}/\text{m}^2/\text{hr}$; R is the total precipitation in mm and AP the total wet deposition in mg/m^2 (adapted from ref. 12).

In addition to the particulate material also SO_2 gas is scavenged and oxidised to sulphate in the presence of H_2O_2 and O_3 . Here, we found (ref. 11) that the sulphate produced in the liquid phase was on the same order of magnitude as the sulphate scavenged below cloud by impaction ($\sim 7\%$). Concerning the sulphate in the rain we found that $2/3$ resulted from particle scavenging and roughly $1/3$ resulted from gas uptake and subsequent oxidation in the liquid phase. Furthermore, we have studied the fate of the pollutants in the liquid phase that do not precipitate. We found that the aerosol particle spectrum released by an evaporating cloud has significantly changed compared with the initial spectrum. The particles are larger and contain more soluble material. This is due on the one hand side to the collision processes among droplets combining water and contained pollution mass in larger hydrometeors and on the other hand due to the gas uptake and oxidation. The released particle spectrum consists, thus, of better CCN which form easily new clouds and even precipitation.

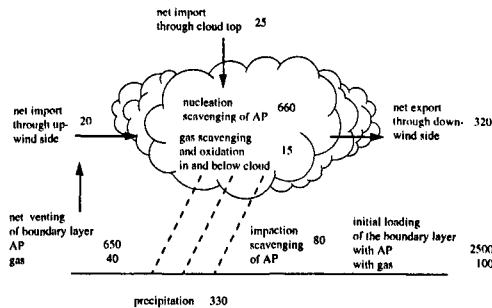


Fig. 4: Net mass transport and scavenging integrated over the 1h of simulation time; the values are given in kg pertaining to a 3-D cloud of 4km depth; for the transport the arrows give the net direction.

Fig. 4 displays some numbers concerning the net effect of the studied medium sized warm cloud on pollution. The numbers are a composite from the various papers discussed above and are extrapolated to a 3-D cloud. Certainly they depend significantly on the type and size of cloud studied as well as on the pollutants present.

CONCLUSION

Taking the example of a medium sized cumulus cloud forming in a remote marine environment the effect of clouds on the redistribution and modification of the chemical load of the atmosphere has been discussed. We find that clouds redistribute particulate and gaseous pollutants mass from the boundary layer to the free troposphere. Furthermore, clouds take up pollution mass into the hydrometeors and microphysical as well as chemical processes modify the chemical load of the drops. When the cloud precipitates the pollution mass is deposited on the ground with the rain. However, clouds never precipitate completely. Thus, a non-negligible amount of pollution stays in the atmosphere and is released back into the air when the cloud evaporates. This pollution loading is significantly altered as compared to the one existing before cloud formation. Thus, it becomes evident that clouds represent an efficient element in the environmental pollution chain.

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REFERENCES

1. H.R. Pruppacher, J.D. Klett. *Microphysics of clouds and precipitation*, 2nd edn, Kluwer Academic Publishers, Dordrecht (1997).
2. P. Warneck. *Chemistry of the natural atmosphere*, International geophysics series, Vol. 41, Academic Press, New York (1988).
3. T.L., Clark. *J. Comput. Phys.* 24, 186 (1977).
4. T.L., Clark. *J. Atmos. Sci.* 36, 2191 (1979).
5. T.L. Clark, R. Gall. *Mon. Weather Rev.* 110, 766 (1982).
6. T.L. Clark, R.D. Farley. *J. Atmos. Sci.* 41, 329 (1984).
7. W.D. Hall. *J. Atmos. Res.* 37, 2486 (1980).
8. A.I. Flossmann, W.D. Hall, H.R. Pruppacher. *J. Atmos. Sci.* 42, 582 (1985).
9. A.I. Flossmann, H.R. Pruppacher, J.H. Topalian. *J. Atmos. Sci.* 44, 2912 (1987).
10. A.I. Flossmann. *Tellus* 43B, 301 (1991).
11. A.I. Flossmann. *J. Atmos. Res.* 32, 255 (1994).
12. A.I. Flossmann. *J. Atmos. Sci.*, 55, 879 (1998).
13. A.I. Flossmann, W. Wobrock. *J. Geophys. Res.* 101, 18639 (1996).
14. D. Baumgardner, W.A. Cooper, L.F. Radke. In *Proceeding of the 12th ICCP*, 19-23 Aug. 1996, Zurich, pp. 308-311 (1996).