IGACtivities Newsletter

of the International Global Atmospheric Chemistry Project

Issue No. 23

April 2001

In this Issue

A Note From the IGAC Chair: *Guy Brasseur*

Atmospheric chemistry, aerosols and climate

Everyone has seen the graph presented by the Intergovernmental Panel for Climate Change (IPCC) illustrating radiative forcing caused by various human-induced perturbations. This diagram illustrates the globally averaged watts per square meter of forcing produced since the pre-industrial era in response to changing atmospheric concentrations of carbon dioxide and other "well mixed" greenhouse gases, stratospheric and tropospheric ozone, and aerosols.

This diagram is somewhat misleading because it does not differentiate between the forcings that are global (e.g., CO_2) and those that clearly have a regional nature (e.g., aerosols). Furthermore, the total forcing (derived by adding the best estimates of IPCC) is not significantly larger than the uncertainty associated with the estimated total forcing. If the geographical inhomogeneity in the radiative forcing is taken into account, the picture becomes even more complicated and uncertain. An important task for the scientific community, therefore, is to define a research agenda that rapidly leads to a clearer picture and, hence, a clearer message for decision-makers.

One major uncertainty is associated with the direct and indirect radiative effects of aerosols. In early climate models this type of forcing was ignored, but more recent investigations have attempted to account for the effects of sulfate particles and other aerosols (dust, soot, etc.). Even this approach remains an oversimplification because in many cases, aerosols are multi-component particles with a chemical composition that can vary in space and time.

Recent field campaigns (e.g., ACE-1, ACE-2, TARFOX and others) have shown the important role of aerosols for the climate system. Local and even regional effects much larger (20 Wm^{-2}) than the globally averaged forcing (a few Wm^{-2}) have been reported, which could modify our current understanding of human-induced climate change. These particles also contribute dramatically to regional pollution, which has become a major issue in many areas of Asia and Africa, especially during the dry season.

Much work involving the atmospheric chemistry and climate communities is needed before fundamental issues related to the microphysics and chemistry of aerosols are fully resolved. It is therefore important that funding agencies recognize the urgency of the problem. Field campaigns such as the IGAC-sponsored ACE-Asia project (which is about to start) will provide new information regarding aerosol formation and fate in eastern Asia, a region where aerosol sources are exceptionally high. The solution to the aerosol/climate question requires a comprehensive approach including laboratory studies, coordinated field campaigns, space observations and modeling.

The present issue of the IGAC Newsletter provides a synthetic view of some important issues related to cloud chemistry and the indirect effects of aerosols.

GLOBAL IGBP CHANGE

CACGP

SCIENCE FEATURES

Clouds in the troposphere

Contributed by **Sandro Fuzzi** *(s.fuzzi@isao.bo.cnr.it), Istituto di Scienze dell'Atmosfera e dell'Oceano, Consiglio Nazionale delle Ricerche, Bologna, Italy.*

Clouds form due to the condensation of water vapor onto atmospheric aerosol particles in air that has become supersaturated. About 60% of the Earth's surface is covered by clouds at any given time, even though clouds occupy only 7% of the troposphere's total volume [Lelieveld *et al.*, 1989; Pruppacher and Jaenicke, 1995] and the volume fraction of liquid water in clouds rarely exceeds 10^{-6}. Although this volume fraction represents a fairly small value, clouds have a major influence on the entire atmosphere.

In fact, clouds redistribute trace compounds emitted at the Earth's surface in the vertical from the boundary layer to the free troposphere and, in some cases, to the stratosphere. They interact with incoming solar radiation and long wave radiation emitted by the Earth, thus affecting both the atmosphere's photochemistry and the Earth's radiation budget. Clouds produce precipitation, an efficient mechanism for removing trace components from the atmosphere. Finally, they constitute an ideal reaction medium, allowing chemical transformations that would otherwise not take place in the gas phase or would proceed at much slower rates. For example, model studies [e.g., Langner and Rodhe, 1991] have shown that, on a global scale, more than 70% of the global oxidation of SO_2 to SO_4^{2-} occurs within cloud droplets.

Chemical constituents in the liquid phase of clouds derive from the incorporation of the soluble species contained in aerosol particles on which cloud droplets nucleate or which are scavenged by the droplets themselves, and from the dissolution of trace gases within the droplets. The different species introduced in cloud droplets can then react in the liquid phase to form other products.

The notion that chemical reactions in a cloud's aqueous phase might be important for atmospheric chemistry was advanced by Junge and Ryan [1958], who called attention to the role of ammonia and the importance of the oxidation of dissolved sulfur dioxide catalyzed by heavy-metals. Chameides and Davis [1982] pointed out the effects on cloud chemistry of free radicals scavenged from the gas phase and / or produced within the droplets.

Two families of chemical species are key participants in the cloud liquid phase chemical reactions: sulfur compounds and organic compounds. While much work has been done on the liquid phase reactions of sulfur species in clouds [see, e.g., Warneck, 1991], the organic chemistry within cloud droplets is still largely unknown. Little knowledge is available even on the actual organic composition of cloud water [Saxena and Hildemann, 1996]. Traditionally, gas phase atmospheric chemistry and cloud chemistry have been two fields of research that have proceeded in parallel for many years, without too many interactions. The atmosphere is a multiphase system, however, where, in addition to the gas phase, the solid (dry aerosol) and liquid phases (wet aerosol, cloud and precipitation elements) coexist; chemical processes in one phase cannot be properly assessed without a comprehensive knowledge of the processes within the multi-phase system. For example, Lelieveld and Crutzen [1990, 1991] drew attention to the effects of clouds on the tropospheric O_3 concentration. Although the quantitative estimations of this study have been questioned [Liang and Jacob, 1997], the importance of addressing atmospheric chemistry processes in a multiphase context clearly emerges from this study and others that followed.

Another relevant issue in cloud chemistry was stressed by Ogren and Charlson [1992], who showed that the chemical composition of cloud droplets is size-dependent. Model results [Hegg and Larson, 1990] have shown, for example, in-cloud S(IV) to S(VI) conversion rates that are three to thirty times higher when explicit droplet size-dependent chemistry is introduced, compared to a bulk approach. While most current cloud models take into account the size-resolved chemistry within cloud droplets, there is still a lack of experimental data for the comparisons with model results or for an investigation of the processes leading to the detected chemical inhomogeneities across the droplet size spectrum [Noone *et al.*, 1988; Collett *et al.*, 1995; Laj *et al.*, 1998; Bower *et al.*, 2000]. In fact, it has been shown that the solute concentration in cloud droplets can either increase or decrease with increasing droplet size [Schell *et al.*, 1997].

It should be pointed out that most current knowledge on cloud chemistry is related to warm (liquid phase) clouds. Ice processes (mixed- and ice-clouds) and their impact on cloud chemistry remain largely unknown, and this topic constitutes an important challenge for the future, since the presence of the ice phase characterizes most clouds, at least over the mid-latitude regions of the globe.

This issue of the IGAC Newsletter provides an overview of some key issues in cloud chemistry and related atmospheric processes. D. Hegg describes how clouds impact aerosol populations. H. Herrmann and co-workers survey S(IV) to S(VI) aqueous phase oxidation by both radical and non-radical pathways. M.C. Facchini reviews current understanding of the organic chemistry of cloudwater and its effect on cloud properties. M. Barth describes how the effects of clouds on atmospheric trace constituents are treated in numerical models. Finally, K. Noone discusses the so-called indirect radiative effect of aerosols, a term which denotes the process(es) by which clouds influence the Earth's radiative budget.

References begin on Pg. 18.

The impact of clouds on aerosol populations

Contributed by **D.A. Hegg** (deanhegg@atmos.washington.edu), *Department of Atmospheric Sciences, University of Washington, Seattle, Washington, USA.*

Introduction

Clouds and precipitation have long been recognized as important sinks for atmospheric aerosol, with size and solubility-induced selective removal affecting both the aerosol size distribution and chemical nature of the aerosol population [cf., Junge, 1963; SMIC, 1971]. The role of clouds as instruments of differential transport of aerosols in the vertical has also been appreciated and studied throughout the history of research on aerosol-cloud interactions [cf., Rodhe, 1983; Kleinman and Daum, 1991; Cautenet and Lefeivre, 1994]. More recently, chemical processes within cloud drops have been shown, in a plethora of experimental and theoretical studies, to be capable of altering the size and composition of aerosol particles processed by them [e.g., Easter and Hobbs, 1974; Hegg *et al*., 1980; Flossmann *et al*., 1987; Hoppel *et al*., 1990, 1994; Leaitch, 1996; Bower *et al*., 1997; Bott, 1999]. Still more recently, support for nucleation of new particles in the near-cloud environment has been forthcoming [e.g., Hegg *et al*., 1990; Frick and Hoppel, 1993; Wiedensohler *et al*., 1997].

Taken as a whole, the above body of research suggests that there are essentially four processes by which clouds can impact aerosol populations:

- Vertical transport
- Scavenging processes (both with water and ice hydrometeors)
- Chemical processes in cloud drops
- Particle formation near clouds

Of course, these mechanisms commonly act in concert and frequently all can significantly impact aerosol populations within a single cloud event (as illustrated schematically in Figure 1). Indeed, it is useful to consider these processes as terms in a continuity equation for particles of a particular size range, i.e., to visualize the problem of cloud processing the way a prognostic model would treat it. Viewed from this perspective, all these processes are clearly operable simultaneously; it is only their relative magnitudes that change with conditions. Furthermore, given that a set of such continuity equations must be utilized (one for each size range), the size-dependent nature and impact of all of these processes becomes clear. For example, chemical processes which add mass to pre-existing particles act as a sink for the relatively small initial particles but are a source of larger particles. It also becomes clear that these processes can act not merely simultaneously but also synergistically, as when scavenging of pre-existing aerosols aids near-cloud particle nucleation. Nevertheless, in the space available, it is only feasible to address these processes separately and delineate the salient aspects of each.

Vertical transport

If vertical transport could be isolated from the other processes just introduced, it would be the most straightforward mechanism by which aerosol populations are altered by clouds. Convective clouds in particular offer a rapid pathway for the vertical transport of air from the boundary layer into the free troposphere. Because nearly all primary aerosol sources are surface-based, this rapid transport affords a means of getting aerosols into the free troposphere without the sometimes substantial changes incurred by aging processes. Furthermore, while such transported aerosols will typically be much reduced in concentration compared to boundary layer values, they can still be sufficiently high to significantly perturb concentrations aloft [e.g., Kleinman and Daum, 1991]. Nevertheless, as noted by Rodhe [1983], such cloud-convective transport must necessarily involve wet-scavenging processes, processes which will generally be the dominant modulators of the aerosol size distribution. Hence, in this brief review, we turn next to these processes.

Scavenging processes

The term ‘scavenging processes’ encompasses a wide variety of cloud-aerosol interactions, as illustrated in

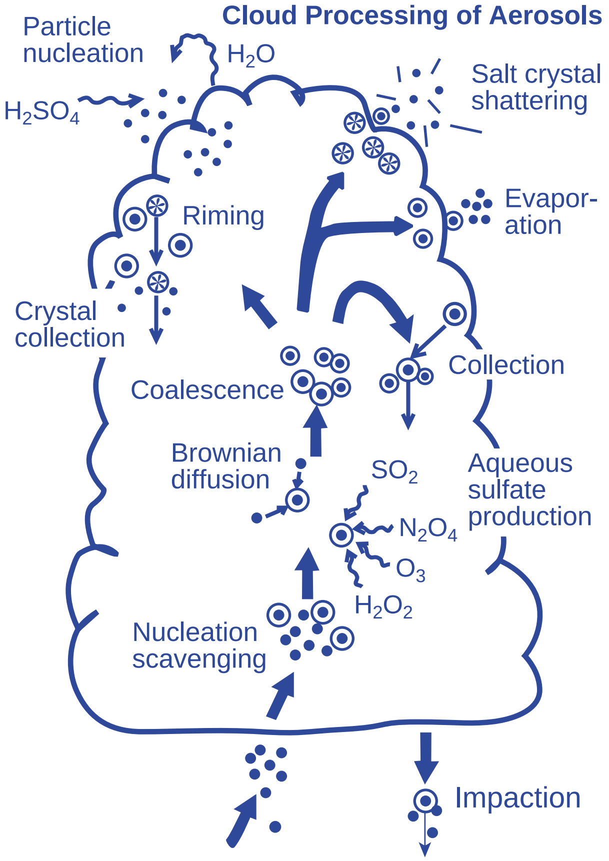

Figure 1. A schematic diagram of the in- or near-cloud processes that can alter the aerosol size distribution.

Figure 1. These include nucleation scavenging of cloud condensation nuclei (CCN), diffusion scavenging of interstitial aerosol by the activated cloud drops (or ice particles) and impaction of aerosols onto both ice and water hydrometeors sufficiently large to have appreciable fall velocities. Furthermore, as noted by Hudson and Frisbie [1991], the collision-coalescence process will act as an effective aerosol modification mechanism because the larger drops formed will yield, in principle, single aerosol particles upon evaporation either below cloud or in detraining air aloft. Similarly, collection processes, which involve capture of cloud drops by larger falling hydrometeors, would yield the same results if subsequent evaporation was significant. Hence, these processes all act as sort of aqueous-enhanced coagulation processes. In consequence, even processing by non-precipitating clouds can significantly alter the aerosol size distribution, though no aerosol mass may actually be removed from the atmosphere in the immediate process. For precipitating clouds, of course, actual removal in precipitation must be added to all the other processes that impact the aerosol size distribution.

The results of the action of these mechanisms will vary from case to case but several broad results can be generally invoked. First, there is a tendency for the size distribution to broaden as well as for number concentrations to decrease [e.g., Flossmann *et al*., 1985; Alheit *et al*., 1990; Pandis *et al*., 1990; Noone *et al*., 1992; Khain *et al*., 1999]. Second, at least for non-precipitating clouds, a marked minimum in the size distribution will form at the particle size corresponding to the effective maximum supersaturation (and the smallest activation radius) achieved in the processing cloud(s) [cf., Fitzgerald *et al*., 1998; Feingold *et al*., 1996]. This arises from the various cloud drop collection processes discussed above and, if rainout is minimal, can actually create a new mode in the size distribution (as can sulfate production, discussed below). There is considerable observational support for this nucleation minimum, at least in marine air [e.g., Hoppel *et al*., 1990]. However, the location (in size) and depth of this minimum will depend not only on the aerosol size distribution but on its chemical composition as a function of size. Hence, this topic leads us next into the general area of differential scavenging due to aerosol composition.

The activation of aerosol particles to form cloud drops, commonly referred to as nucleation scavenging, is by far the most important mechanism for aerosol mass scavenging and commonly results in a drastic depletion of the accumulation mode in cloud. The well-known Köhler equation, which governs this process, clearly shows the dependence of the process on aerosol composition and, in fact, numerous field studies have documented this dependence for atmospheric aerosols [e.g., Noone *et al*., 1992; Svenningsson *et al*., 1997; Martinsson *et al*., 1999]. These studies have demonstrated a favorable partitioning of soluble aerosols into cloud drops and, conversely, relatively inefficient scavenging of insoluble aerosols. However, a number of caveats must be imposed on this general picture. Atmospheric aerosols are commonly internal mixtures with both soluble and insoluble components. For example, elemental carbon, which is hydrophobic, is frequently coated with a soluble layer of sulfate or nitrate with a resultant higher nucleation scavenging efficiency than would be expected from its structure. Another factor, which is important to keep in mind, is the variability in the internal microphysical and dynamical structure of clouds. For example, Gieray *et al.* [1997], even after taking into account the composition and internal mixing of aerosols, found anomalies in scavenging which they attributed to spatial variability of water vapor supersaturation. Finally, much of both the experimental and field work just discussed dealt solely with "warm" or purely water clouds. Mixed-phase clouds present a still more complex picture.

Mixed-phase clouds are more prevalent than either pure water or ice clouds, much more so in the mid-latitude bands of the Northern Hemisphere where aerosol concentrations are highest. From the standpoint of aerosol removal from the atmosphere, such mixed-phase clouds are considerably more efficient than single-phase clouds due to the relative efficiency of the riming and accretion processes, particularly riming [e.g., Hegg *et al*., 1989; Respondek *et al*., 1995]. But beyond this is the issue of effective scavenging of otherwise poorly scavenged aerosols by ice particles. Insoluble aerosols such as soil dust, elemental carbon and relatively hygrophobic organics, largely impervious to nucleation scavenging in their own right, have long been known to be favorable nuclei for ice crystal growth from the vapor phase [cf., Pruppacher and Klett, 1997]. Furthermore, such crystals, when formed, have been demonstrated to be rather effective scavengers of interstitial aerosols, including insoluble ones [Bell and Saunders, 1995; Song and Lamb, 1994]. Hence, mixed-phase clouds will tend to have a less composition-dependent impact on aerosol scavenging than single-phase clouds.

Chemical processes in cloud drops

By far the most studied cloud chemical process capable of significantly modifying aerosol size is the aqueous conversion of SO_2 to sulfate. Evidence of the significance of this process has been accumulating steadily for decades and it may now be regarded as well established. However, both modeling and observational studies have suggested considerable variability as to precisely where in the size distribution the prospective new sulfate mass will reside [cf., Hegg *et al*., 1980, 1992; Yuen *et al*., 1994; Bower *et al*., 1997], with considerable dependence on the initial composition and size distribution of the cloud forming aerosol. Additionally, of course, will be factors external to the aerosol itself, such as maximum cloud updraft, that will determine the size demarcation between activated and inactivated particles and thus the initial aerosol sizes only above which appreciable aqueous oxidation can take place.

Nevertheless, once again some general (and interesting) conclusions can be drawn. Most studies have concluded that in-cloud sulfate production adds mass most effectively at sizes just above the minimum activation radius achieved in cloud. For example, chamber studies conducted by Hoppel *et al.* [1994] show this quite clearly, and it is suggested in several field studies as well [e.g., Hegg *et al.*, 1980; Leaitch, 1997]. While there are both observational [cf., Bower *et al.*, 1997] and theoretical [Flossmann *et al.*, 1987] studies which suggest significant variations at further distances from the mean activation radius (larger), all studies are in agreement that the enhancement will occur for particles on the order of 0.1 µm or larger. This is of considerable significance in that all such particles will likely be effective CCN in most atmospheric clouds. Hence, while the number of CCN does not in principle change, their activation supersaturation will be lower, thus raising the possibility of activation in successor clouds with lower supersaturation [cf., Hegg, 1990; Kaufman and Tanre, 1994]. Indeed, numerous studies, both observational and theoretical, suggest substantial changes in the cloud condensation nuclei (CCN) activation spectrum due to cloud processing [e.g., Hegg *et al.*, 1980; Fitzgerald *et al.*, 1998; Broadbury *et al.*, 1999; Zhang *et al.*, 1999]. Feingold *et al.* [1996] have proposed that such sulfate production would increase the new size of CCN in a similar manner to the collision-coalescence process discussed above. It has been suggested that the location in the size distribution of the additional sulfate mass produced by aqueous sulfate production enhances the light-scattering efficiency of cloud processed aerosols and thus affects the direct aerosol forcing of climate [Heintzenberg and Lelieveld, 1992].

One aspect of most of the studies discussed above, which is of considerable moment, is their applicability to, or exclusive concern with, non-precipitating clouds. Certainly the removal of any substantial number of cloud drops, particularly the preferential removal of larger drops, will impact modification of size distribution and CCN activation spectrum. This can be seen in the study of Khain *et al.* [1999] where, by and large, the aerosol accumulation mode is much reduced rather than enhanced by cloud processing. Nevertheless, other studies have suggested significant cloud microphysical impacts due to sulfate production even taking precipitation into account [e.g., Flossmann *et al.*, 1987; Kogan *et al.*, 1994]. Furthermore, many clouds are largely nonprecipitating.

Particle formation

The observational record of enhanced particle concentrations in the vicinity of clouds is now quite lengthy [e.g., Dinger *et al.*, 1970; Saxena *et al.*, 1970; Saxena and Gravenstein, 1994; Hegg *et al.*, 1990; Hoppel *et al.*, 1994; Saxena, 1996]. Early work, which dealt largely with increases in CCN, predominantly hypothesized enhancements in pre-existing particle size due to in-cloud sulfate production to explain the phenomenon; although the possibility of shattering of supersaturated salt droplets formed by rapid evaporation of cloud drops (as per Dessens [1949]) was also considered [e.g., Radke and Hegg, 1972]. However, the viability of this latter process is not entirely clear [Mitra *et al.*, 1992]. More recently, advances in particle sizing instrumentation have permitted more complete characterization of near-cloud particle formation and support the formation, at least on occasion, of quite small particles rather than the larger particles that constitute the effective CCN population. The mechanistic explanation for such small particle production has generally involved homogeneous nucleation from the gas phase. While there is some debate on the extent to, and manner in which the new particle formation is an example of "cloud processing," it seems quite clear that clouds are involved. For example, Shaw [1989] postulated that only in very clean air in which virtually all pre-existing aerosol had been removed by cloud scavenging could binary nucleation of H_2O-H_2SO_4 particles occur. Hegg *et al.* [1990], in a diagnostic modeling study of observed high ultra-fine particle concentrations above marine stratocumulus, found that high water vapor concentrations detrained from the cloud deck coupled with an unusually high actinic flux (conducive to OH formation and thus H_2SO_4 production) due to isotropic backscatter from the cloud droplets were the main contributors to particle formation, though somewhat reduced particle surface area played some role. Similar observations of new particle formation adjacent to stratiform clouds have been made by Frick and Hoppel [1993] and Kutz and Dubais [1997] with attribution to the same mechanisms. It is also possible that the nucleation is ternary, involving NH_3, rather than binary [cf., Coffman and Hegg, 1994; Weber *et al.*, 1995].

A slightly different priority with respect to contributing factors is likely present in the observations of particle formation in evaporating Antarctic stratus by Saxena [1996] where low temperature and the low pre-existing aerosol surface area were no doubt of considerable importance. Similarly, the phenomenon observed by Perry and Hobbs [1994], of particle formation in air detraining aloft from convective clouds, was partially attributable to the low temperatures and low aerosol surface area aloft on the basis of diagnostic modeling carried out on the cases studied. The overall scenario suggested by Perry and Hobbs, in which convective clouds bring up SO_2 to higher levels aloft while simultaneously removing particles, followed by H_2SO_4 production and particle nucleation in the cold, moist detraining air, has been adopted to explain still larger-scale phenomena by Clarke *et al.* [1998]. These workers found evidence of par-

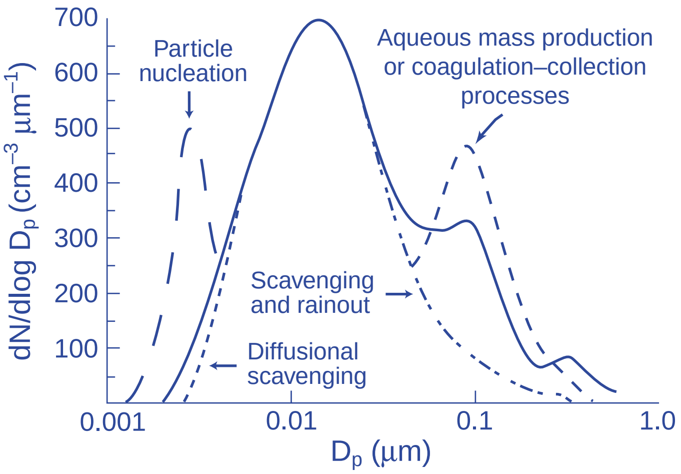

Figure 2. A qualitative schematic illustrating the impact of the various processes discussed in the text on the aerosol size distribution. The magnitude of the individual effects will be scenario dependent and could be either substantially larger or smaller than those shown here.

ticle formation aloft associated with detraining air from moderate to large convective clouds and proposed a scenario similar to the Perry-Hobbs scheme but applied to a much larger scale and involving growth after formation with gradual cyclic subsidence and re-introduction into the boundary layer as CCN. The extent to which this larger scale phenomenon can be considered as modulation of the aerosol size distribution due to cloud processing is not entirely clear but certainly clouds play a vital role in the process as presented by Clarke *et al.* [1998] and it is therefore included here.

Synthesis of mechanisms

Given the multiplicity of mechanisms that must be considered, what might one expect for an overall effect? Clearly this will depend on the particular scenario to be evaluated and, indeed, the phenomenology of cloud effects on the aerosol size distribution and composition is diverse. In many instances in which non-precipitating clouds of small extent and liquid water content form on aerosols, little effect is to be expected; in others, with high actinic flux at cloud top, sufficient SO_2 (and possibly NH_3) and detraining water vapor, nucleation is to be expected; sufficient SO_2 and time in-cloud should normally produce significant sulfate mass; rapidly precipitating clouds with little SO_2 present should strongly deplete the accumulation mode; and so forth.

Figure 2 serves as a schematic to illustrate the potential impact of all the processes discussed here, assuming favorable conditions. The actual spectral modification to be expected for any particular event will be, once again, dependent on the specific conditions for that particular scenario and how they amplify or retard the impact of each process. Perhaps the most important single point to keep in mind is that clouds can have a profound local impact on both the size distribution and composition of aerosols, and that on larger scales clouds are major factors in the determination of aerosol properties.

Acknowledgment

This paper was prepared with support from the Office of Naval Research, grant N00014-97-0132. The author thanks Professor Marcia Baker for useful comments.

Sulfur chemistry in clouds

Contributed by **H. Herrmann** (herrmann@tropos.de), **B. Ervens** and **D. Weise**, *Institut für Troposphärenforschung, Leipzig, Germany.*

Introduction

Clouds are a tropospheric environment for multiphase chemical transformations. Chemical constituents in the liquid phase of clouds derive from the incorporation of soluble species contained in the aerosol particles on which cloud droplets grow (cloud condensation nuclei, CCN) and from the dissolution of trace gases in cloud water. The different species introduced in cloud droplets can eventually react in the liquid phase to form other products. The processing of chemical compounds in liquid water droplets influences the chemical composition of the tropospheric gas phase as well as the properties of the aerosol after cloud processing. A proper description of liquid phase chemical processes is therefore necessary to assess the role of clouds in a changing atmosphere. Understanding the chemistry of clouds requires a detailed knowledge of the factors controlling chemical composition and concentration of chemical species in droplets.

Sulfur(IV) oxidation reactions occur at a much faster rate in clouds than in the clear air. Model calculations [e.g., Langner and Rodhe, 1991] have shown that, on a global scale, tropospheric in-cloud S(IV) oxidation is 2-5 times more important than out-of-cloud oxidation. Many details of the processes involved, however, are still the subject of a wide variety of laboratory studies in multiphase modeling and field measurements.

Chemical systems

S(IV) oxidation by non-radical oxidants

Appreciable progress has been made over the last decade by laboratory studies in identifying the reactions responsible for S(IV) oxidation in the atmospheric liquid phase, and in determining the associated rate coefficients [Warneck, 1991]. Reviews are available on S(IV)-oxidation by H_2O_2 and other peroxides [Warneck *et al.*, 1996a] or by ozone [Hoffmann, 1986]. It should be noted that organic peroxides can also potentially contribute to sulfur oxidation. Because the hydrogen peroxide concentration will generally exceed the concentration of organic peroxides, oxidation by H_2O_2 will dominate.

As the oxidation of S(IV) by hydrogen peroxide appears to be the most effective pathway in cloudwater, special attention needs to be paid to assess all potential sinks and sources which may not only be incorporated from the gas phase but also formed by (1) reaction of HO_2 / O_2^- with Fe^{2+} and Cu^+, or (2) peroxyl radical recombination in solution. Because of this, a coupling to organic cloud chemistry exists (see below).

A data and literature compilation with regards to oxidation of S(IV) by non-radical oxidants is found in the HALIPP final report [Warneck *et al.*, 1996a].

Table 1. Comparison of sulfite radical anion generation processes initiated by free radicals and radical anions. S denotes the source strength of each process, τ_X is the half–life of the radical X with regards to its reaction with HSO_3^- (T = 298 K, applying $[HSO_3^-] = 5 \times 10^{-7}$ mol l^{-1} after Warneck [1992]).

Radical X	[X] [mol/l], Ref.	k (X + HSO_3^-) [l mol^{-1} s^{-1}], Ref.	S_X (SO_3^-) mol l^{-1} s^{-1}	S_X (SO_3^-) / ΣS_X (SO_3^-)	τ_X [ms]
OH	6×10^{-13}, (1)	4.5×10^9, (5)	1.4×10^{-9}	0.39	0.44
NO3	1×10^{-13}, (1)	1.4×10^9, (6)	7.0×10^{-11}	0.02	1.4
SO_4^-	1×10^{-12}, (2)	6.8×10^8, (7)	3.4×10^{-10}	0.10	2.9
Cl_2^-	8×10^{-12}, (3)	3.4×10^8, (5)	1.4×10^{-9}	0.39	5.9
CO_3^-	1.4×10^{-10}, (4)	5.0×10^6, (8)	3.5×10^{-10}	0.10	400

References: [1]Lelieveld and Crutzen, 1991; [2]Jacob *et al.*, 1989; [3]Chameides, 1986; [4]Chameides and Davis, 1982; [5]Huie and Neta, 1987; [6]Exner *et al.*, 1992; [7]Buxton *et al.*, 1993; [8]Herrmann *et al.*, 1991.

S(IV) oxidation by radical oxidants

Aqueous chemical conversions may not only be driven by the above-mentioned classical oxidants but also by free radicals. Radicals may originate from the gas phase as OH, HO_2, NO_3, CH_3O_2 and others [Davidovits *et al.*, 1995] or from photolysis within solution [Zellner *et al.*, 1990]. These species are referred to as primary radicals, as opposed to secondary radicals which are solely formed within aqueous atmospheric particles such as SO_X^- (x = 3,4,5), Cl / Cl_2^-, Br / Br_2^- and CO_3^-. Radicals exist in solution in very small concentrations which can currently only be assessed from box models, however, they exhibit a very high reactivity towards inorganic and organic constituents of cloud droplets.

Radical reactions in diluted aqueous solutions can only be of importance in the troposphere. A classic compilation is the review of Graedel and Weschler [1981], which still gives a good overview on the topic of this contribution. In addition, two more recent treatments by Huie [1995] and Zellner and Herrmann [1995] summarize the state of knowledge as of 1995. The radical oxidation may be initiated by thermal decomposition of transition metal complexes or by direct reaction of radicals X with S(IV), i.e., for cloud conditions mainly bisulfite:

$$X + HSO_3^- \rightarrow X^- + H^+ + SO_3^- \qquad \text{(R-1)}$$

Table 1 gives a comparison of fluxes for the most important tropospheric aqueous phase radical oxidants.

The hydroxyl radical appears to be most efficient in initiating S(IV) oxidation. It should be noted, however, that radical concentrations for the calculation of fluxes in Table 1 have been estimated based on available considerations from literature. More details are found in Zellner and Herrmann [1995].

Under the conditions of the atmospheric aqueous phase sulfite radical anions (SO_3^-) are converted to peroxomonosulfate radical anions (SO_5^-) by reaction (R-2):

$$SO_3^- + O_2 \rightarrow SO_5^- \qquad \text{(R-2)}$$

The peroxomonosulfate radical anion itself may react with HSO_3^-:

$$\begin{aligned} SO_5^- + HSO_3^- &\rightarrow SO_3^- + HSO_5^- &\text{(R-3a)}\\ &\rightarrow SO_4^- + HSO_4^- &\text{(R-3b)} \end{aligned}$$

This branching reaction (R-3 a,b) apparently is a key process in the conversion of S(IV) whenever sulfur-oxy radicals and no transition metal ions are involved. However, the currently available kinetic data base shows considerable scatter (Table 2). In reaction (3a) the peroxomonosulfate anion will undergo a non-radical oxidation of HSO_3^-. The sulfate radical anion on the other hand is produced by reaction (3b). It will subsequently react with HSO_3^- according to reaction (R-1) for X = SO_4^-.

Termination of the chain reaction will occur in radical-radical recombination reactions. Under laboratory conditions, these may involve reactions of the sulfur-oxy radical anions formed in the system. Under natural conditions, however, recombination with HO_2 or O_2^- will become much more important due to their high solution phase concentrations. See Huie [1995] and Zellner and Herrmann [1995] for a discussion of processes, and Herrmann *et al.* [2000] for a more recent modeling study.

Interactions with transition metal ions (TMI's)

Transition metals are common constituents of atmospheric water [see Warneck, 1992; Graedel *et al.*, 1986; Weschler *et al.*, 1986; Pehkonen *et al.*, 1992, 1993]. The most important of these species apparently is Fe with concentrations in the aqueous atmospheric phase of

Table 2. Kinetic data for the reaction of peroxomonosulfate radical anions with bisulfite

k_{3a} $[l\ mol^{-1}\ s^{-1}]$	k_{3b} $[l\ mol^{-1}\ s^{-1}]$	$k_{3a} + k_{3b}$ $[l\ mol^{-1}\ s^{-1}]$	BR (a)	Exp. Method	Ref.
$3x10^8$	$1.5x10^8$	$4.5x10^8$	0.33	Estimate, PR (b)	(1)
		$< 3x10^5$	0.75	PR, BR estimated (c)	(2)
		$(1.2 \pm 0.1)x10^5$		SS-γ-Rad. (d)	(3, 4)
			0.08	Scav. Exp. (e)	(5)

Remarks: (a) Branching ratio $k_{3b} / (k_{3a} + k_{3b})$, (b) Estimated, based on pulse radiolysis experiments, (c) Measured upper limit for the overall reaction (3), branching ratio estimated, (d) Value derived from steady-state radiolysis experiment, (e) Value determined from scavenger experiments, absolute rate constant not determined.

Table 3. Mechanism of the iron catalyzed oxidation of S(IV) at pH = 3 after Ziajka *et al*. [1993, 1994] and Warneck *et al*. [1996b].

No.	Reaction	Rate Coefficient(a)
(R—4)	$FeOH^{2+} + HSO_3^- = [FeOHSO_3H]^+$	$K_0 \approx 600$ l / mol
(R—5)	$[FeOHSO_3H]^+ \rightarrow Fe^{2+} + SO_3^- + H_2O$	$0.065\ s^{-1}$
(R—2)	$SO_3^- + O_2 \rightarrow SO_5^-$	$2.5x10^9$
(R—6)	$Fe_2 + SO_5^- (+H_2O) \rightarrow FeOH^{2+} + HSO_5^-$	$6.5x10^5$ (b)
(R—7)	$Fe^{2+} + HSO_5^- \rightarrow FeOH^{2+} + SO_4^-$	$3.0x10^4$ (b)
(R—8)	$FeOH^{2+} + HO_2 \rightarrow Fe^{2+} + O_2 + H_2O$	$1.3x10^5$
(R—9)	$Fe^{2+} + HO_2\ (+H_2O) \rightarrow FeOH^{2+} + H_2O_2$	$1.2x10^6$
(R—10)	$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + OH$	75
(R—11)	$Fe^{2+} + SO_4^- (+H_2O) \rightarrow FeOH^{2+} + SO_4^{2-} + H^+$	$3.5x10^7$
(R—12)	$Fe^{2+} + S_2O_8^{2-} (+H_2O) \rightarrow FeOH^{2+} + SO_4^{2-} + SO_4^- + H^+$	12
(R—3a)	$SO_5^- + HSO_3^- \quad \rightarrow HSO_5^- + SO_3^-$	$1.2x10^4$ (c)
(R—3b)	$SO_5^- + HSO_3^- \quad \rightarrow SO_4^{2-} + SO_4^- + H^+$	$4.8x10^2$ (b)
(R—13)	$SO_4^- + HSO_3^- \rightarrow SO_4^{2-} + SO_3^- + H^+$	$6.8x10^8$
(R—14)	$SO_5^- + SO_5^- \rightarrow S_2O_8^{2-} + O_2$	$7.0x10^7$
(R—15)	$HO_2 + SO_5^- \rightarrow HSO_5^- + O_2$	$2.5x10^9$ (b)
(R—16)	$HSO_5^- + HSO_3^- + H^+ \rightarrow 2\ SO_4^{2-} + 3\ H^+$	~ 10^4 at pH 3
(R—17)	$H_2O_2 + HSO_3^- + H^+ \rightarrow SO_4^{2-} + H_2O + 2\ H^+$	~ 10^4 at pH 3

Remarks: (a) In units of $l\ mol^{-1}s^{-1}$ unless otherwise stated, data from Ziajka *et al*. [1993]; (b) see Warneck *et al*. [1996b] and references therein; (c) Rate constant for the overall reaction (3a)+(3b).

about $1x10^{-6}$ mol l^{-1} [Warneck, 1992]. However, field measurements indicate that the concentration of Fe may vary by several orders of magnitude, i.e., between nanomolar and micromolar in rain and between micromolar and millimolar in fogwater [Hoigné *et al*., 1993]. The Fe content of tropospheric droplets originates from Fe_2O_3 which dissolves in acidic solutions (pH < 4). A method is available for the simultaneous determination of Fe(II) and Fe(III) from Pehkonen *et al*. [1992]. Recent field experiments showed a large fraction of Fe in tropospheric droplets to exist in the form of Fe(II) [Behra and Sigg, 1990; Erel *et al*., 1993]. For the Fe-catalysed oxidation of sulfur (IV) at pH=3 the reaction scheme shown in Table 3 is suggested by Ziajka *et al*. [1993] and Warneck *et al*. [1996].

In general the mechanism of Table 3 represents a combination of the thermal generation of sulfite radical anions followed by the reaction of sulfur-oxy radical anions. During the course of the reaction chain Fe(III) is recycled by the reactions of Fe(II) with HO_2, H_2O_2 (reactions (R-9) and (R-10)) as well as with peroxomonosulfate and sulfate radical anions (reactions (R-6) and (R-11)). The role of HO_2 radicals in this mechanism is both that of an oxidant (reaction (R-9)) and also that of a reductant (reaction (R-8)). Due to this effect, the HO_2 / O_2^- system is expected to maintain Fe(II) at steady state [Warneck, 1992]. For completeness, the reaction scheme also contains several non-radical reactions in which S(IV) is converted to S(VI), i.e., reactions (R-16) and (R-17).

It has been suggested that manganese (II) [Berglund and Elding, 1993] and cobalt (II) [Coichev and van Eldik, 1991] may react with S(IV) in a manner similar to Fe(II). The addition of Mn(II) to systems as shown in Table 3 has been shown to have a synergistic effect [van Eldik *et al*., 1992; Coichev *et al*., 1992], i.e., the efficiency of catalytic cycling is strongly enhanced.

Copper is believed to be present in the atmospheric aqueous phase in concentrations of about one tenth the concentration of dissolved Fe [Sedlak and Hoignè, 1993]. It has been suggested that Cu might significantly influence the interactions of dissolved S(IV) with other transition metal ions and also free radicals because it is expected to react efficiently with HO_2 / O_2^- according to Hoignè *et al*. [1993] and Sedlak and Hoignè [1993]:

$$Cu^{2+} + HO_2 \rightarrow Cu^+ + H^+ + O_2 \qquad \text{(R-18)}$$

The rate constant for (R-18) has been determined by pulse radiolysis as $k_{18} = 1x10^8\ l\ mol^{-1}s^{-1}$ [Rabani *et al*., 1973]. Copper may not only be reduced by HO_2 but it may also be oxidized from the Cu (I) to the Cu (II) oxidation state by HO_2/O_2^-, i.e.:

$$Cu^+ + O_2^- + 2\,H^+ \rightarrow Cu^{2+} + H_2O_2 \tag{R-19}$$

with $k_{19} = 1 \times 10^{10}\ l\ mol^{-1} s^{-1}$ [Rabani *et al.*, 1973]. It has hence been concluded that due to the high rate coefficients of these reactions the effect of the considerably smaller concentration of Cu in comparison to Fe is compensated and HO_2/O_2^- is expected to be efficiently converted to either molecular oxygen or hydrogen peroxide by the Cu^+/Cu^{2+} redox pair. The interaction of Cu^+/Cu^{2+} with hydroperoxyl radicals has to be considered also in the context of the production of HO_2 formed following the photolysis of iron-oxalato complexes. HO_2 radicals produced in the catalytic cycle will be converted to O_2 and H_2O_2. The H_2O_2 produced will subsequently react with S(IV) in a non-radical process. Alternately, H_2O_2 may be subject to photolysis [Zellner *et al.*, 1990] and produce OH radicals which in turn initiate the radical induced oxidation of S(IV) in polluted air masses. As a consequence, the catalytic decomposition of iron-oxalato complexes in the presence of Cu has to be regarded as an *in situ* source of hydrogen peroxide rather than only a source of hydroperoxyl radicals (see also above).

For a very detailed treatment of the transition–metal catalyzed S(IV) oxidation, the reader is referred to Brandt and van Eldik [1995].

Peroxynitric Acid (PNA) as an oxidant

Recombination of NO_2 and HO_2 in the gas phase leads to the formation of peroxynitric acid (PNA):

$$NO_2 + HO_2 \rightleftharpoons HNO_4 \tag{R-20}$$

PNA can be taken up by aqueous particles very effectively and then contribute to the oxidation of S(IV):

$$HNO_4 + HSO_3^- \rightarrow HNO_3 + HSO_4^- \tag{R-21}$$

It has been suggested by Amels *et al.* [1996] based on laboratory experiments and demonstrated in a modeling study by Warneck [1999] that this sequence could on the one hand substantially contribute to the removal of NO_X from the troposphere as well as to aqueous phase sulfur oxidation.

Interaction of cloud sulfur oxidation with organic chemistry

S(IV) species may form complexes with aldehydes commonly encountered in tropospheric clouds. This subject is described in detail by Olson and Hoffmann [1989]. The complexes formed are no longer subject to effective oxidation by hydrogen peroxide or ozone. Possible losses are thermal decomposition and degradation by radicals.

Only for the most simple adduct, i.e., hydroxymethanesulfonate, are kinetic data for the most important radical reactions available. For cloud chemistry models to be further developed to include higher organics, rate parameters are needed to better describe the possible degradation of condensation products of aldehydes and S(IV). It is interesting to note that such S(IV)/aldehyde condensation products are not only formed by aliphatic aldehydes but also by aromatic species such as benzaldehyde.

Another coupling of organic cloud chemistry to sulfur oxidation in clouds exists because oxidation of organics will lead to the formation of hydroperoxyl radicals, whose ultimate sink will be reaction with TMIs or recombination to form H_2O_2 which effectively will oxidize S(IV).

Recent box model results

Recent model results with CAPRAM 2.4 (MODAC mechanism, an updated and enlarged version of CAPRAM 2.3 (see Herrmann *et al.* [2000], Ervens *et al.* [2001] and the CAPRAM website (http://www.tropos.de)) show that for the used set of initial concentrations and emissions for an urban scenario, oxidation by hydrogen peroxide is most efficient. Results for the integrated production fluxes for S(VI) over 24 hours from the different S(IV) oxidation pathways for a permanent cloud and a cloud existing for 18 minutes are shown in Figure 1.

As can be seen, the oxidation by H_2O_2 is most efficient in both cases. It is very interesting to note that for the more realistic case of an 18 minute cloud duration about half of the S(IV) oxidized in total is converted by H_2O_2 in cloud water. The second most important pathway is then oxidation by the gas phase reaction of OH with SO_2 followed by the peroxynitric acid oxidation reaction. The

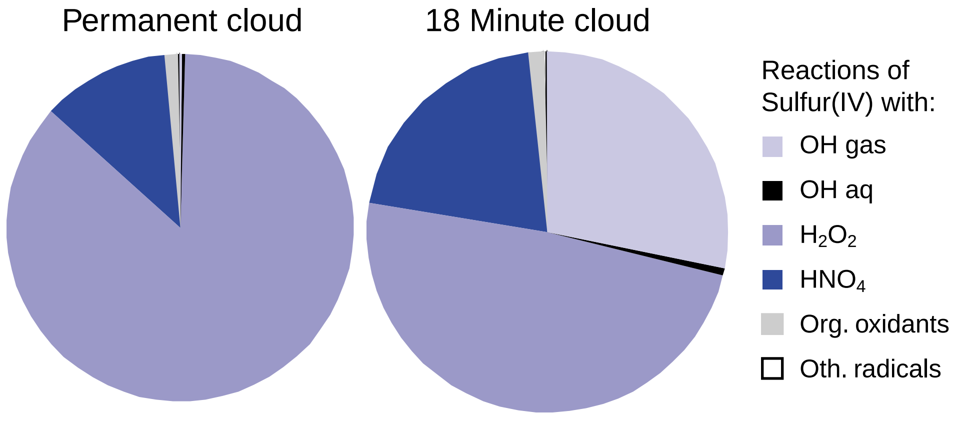

Figure 1. Contributions of different oxidation pathways to sulfur (VI) formation. CAPRAM 2.4 (MODAC mech.) urban case, with emissions and deposition.

reason for the smaller relative contribution of hydrogen peroxide for the shorter cloud period is the much smaller aqueous phase concentration of H_2O_2 compared to the continuous cloud case.

Organic oxidants such as methylhydroperoxide (CH_3OOH) constitute only a minor contribution. It has to be noted that the outcome of such reaction pathway comparisons is highly dependent on the concentration scenario established in the considered air mass. For the effect of clouds on tropospheric ozone this has been clearly demonstrated by Walcek *et al.* [1997].

Oxidation of reduced sulfur species

It should be noted that DMS oxidation might yield products such as DMSO, $DMSO_2$, methanesulfonic acid (MSA) and methanesulfinic acid (MSI), which may partition into marine aqueous particles, i.e., cloud droplets and marine aerosols [for DMSO in rainwater, see Sciare *et al.*, 1998]. In solution, these species might undergo fast radical reactions as has been shown by Sehested and Holcman [1996]. Initial multiphase modeling studies have been undertaken [see Campolongo *et al.*, 1999]. Many elementary rate coefficients needed for a better understanding of multiphase DMS oxidation and its coupling to tropospheric cloud and aerosol chemistry still need to be characterized. Apparently, another field of sulfur multiphase chemical conversions starting from species more reduced than S(IV) is emerging here. It combines both radical reactions with organics but then also couples to 'conventional' S(IV) conversion because this is an intermediate step in the oxidation chain from S(-II) as found in DMS to S(VI) as found in MSA or sulfate.

Summary and outlook

The radical-driven oxidation of S(IV) to S(VI), after a great deal of research in the last hundred years, still constitutes an extensive research topic of its own. Open questions exist with regards to the dependencies of elementary reaction rate constants on temperature and also to ionic strengths and ionic composition of solution. Aqueous phase process studies turn more and more to investigating the effects of organics. Organic chemistry in cloud water may influence the rate of S(IV) oxidation in droplets [Warneck, 1996a], alter the pattern of precipitation composition, and may also lead to the production of harmful substances (see, e.g., Lüttke *et al.* [1997] for the special case of nitrophenols as well as other contributions in this newsletter). Another potentially very interesting coupling to organic chemistry exists in the area of multiphase DMS oxidation.

For a more systematic understanding of multiphase sulfur oxidation, the broader solution phase chemistry needs to be better characterized in laboratory studies, with results implemented into tropospheric multiphase chemistry models. These, subsequently, have to be coupled to microphysical models, to be tested in field experiments with regards to their ability to describe measured gas phase trace gas and oxidant concentrations, cloud water constituent concentrations and chemical aerosol composition in the tropospheric multiphase system.

Organic compounds in clouds: Present knowledge and future perspectives

Contributed by **M.C. Facchini** (mc.facchini@isao.bo.cnr.it), *Istituto di Scienze dell'Atmosfera e dell'Oceano, Consiglio Nazionale delle Ricerche, Bologna, Italy.*

Introduction

The potential role of organic compounds in the chemistry of wet aerosols and raindrops was investigated by Graedel and Weschler [1981] already twenty years ago. They presented a conceptual model of an aqueous droplet containing an insoluble core, an aqueous solution of both organic and inorganic species, and an organic surface film with "any polar portion of the organic molecule preferentially oriented toward the core as the result of solution bondings." This model represented a complex and heterogeneous system in which the organic compounds would produce important consequences on the chemical and physical properties of the droplets. In particular, a potential for photochemical reactions in the aqueous phase and air-solution interface effects was evidenced among the processes involving organic species.

Over the last two decades, only soluble organic molecules derived from the gas phase have commonly been measured in cloudwater. Formic, acetic and other lightweight carboxylic acids, formaldehyde and other gas phase-derived carbonyls were reported to constitute the main dissolved organic compounds [Grosjean and Wright, 1983; Munger *et al.*, 1984; Winiwarter *et al.*, 1988; Collett *et al.*, 1990; Facchini *et al.*, 1992]. Important liquid-phase reactions involving these compounds were also studied as, for example, the formation of bisulfite-formaldehyde adducts [Boyce and Hoffmann, 1984; Dong and Dasgupta, 1986] and the photochemical formation of formic acid in clouds [Jacob, 1986]. All these reactions have implications in the process of acidification of precipitation.

The remaining part of organic carbon in the aerosol was considered mostly insoluble in cloudwater and, therefore, the possible effects of organic compounds on cloud chemistry were those connected to the formation of insoluble organic films [Gill *et al.*, 1983] or some catalytic soot–metal effects on aqueous-phase SO_2 oxidation [Jacob and Hoffmann, 1983].

For these reasons, the above model of aqueous droplets proposed by Graedel and Weschler [1981] remained more

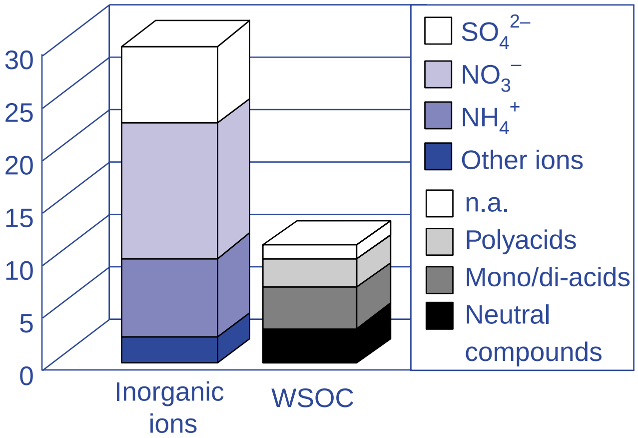

Figure 1. Average concentration of the main classes of inorganic and organic water-soluble species in fog water samples collected in the Po Valley, Italy. Data are expressed in µg m^{-3}, calculated by multiplying the measured liquid phase concentrations by the fog liquid water content [Decesari *et al*., 2000b].

of a conceptual frame rather than a study system supported by observations.

Organic compounds in cloud water

In the early 1980s, a pioneer paper appeared [Likens *et al*., 1983] reporting on the composition of organic compounds in precipitation. These authors measured total organic carbon (TOC) concentration in precipitation samples and found that the dissolved organic fraction (DOC) was very high: ca. 80% of the TOC measured. Particulate organic carbon (POC) plus dissolved macromolecular compounds (> 1000 dalton) accounted for 50-60% of the TOC. Carboxylic acids, alhehydes, polysaccharides and tannin-lignin comprised most of the remaining carbon. These results suggested that the major fraction of organic carbon in precipitation was derived from particle scavenging rather than from the gas phase.

Over the last ten years, considerable time and effort has been devoted to the characterization of the organic composition of aerosols and cloudwater. However, the difficulties encountered in the analysis of the polar, water soluble organic species, the ones important for the aerosol-cloud interaction, have represented a technical limit to understanding the role of organic compounds in cloud chemistry [Jacobson *et al*., 2000]. The traditionally used analytical technique for organic compound speciation—solvent extraction followed by gas chromatography coupled to mass spectrometry (GC–MS) analysis—fails to identify most of the water soluble organic compounds (WSOC), since this method is not aimed at analyzing very polar species. Typically, less than 5% of the total mass of aerosol WSOC was resolved into individual species [see e.g., Rogge *et al*., 1993]. These difficulties were evidenced in a review by Saxena and Hildemann [1996, and references therein]: their paper investigated theoretically the characteristics of WSOC and identified the specific classes of compounds that had either been detected or that were likely to contribute to aerosol WSOC on the basis of their thermodynamic properties. Mono- and di-carboxylic acids, carbonyls, alcohols and some other classes of compounds, e.g., polyols, amino acids and other multifunctional organic compounds were indicated as potential candidates for the organic composition of aerosol WSOC and cloudwater.

Recently, a new class of macromolecular polycarboxylic acids has been detected in aerosol samples [Mukai and Ambe, 1996; Havers *et al*., 1998; Zappoli *et al*., 1999], accounting for a significant fraction of the aerosol WSOC [Facchini *et al*., 1999a; Kiss *et al*., 2001; Decesari *et al*., 2001]. This class of macromolecular compounds has physical and chemical properties similar to those of humic (or fulvic) acids, the main constituent of dissolved organic carbon in natural waters [Stumm and Morgan, 1981], and for this reason they are sometimes referred to in the literature as HULIS [humic-like substances]. Combustion processes, in particular biomass burning, have been indicated as possible sources of HULIS [Mukai and Ambe, 1986; Zappoli *et al*., 1999; Mayol-Bracero *et al*., 2001].

In view of the difficulty of pursuing individual compound speciation of WSOC employing traditional GC-MS techniques, Decesari *et al*. [2000a] have proposed a new approach for the analysis of WSOC in aerosol and cloudwater, which aims to characterise the main functional groups and chemical properties of WSOC. The procedure is based on a combination of: a) chromatographic separation; b) TOC analysis; and c) organic functional group analysis. The complex WSOC mixture is separated into three main classes of compounds classified according to their acidic character: i) neutral / basic compounds; ii) mono- and di-carboxylic acids; iii) polycarboxylic acids. The TOC of each of the three fractions is determined, and organic functional group analysis is then performed on the separated fractions by means of Proton Nuclear Magnetic Resonance (PNMR). In the case of aerosol and fog water samples from the Po Valley, Italy, the neutral / basic fraction was found to be composed mainly of polyols and sugars, while mono- and dicarboxylic acids were mainly hydroxylated aliphatic compounds and polyacids were highly unsaturated compounds, both aliphatic and aromatic, with a smaller content of hydroxyl groups. It is suggested that the structure of the latter class of compounds may correspond to the above mentioned HULIS [Mayol-Bracero *et al*., 2001].

Decesari *et al*. [2000b] further investigated a number of Po Valley fog samples and found that the above three classes of organic compounds account for an average 88% of the total WSOC within the samples (Figure 1). Acidic compounds (mono / dicarboxylic acids and polyacids) are the dominant WSOC, accounting for an average 59% of soluble organic species; while neutral compounds account for ca. 30% of the total WSOC. Although the inorganic ions represent an average 75% of total fog water soluble mass, the WSOC concentration is by no means negligible.

While the above characterization of WSOC supplies a less detailed picture compared to individual compound speciation, it certainly provides more comprehensive information for modeling purposes and is particularly helpful when aerosol chemical mass closure is pursued, since the procedure accounts for almost 90% of WSOC.

Organic cloud condensation nuclei and cloud microphysics

Over the last few years, the contribution of organic aerosols to the mass of cloud condensation nuclei [CCN] has been investigated by several authors [Novakov and Penner, 1993; Rivera-Carpio *et al.*, 1996; Corrigan and Novakov, 1999]. In particular, Novakov and Corrigan [1996] reported that pure organic smoke aerosols from cellulose combustion are efficient CCN without being associated to inorganic salts. Penner *et al.* [1996] pointed out that organic compounds derived from biomass burning may also act as CCN, thus influencing indirect aerosol forcing. The hygroscopic properties of atmospheric particles containing organic and inorganic compounds and their ability to act as CCN have been extensively investigated by the Tandem Differential Mobility Analyzer (TDMA) technique, in both laboratory and field experiments [Saxena *et al.*, 1995; Cruz and Pandis, 1996; Hansson *et al.*, 1998]. Other methods like electrodynamic balance [Andrew and Larson, 1993; Peng and Chan, 2001] or molecular-controlled semiconductor resistor [Rudich *et al.*, 2000] have been used to study the interaction of organic compounds with water vapor. The results of these studies have shown that organic compounds can either enhance or inhibit water absorption and that the hygroscopicity is strongly dependent on the specific organic mixture (the different origin of the particles, in the case of real samples).

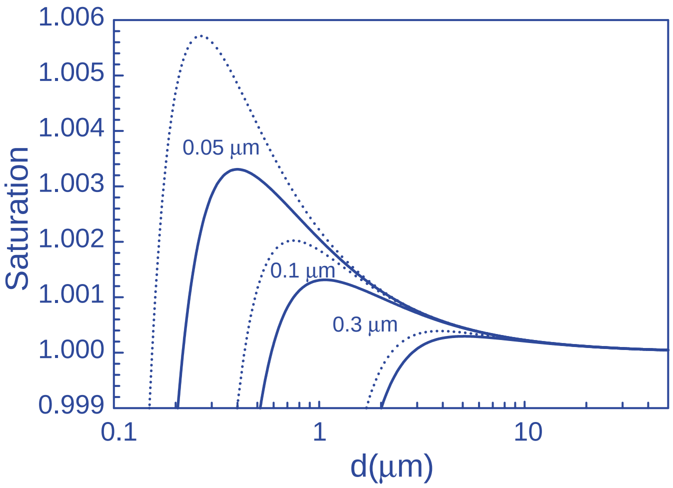

Figure 2. Köhler curves calculated for three aerosol dry sizes and two different aerosol chemical compositions. The dotted lines correspond to a purely inorganic aerosol composition with surface tension equal to that of pure water, while the solid lines represent an inorganic + organic aerosol composition and variable surface tension. The concentration for inorganic and organic species and the surface tension depression were retrieved from measurements of real aerosol and fog water samples collected in the Po Valley, Italy [Mircea *et al.*, 2001].

It is known that some organic compounds present in aerosols are surface active and that their presence in CCN particles can significantly affect the surface tension of cloud droplets [Gill *et al.*, 1983; Capel *et al.*, 1990; Shulman *et al.*, 1996]. Facchini *et al.* [1999b] have shown that the lowering of surface tension due to organic compounds dissolved within cloud droplets may influence droplet nucleation and growth, hence affecting the droplet population. Facchini *et al.* [2000] have also shown that, in the case of Po Valley fog water, among the three kinds of compounds classified according to the procedure of Decesari *et al.* [2000], the polycarboxylic acid fraction exhibited the most pronounced surface active behavior: four times higher than the mono- and dicarboxylic acids and one order of magnitude higher than the neutral compounds.

The effect of organic composition and surface tension depression on cloud droplet formation is shown in Figure 2, which illustrates for three different aerosol dry sizes the equilibrium growth predicted by the Köhler theory [Köhler, 1936] of CCN with two different chemical compositions; i) a purely inorganic composition with constant surface tension equal to that of pure water and ii) organic + inorganic composition and variable surface tension as a function of WSOC concentration [Mircea *et al.*, 2001]. The effect of organic composition on CCN activation becomes evident by comparing the two families of curves in the vicinity of the critical radius: the decrease in critical supersaturation produces a difference of roughly 20% in the calculated droplet number concentration (or a decrease of ca. 6% in the estimated effective radius). This example shows that organic CCN composition and surface tension effects should be taken into account in cloud models for describing cloud formation and evolution. On the other hand, it has also been shown that slightly soluble organic compounds may inhibit cloud droplet growth [Shulman *et al.*, 1996; Laaksonen *et al.*, 1997], although the lack of measurements on real cloud / aerosol organic chemical composition and of solubility data prevents a more thorough analysis on this point.

Emerging issues concerning organic compounds in clouds

The presence of many different classes of polyfunctional organic compounds in clouds with a wide range of molecular weights opens new scenarios in cloud chemistry.

In the first place, it can be speculated that the polar water-soluble organic species in cloudwater not only derive from gas phase scavenging or the dissolution of polar products of gas-to-particle-conversion, but that they also derive from the scavenging of carbonaceous particles from combustion sources oxidized in the atmosphere [Chugthai *et al.*, 1991; Lary *et al.*,1999]. The oxidation of carbonaceous surfaces leads to the formation of polar groups such as carboxylates, which cause the aerosol to become more hydrophilic and hence effective as CCN.

Lary *et al.* [1999] also pointed out that, once in cloud, the carbonaceous material (both the soluble part and the insoluble core) can be photo-reactive. Furthermore, Anastasio *et al.* [1997] have suggested that non-phenolic aromatic carbonyl compounds and phenols can be a source of hydrogen peroxide in the aqueous phase via photochemical reactions. Aromatic carbonyls and phenols are formed by biomass burning processes and the same kind of moieties are present in lignin photodegradation products and in the HULIS.

The tendency of natural humic substance to form stable complexes with metal ions is well known [Stumm and Morgan, 1981] and it is possible that similar processes also occur within cloud droplets containing HULIS. Another important property of polycarboxylic acids in natural waters is their colloid behavior, and they tend to precipitate in the presence of Ca^{2+} and Mg^{2+} ions [Stumm and Morgan, 1981]. Such processes may also be important within cloud droplets, influencing the partitioning of material from the aqueous phase to the insoluble phase, in analogy to the chemistry of natural waters.

Beside the fact that surfactants are present in cloud water [Facchini *et al.*, 2000], their role in cloud chemistry is completely unknown, as also are their likely sources. These complex materials may operate as concentration or transport agents for other non polar organic compounds or for hydrous oxide clays [P. Brimblecombe, personal communication; see also the URL: http://www.uea.ac.uk/~e490/future.htm].

The limitation of reliable chemical methodologies to fully elucidate the complex composition of organic aerosol and cloudwater and the fact that the organic composition cannot be attributed to a few major species alone (unlike inorganic compounds) make the choice of a reference inorganic + organic composition to be used in numerical simulations and in laboratory experiments very challenging [Blando and Turpin, 2000], and the choice of model compounds to represent the whole WSOC mass should be done with caution. In addition, it is necessary to acquire experimental and theoretical information on other important thermodynamic properties of WSOC, such as actual solubility and water activity, in order to obtain the necessary input parameters for correct model simulations of cloud physical and chemical processes.

Modeling the effects of clouds on chemical constituents

Contributed by **M.C. Barth** (barthm@ncar.ucar.edu), *National Center for Atmospheric Research, Boulder, CO, USA.*

Introduction

To understand how clouds affect chemical constituents, modeling the chemistry in clouds has been an active area of research. Many processes must be taken into account to describe accurately the effect of clouds on tropospheric chemistry, including cloud dynamics, microphysics, chemistry, radiation effects and, for simulations of thunderstorms, nitrogen oxide production from lightning. To better understand the influence of clouds on chemistry, these processes should be integrated in three-dimensional numerical simulations that resolve the cloud scale yet cover synoptic-scale domains such that long-term effects of clouds on chemical species can be tracked.

Alternatively, box models and parcel models provide a useful means to focus on individual processes (e.g., chemistry) such that the process can be assessed in more detail. This paper focuses on three processes: 1) the chemistry in and around cloud drops, 2) interactions between aerosols and aqueous chemistry, and 3) cloud microphysics to exemplify how a non-chemical process changes the spatial distribution of chemical species.

Aqueous chemistry

In clear air, the chemical sources and sinks of gas-phase species, C_g, are represented as

$$\frac{dC_g}{dt} = P_g - L_g C_g \qquad (1)$$

where P_g is the gas-phase production of C_g and L_g is the first order gas-phase loss of C_g. If only non-precipitating water clouds are considered, the chemical sources and sinks of the gas-phase species are modified to

$$\frac{dC_g}{dt} = P_g - L_g C_g - k_t \mathbf{L} C_g + \frac{k_t}{H_{eff}} C_a \qquad (2)$$

where k_t is the first order mass transfer rate, **L** is the liquid water content, and H_{eff} is the dimensionless effective Henry's Law constant. A similar equation can be written for the aqueous-phase species, C_a,

$$\frac{dC_a}{dt} = P_a - L_a C_a + k_t \mathbf{L} C_g - \frac{k_t}{H_{eff}} C_a \qquad (3)$$

Adding equations 2 and 3 gives the total concentration of the species, $C_{tot} = C_g + C_a$,

$$\frac{dC_{tot}}{dt} = P_g + P_a - L_g C_g - L_a C_a \qquad (4)$$

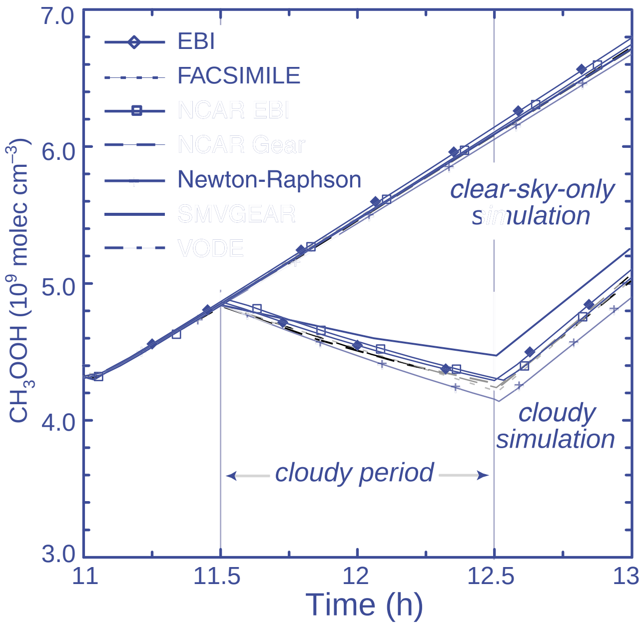

Figure 1. Time versus total CH_3OOH concentration from several box model simulations. The simulated cloud is appropriate for stratus at 1.5 km altitude.

Either equations 2 and 3 can be solved to predict C_g and C_a, or equation 4 can be solved and C_g and C_a determined by assuming Henry's Law equilibrium between phases. The production and loss terms in these equations depend on the concentration of other chemical species, thus a set of interdependent stiff equations must be solved. Several numerical techniques—e.g., predictor-corrector methods, implicit methods, or hybrid explicit-implicit methods—could be utilized to solve this set of equations.

During the 5th International Cloud Modeling Workshop (Glenwood Springs, CO, USA, August 2000), the cloud chemistry case compared numerical solver techniques for the system outlined above. Seven solvers were tested: four based on the Gear predictor-corrector method, two using an Euler Backward Iterative (EBI) method, and one using the Newton-Raphson method. Excellent agreement between model results was found for the clear-sky-only simulation. For the simulation in which a cloud with **L** = 0.3 x 10^{-6} cm^3 cm^{-3} was imposed for a one-hour period, agreement between model results was quite good. Greater variability was found for species such as CH_3OOH (Figure 1), CH_2O, and HCOOH. When aqueous chemistry was introduced, increased variability between models resulted whether equations 2-3 or equation 4 (and determining C_g and C_a from equilibrium calculations) were solved, or whether a dissociated species (e.g., O_2^-) was treated as part of a family and determined by equilibrium, or whether it was predicted separately from the other members of the family.

A summary of the results of this intercomparison will be published in the Cloud Modeling Workshop's report to the World Meteorological Organization, and a manuscript discussing the results in detail is in preparation.

Aerosols and aqueous chemistry

The cloud chemistry case of the Cloud Modeling Workshop also compared results of aerosol parcel models that simulated S(IV) oxidation. Not only do these parcel models need to use equations 2-4 to predict SO_2, H_2O_2 and O_3 concentrations, but they need to predict the activation of the aerosol to cloud drops and the liquid water content (**L**) in the air parcel.

The activation of cloud condensation nuclei (CCN) depends on the size of the CCN and its composition. Droplet growth equations can be found in textbooks on cloud physics and chemistry [e.g., Seinfeld and Pandis, 1998]. Many aerosol parcels models discretize the aerosol and cloud drop size distribution into bins. Thus, the total concentration of a species, C_{pa}, in the activated aerosol (i.e., cloud drops) can be determined by summing over the size range of CCN that were activated,

$$C_{pa}\Big|_{act} = \sum_{n=m_c}^{n=mtot} C_{pg}(n) \qquad (5)$$

where $C_{pg}(n)$ is the concentration of species in the aerosol in bin n, m_c is the aerosol bin number that is associated with the critical diameter for activation, and *mtot* is the total number of bins. The liquid water content can be found from the supersaturation, which is determined from the Clausius-Clapeyron equation [e.g., see Seinfeld and Pandis, 1998].

Results from this initial aerosol parcel model intercomparison showed that there was much disagreement in predicting pH and final SO_2 concentration. Two types of simulations were performed: 1) where the cloud drop size is fixed at 10 mm, and 2) where the cloud drop population is distributed over size. One consistent outcome was that the results from the simulations with a size-varying cloud drop population oxidized 20% more SO_2 than the simulations that assumed a fixed cloud drop size. For a size-varying cloud droplet population, the pH is allowed to vary with drop size and reaction rates that depend on pH (e.g., S(IV) oxidation by O_3) vary with drop size. Thus, for the larger droplets that have higher pH values, O_3 oxidation by S(IV) proceeds rapidly causing greater SO_2 depletion than if a fixed cloud drop size is used. As has been noted in other studies [Hegg and Larson, 1990; Roelofs, 1993], it is important to characterize a population of cloud drops rather than fixing the cloud drop size.

Cloud physics and chemical species

The physical characteristics of clouds are quite varied and can influence the chemical distribution of species. As noted in the previous section, the effect of drop size on cloud chemistry is important to the pH-dependent chemistry. The effect of size on cloud chemistry can most notably be seen when comparing cloud drop chemistry to rain drop chemistry [Audiffren *et al.*, 1996]. The larger-sized raindrops usually have higher pH values, which increases the extent of S(IV) oxidation, oxidation of formate and oxidation of species by the superoxide ion (O_2^-).

Ice hydrometeors also need to be considered when describing cloud chemistry because of the interaction of the ice particles with cloud drops and because of possible direct interactions with chemical species. Cloud physics texts detail the methodology used to describe microphysical processes in cloud models. When cloud drops or rain freeze to form ice, snow or hail (whether by direct freezing or by freezing during the riming process), the chemical species in the cloud water or rain may or may not be captured by the frozen hydrometeor. As an example, the transfer of a chemical constituent from cloud water to snow can be depicted to be proportional to the amount of water transferred [Hegg *et al.*, 1984],

$$\left.\frac{dC_s}{dt}\right|_{MP} = \frac{C_a}{q_c}\frac{dq_c}{dt} \qquad (6)$$

where C_s is the concentration of the species in snow, MP refers to the microphysical process of interest, q_c is the cloud water mass mixing ratio, dq_c/dt is the microphysical process affecting the hydrometeors (in this example, snow collecting cloud water).

In the frozen hydrometeors, chemical reactions that readily occurred in the aqueous phase are stopped. Further, because snow and hail have fall speeds quite different from each other and from rain, the chemical species that are captured by the frozen hydrometeors will be redistributed very differently than if the species were degassed during the freezing process. To exemplify the potential importance of the ice on the distribution of soluble species, results from simulations [Barth *et al.*, 2000] of a thunderstorm that included cloud chemistry and tested the importance of a species being captured by the frozen hydrometeors show that H_2O_2 is somewhat reduced in the outflow region of the storm by aqueous chemistry but is substantially reduced when the frozen hydrometeors are allowed to capture H_2O_2 (Figure 2).

Conclusions

To understand how cloud processes influence chemical species, numerical simulations can be performed. Box model studies of cloud chemistry can illuminate the significance of aqueous-phase reactions on tropospheric chemistry, but first must be evaluated to assess the model's ability to predict the chemistry accurately. Results from the cloud chemistry case of the 5th International Cloud Modeling Workshop indicate good agreement between different box models.

Parcel models allow the researcher to understand the importance of cloud condensation nuclei on cloud drop activation and cloud chemistry. The intercomparison of parcel models showed some disagreement between different models and suggests the need for continued comparisons.

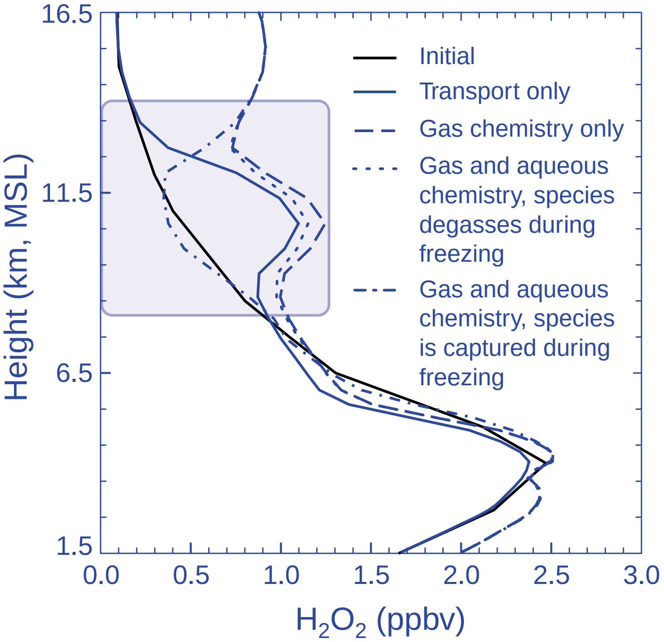

Figure 2. Spatially-averaged H_2O_2 versus height in the outflow region (shaded area) of a simulated thunderstorm.

The cloud chemistry intercomparison was very successful; however, its usefulness would be even greater if the results could be compared to observations. Thus we hope to combine parcel models of cloud and aerosol chemistry with cloud chemistry observations of orographic clouds.

To understand more complex clouds, e.g., cumulonimbus, multi-dimensional cloud models are used to describe several processes. Sensitivity studies of how cloud microphysics affects the spatial distribution of soluble species indicate that the concentrations of some constituents can be substantially altered in the anvil region of a storm. Observations of these soluble species need to be made to improve our understanding of how thunderstorms influence soluble species.

Not only should cloud chemistry and microphysics be accurately described in cloud chemistry models, but transport, radiative influences, and lightning-produced NO_X must also be depicted properly. Simulations of individual clouds teach us what occurs in a short period of time for particular cases. However, long-term effects of clouds on chemical species must also be examined by resolving cloud-scale processes on large model domains.

Acknowledgments

Participants of the cloud chemistry case, box model intercomparison of photochemistry included the author, Anne Monod, Cheol-Hee Kim, Mark Jacobson, Jinyou Liang, Sandy Sillman, and Rynda Hudman. Their contribution and the contribution by Sonia Kreidenweis to this article is greatly appreciated. Charles Brock, Geoff Tyndall and Brian Ridley are thanked for their comments on this manuscript. NCAR is sponsored by the National Science Foundation.

The indirect radiative effect of aerosols

Contributed by **K. Noone** (zippy@misu.su.se), *Department of Meteorology, Stockholm University, Sweden.*

Determining the radiative effects of aerosols is currently one of the most active areas in climate research. Aerosols influence the Earth's radiative balance *directly* by scattering incoming shortwave radiation back to space, or *indirectly* through their influence on cloud properties. The indirect effect is considered to be one of the largest uncertainties in current global climate models (GCMs). Correctly predicting the indirect radiative effect of aerosols requires that we understand the interactions between aerosols and clouds that determine cloud properties.

There has been a large amount of very interesting new work done recently on the subject of indirect radiative effects—far too much to attempt to present a comprehensive review here. Rather, the purpose of this note is to present a short tutorial on the subject, and to highlight a few of the original papers and recent advances.

Different facets of the indirect effect

There are several indirect ways that aerosols influence the radiative balance of the Earth. Aerosols contribute to determining the reflectivity of clouds—cloud albedo. They also affect precipitation processes. Aerosols influence the initial droplet size distributions produced close to cloud base, and can subsequently influence the effectiveness of coalescence at a later stage of cloud development through changing the spread in drop sizes. Aerosols also influence freezing processes in mixed-phase clouds. Both these mechanisms (coalescence and freezing) influence precipitation development. Precipitation is a key component in determining the lifetime and extent of clouds. It also is a key component in the atmospheric energy balance through the redistribution of latent heat. Finally, it is possible that aerosols can influence the dynamical processes in the atmosphere that drive cloud formation and development.

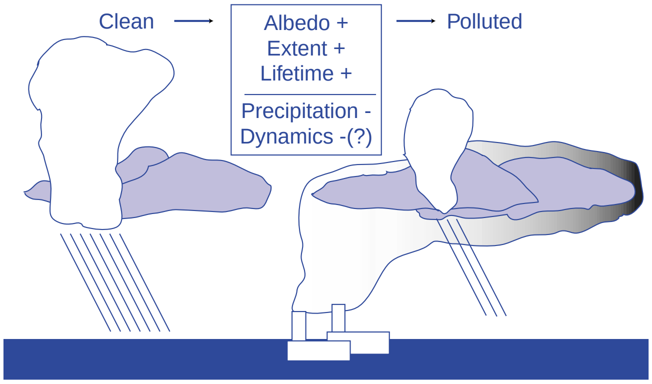

Figure 1. Cartoon illustrating the different kinds of indirect effects of aerosols.

These phenomena are illustrated in Figure 1, a cartoon of aerosol influences on cloud properties. The left panel represents a clean (background) case with a given cloud albedo, extent, precipitation intensity and dynamic structure. The right panel depicts the case where all of the indirect effects of aerosols act at the same time (an unlikely scenario, but then it *is* just a cartoon!). In the polluted case, cloud albedo has increased. Precipitation has decreased due to changes in cloud microphysics as well as a weakening in the overall dynamic driving force for convection. The rectangle in the center of the figure indicates the expected sign of the indirect effect (increase or decrease) going from clean to polluted conditions.

The Albedo Effect

Perhaps the first to be recognized (and receive the most attention) is the *albedo* or "Twomey" effect—the increase in cloud albedo due to an increase in aerosol concentration. For a dynamic forcing that creates a cloud with a given vertical extent and liquid water content, an increase in aerosol concentration going into the cloud can result in the formation of a larger number of smaller droplets as compared to an unperturbed cloud. The end result is in an increase in cloud albedo [Twomey, 1974, 1977a].

An early observation that anthropogenically-produced aerosols could change cloud properties came when "anomalous cloud lines"—bright curvilinear structures in low clouds—were seen in early TIROS satellite imagery [Conover, 1966]. The suspicion was that these areas of increased cloud albedo were caused by aerosol emissions from ships [Conover, 1966; Twomey *et al.*, 1968]. These features have subsequently become known as ship tracks and serve as a textbook example of the effect pollution aerosols can have on the albedo of warm clouds.

Experiments in marine stratocumulus clouds have confirmed the general conceptual model of this effect [Coakley *et al.*, 1987; King *et al.*, 1993; Radke *et al.*, 1989]. Several recent large process-oriented field experiments have been dedicated to investigating the relationship between aerosols and cloud albedo [Brenguier *et al.*, 2000; Durkee *et al.*, 2000].

The albedo effect does not necessarily imply an increase in cloud reflectivity. The reflectance (R) of a cloud is a function of several variables: $R = R(\tau, \omega_0\ g)$ where τ is the optical depth of the cloud, ω_0 is the single scattering albedo of the droplets, and g is the asymmetry parameter (describing the fraction of energy scattered into the forward direction). An aerosol/cloud interaction that can change any of these parameters can also affect cloud reflectivity. For instance, ω_0 is approximately unity for water droplets at visible wavelengths. If a significant amount of absorbing aerosol were to be incorporated into cloud droplets, it could reduce ω_0 and decrease R. On the whole, however, increasing aerosol concentrations are expected to increase cloud albedo for all but the thickest clouds [Twomey, 1977b].

Precipitation: Cloud lifetime, extent and energy redistribution

The same processes that increase cloud albedo in low-level clouds (a production of more and smaller droplets) tend to decrease the efficiency with which precipitation is formed. Albrecht [1989] proposed that a decrease in drizzle production in these kinds of clouds could increase both the cloud liquid water content (and thus liquid water path) and the fractional cloudiness. Aerosol-induced precipitation suppression has been observed both with *in situ* measurements [Ferek *et al*., 2000], and in satellite observations [Rosenfeld, 2000] showing that the effect does in fact occur in the atmosphere. Some time ago, Warner [1968] deduced that aerosol emissions from sugar cane fires were affecting precipitation by examining rainfall records from western Australia.

If precipitation is suppressed, water that would have been removed from the atmosphere remains aloft and can be transported to other locations before it is deposited to the surface. The same is true for the energy associated with this water—the latent heat released on condensation in clouds and the energy required for evaporation of water from the surface. This redistribution of water and latent heat due to precipitation suppression may have the potential to influence circulation patterns.

Another kind of indirect effect may arise due to the presence of absorbing aerosols. It has been hypothesized that heating of the boundary layer by absorbing aerosols may influence cumulus cloud formation by stabilizing the layer and reducing relative humidity [Ackerman *et al*., 2000]. GCM calculations indicate that while this effect may reduce cloudiness in some highly polluted locations, the increase in cloud albedo and lifetime are still predicted to dominate on the global scale [Lohmann and Feichter, 2000]. Field experiments in polluted winter fogs showed that despite the presence of considerable amounts of absorbing aerosol, fog still persisted for several days [Hallberg *et al*., 1992; Noone *et al*., 1992].

These results are not necessarily contradictory—what they *do* show is that this subject is not yet very well understood. The number and complexity of the steps in the causal relationship between aerosols and precipitation makes quantifying this indirect radiative effect very challenging. Even more challenging is understanding and quantifying the consequences of the effect in terms of circulation patterns and energy redistribution. Clearly, there is still plenty of work to be done in this area.

High clouds

The previous discussion has implicitly been related to clouds in (or at least originating in) the lower troposphere—e.g., marine stratocumulus and tropical cumulus clouds. Aerosols affect cirrus cloud properties as well. Here, our knowledge of aerosol indirect effects is even more rudimentary than for the case of warm clouds. In fact, it is difficult to even come up with a sign for the effect, much less quantify its nature and magnitude. The difficulty arises because cirrus clouds can act very differently in terms of their radiative properties depending on their optical thickness. Optically thin cirrus clouds let most of the incoming solar radiation pass through, but tend to absorb outgoing infrared radiation emitted from the Earth's surface. They re-radiate this energy—but at a much lower temperature. In this way, they behave similarly to greenhouse gases, and can have a net warming effect. Optically thick cirrus clouds, on the other hand, reflect much of the incoming solar radiation. They too absorb and re-radiate outgoing infrared radiation, but if the loss of solar radiation dominates the energy balance, the net effect is cooling. An additional complication arises from the fact that cirrus clouds contain non-spherical crystals, the optical properties of which are more difficult to describe compared with homogeneous liquid spheres.

Of particular interest in this regard is the effect of aircraft emissions on cirrus cloud properties. Several field campaigns and modeling efforts have been undertaken recently to examine how aircraft emissions influence cirrus clouds [e.g., Brasseur *et al*., 1998; Schumann *et al*., 2000; Toon and Miake-Lye, 1998]. In one study, Ström and Ohlsson [1998] used measurements of absorbing aerosol material inside cirrus cloud elements to show that crystal concentrations were enhanced in areas affected by aircraft exhaust. Like ship tracks, this is a case where a clear causal link between a specific aerosol emission and a cloud effect was identified. Unfortunately, our knowledge of the microphysical properties and chemical composition of the particles emitted by jet engines is extremely limited. Without this information, understanding and predicting the effects of aircraft emissions on cirrus cloudiness will remain an uncertain endeavor. As with the case for precipitation effects, a great deal of work remains to be done to determine the indirect radiative effects of aerosols on cirrus clouds.

Concluding remarks

The process that ultimately drives the indirect radiative effect of aerosols—that of cloud droplet (or crystal) formation—happens on time scales of seconds and spatial scales of micrometers. Yet the end result of this process—the clouds themselves—is a global scale phenomenon. One of the largest challenges in understanding and predicting the indirect radiative effect of aerosols is bridging the gap between these spatial and temporal scales in terms of both our understanding of the processes involved, and in our descriptions of the processes in global-scale models. Making progress in this area requires that modelers and experimentalists work together and communicate effectively with each other. IGAC has played a tremendously important role in bringing these communities together to make real advances in the area of atmospheric chemistry. It can also serve as a unifying forum for the exchange of information and ideas in the area of climate research as well.

References

Ackerman, A.S., O.B. Toon, D.E. Stevens, A.J. Heymsfield, V. Ramanathan, and E.J. Welton, Reduction of tropical cloudiness by soot, *Science*, **288**, 1042-1047, 2000.

Albrecht, B.A., Aerosols, cloud microphysics, and fractional cloudiness, *Science*, **245**, 1227-1230, 1989.

Alheit, R.R., A.I. Flossmann, and H.R. Pruppacher, A theoretical study of the wet removal of atmospheric pollutants, IV, The uptake and redistribution of aerosol particles through nucleation and impaction scavenging by growing cloud drops and ice particles, *J. Atmos. Sci.*, **47**, 870-887, 1990.

Amels, P., H. Elias, U. Götz, U. Steinges and K.J. Wannowius, Kinetic investigation of the stability of peroxonitric acid and of its reaction with sulfur(IV) in aqueous solution, in Heterogeneous and Liquid Phase Processes, edited by P. Warneck, pp. 77-88, Springer, Berlin, 1996.

Anastasio, C., B.C. Faust and C.J. Rao, Aromatic carbonyl compounds as aqueous-phase photochemical sources of hydrogen peroxide in acidic sulfate aerosols, fogs, and clouds. 1. Non-phenolic methoxybenzaldehydes and methoxyacetophenoneswith reductants [phenols], *Environ. Sci. Technol.*, **31**, 218-232, 1997.

Andrews, E. and S. M. Larson, Effect of surfactant layers on the size change of aerosol particles as a function of relative humidity, *Environ. Sci. Technol.*, **27**, 857-865, 1993.

Audiffren, N., N. Chaumerliac, and M. Renard, Effects of a polydisperse cloud on tropospheric chemistry, *J. Geophys. Res.*, **101**, 25,949-25,965, 1996.

Barlow, S., J. Berglund, G.V. Buxton, S. Mc Gowan and G.A. Salmon, Kinetics and mechanisms of acid generation in clouds and precipitation, in Annual EUROTRAC Report 1992, Part 6, GCE / HALIPP, EUROTRAC ISS, pp. 49-56, Garmisch-Partenkirchen, 1993.

Barth, M.C., W.C. Skamarock, and A.L. Stuart, The influence of cloud processes on the distribution of chemical species for the 10 July 1996 STERAO / Deep Convection Storm, in International Conference on Clouds and Precipitation Proceedings, pp. 960-963, Reno, Nevada, USA, 14-18 August 2000.

Behra, P. and L. Sigg, Evidence for redox cycling of iron in atmospheric water droplets, *Nature*, **344**, 419-421.

Bell, D.A., and C.P.R. Saunders, An experimental study of aerosol scavenging by hexagonal plate ice crystals, *Atmos. Res.*, **38**, 9-19, 1995.

Berglund, J. and L.I. Elding, Kinetics and mechanism for metal catalysed oxidation of sulfur(IV) by oxygen in aqueous solution, in Annual EUROTRAC Report 1992, Part 6, GCE / HALIPP, EUROTRAC ISS, pp. 19-22, Garmisch-Partenkirchen, 1993.

Blando, J.D. and B.J. Turpin, Secondary organic aerosol formation in cloud and fog droplets: A literature evaluation of plausibility, *Atmos. Environ.*, 34, 1623-1632, 2000.

Bott, A., A numerical model of the cloud-topped planetary boundary-layer: Chemistry in marine stratus and the effects on aerosol particles, *Atmos. Environ.*, **33**, 1921-1936, 1999.

Bower, K.N., *et al.*, Observations and modeling of the processing of aerosol by a hill cap cloud, *Atmos. Environ.*, **31**, 2527-2543, 1997.

Bower, K.N., et al., ACE-2 HILLCLOUD. An overview of the ACE-2 ground-based cloud experiment, *Tellus*, **52B**, 750-778, 2000.

Boyce S. and M.R. Hoffmann, Kinetics and mechanism of the formation of hydroxymethanesulfonic acid at low pH, *J. Phys. Chem.*, **88**, 4740-4746, 1984.

Bradbury, C., K.N. Bower, T.W. Choularton, E. Swietlicki, W. Birmili, A. Wiedensohler, B. Yuskiewicz, A. Berner, U. Dusek, C. Dore, and G.G. Mcfadyen, Modeling of aerosol modification resulting from passage through a hill cap cloud, *Atmos. Res.*, **50**, 185-204, 1999.

Brandt, C. and R. van Eldik, Transition metal-catalysed oxidation of sulfur(IV)oxides, Atmospheric relevant processes and mechanisms, *Chem. Rev.*, **95**, 119-190, 1995.

Brasseur, G.P., R.A. Cox, D. Hauglustaine, I. Isaksen, J. Lelieveld, D.H. Lister, R. Sausen, U. Schumann, A. Wahner, and P. Wiesen, European Scientific Assessment of the Atmospheric Effects of Aircraft Emissions, *Atmos. Env.*, **32**, 2329-2418, 1998.

Brenguier, J.L., P.Y. Chuang, Y. Fouquart, D.W. Johnson, F. Parol, H. Pawlowska, J. Pelon, L. Schuller, F. Schroder, and J. Snider, An overview of the ACE-2 CLOUDYCOLUMN closure experiment, *Tellus Series B-Chemical and Physical Meteorology*, **52** (2), 815-827, 2000.

Buxton, G.V., G.A. Salmon, N.D. Wood, S. Croft and S. McGowan, Kinetics and mechanisms of acid generation in clouds and precipitation, in Annual EUROTRAC Report 1990, Part 6, HALIPP, EUROTRAC ISS, pp.38-43, Garmisch-Partenkirchen, 1991.

Buxton, G.V., S. McGowan and G.A. Salmon, The free radical chain oxidation of S(IV), in The Proceedings of EUROTRAC Symposium '92, edited by P.M. Borrell, P. Borell, T. Cvitas and W. Seiler, pp. 599-604, SPB Academic Publishing bv, The Hague, 1993.

Campolongo, F., A. Saltelli, N.R. Jensen, J. Wilson and J. Hjorth, The role of multiphase chemistry in the oxidation of dimethylsulphide (DMS). A latitude dependent analysis, *J. Atmos. Chem.*, **32**, 327-356, 1999.

Capel, P.D., R. Gunde, F. Zürcher and W. Giger, Carbon speciation and surface tension of fog, *Environ. Sci. Technol.*, **24**, 722-727,1990.

Cautenet, S., and B. Lefeivre, Contrasting behavior of gas and aerosol scavenging in convective rain: A numerical and experimental study in the African equatorial forest, *J. Geophys. Res.*, **99**,13,013-13,024, 1994.

Chameides, W.L., Photochemistry of the atmospheric aqueous phase, in Chemistry of Multiphase Atmospheric Systems, edited by W. Jaeschke, pp. 369-414, Springer, Berlin, 1986.

Chameides, W.L., and D.D. Davis, The free radical chemistry of cloud droplets and its impact upon the composition of rain, *J. Geophys. Res.*, **87**, 4863-4877, 1982.

Chugthai, A.R., J.A. Jassim, J.H. Peterson, D.H. Stedman and D.M. Smith, Spectroscopic and solubility characteristics of oxidized soots, *Aerosol Sci. Technol.*, **15**, 112-126, 1991.

Clarke, A.D., J.L. Varner, F. Eisele, R.L. Wauldin, D. Tanner, and M. Litchy, Particle production in the remote marine atmosphere: Cloud outflow and subsidence during ACE1, *J. Geophys. Res.*, **103**, 16,397-16,409, 1998.

Coakley Jr., J.A., R.L. Bernstein, and P.A. Durkee, Effect of ship-stack effluents on cloud reflectivity, *Science*, ***237***, 1020-1022, 1987.

Coffman, D.J., and D.A. Hegg, A preliminary study of the effect of ammonia on particle nucleation in the marine boundary layer, *J. Geophys. Res.*, **100**, 7147-7160, 1995.

Coichev, N. and R. van Eldik, Kinetics and mechanism of the sulfite-induced autoxidation of Co(II) in aqueous azide medium, *Inorg. Chem.*, **30**, 2375-2380, 1991.

Coichev, N., K. Bal Reddy and R. van Eldik, The synergistic effect of manganese (II) in the sulfite-induced autoxidation of metal ions and complexes in aqueous solution, *Atmos. Environ.*, **26A**, 2295-2300, 1992.

Collett J., B. Daube, D. Gunz and M. Hoffmann, Intensive studies of Sierra Nevada cloudwater chemistry and its relationship to precursor aerosol and gas concentrations, Atmos. Environ., 24A, 1741-1757, 1990.

Collett, J.L. Jr., R. Iovinelli, and B. Demoz, A three-stage cloud impactor for size-resolved measurement of cloud droplet chemistry, *Atmos. Environ.*, **29**, 1145-1154, 1995.

Conover, J.H., Anomalous cloud lines, *J. Atm. Sci., 23*, 778-785, 1966.

Corrigan, C. E. and T. Novakov, Cloud condensation nucleus activity of organic compounds: a laboratory study, *Atmos. Environ.*, ***33***, 2661-2668, 1999.

Cruz, C. N. and S.N Pandis, A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei, *Atmos. Environ.*, **31**, 2205-2214, 1997.

Davidovits, M., Hu, J. H., Worsnop, D. R., Zahniser, M. S. and Kolb, C. E., Entry of gas molecules into liquids, *Faraday Discuss.*, **100**, 65-82, 1995.

Decesari, S., M.C. Facchini, E. Matta and S. Fuzzi, Organic and inorganic solutes in fog droplets: A full characterization approach, Proceedings of 13th International Conference on Clouds and Precipitation, Reno, Nevada, USA, August 14-18, 2000b.

Decesari, S., M.C. Facchini, E. Matta, F. Lettini, M. Mircea, S. Fuzzi, E. Tagliavini and J.-P. Putaud, Chemical features and seasonal trend of water soluble organic compounds in the Po Valley fine aerosol, *Atmos. Environ.*, in press, 2001.

Decesari, S., M.C. Facchini, S. Fuzzi and E. Tagliavini, Characterization of water soluble organic compounds in atmospheric aerosol: a new approach, *J. Geophys. Res.*, **105**, 1481-1489, 2000a.

Dessens, H., The use of spider's threads in the study of condensation nuclei, *Quart. J. Roy. Met. Soc.*,**75**, 23-27, 1949.

Dinger, J.E., H.B. Howell, and T.A. Wojciechowski, On the sources and composition of cloud condensation nuclei in the subsidence air mass over the North Atlantic, *J. Atmos. Sci.*, **27**, 791-797, 1970.

Dong, S. and P.K. Dasgupta, On the formaldehyde bisulfite hydroxymetansulfonate equilibrium, *Atmos. Environ.*, **20**, 1635-1637, 1986.

Durkee, P.A., K.J. Noone, and R.T. Bluth, The Monterey Area Ship Track (MAST) Experiment, *J. Atmos. Sci.*, **57** (16), 2523-2541, 2000.

Easter, R.C., and P.V. Hobbs, The formation of sulfate and the enhancement of cloud condensation nuclei in clouds, *J. Atmos. Sci.*, **31**, 1586-1591, 1974.

Erel, Y., S.O. Pehkonen and M.R. Hoffmann, Redox chemistry of iron in fog and stratus clouds, *J. Geophys. Res.*, **98**, 18423-18434, 1993.

Ervens, B., H. Herrmann, G.V. Buxton, G.A. Salmon, J. Williams, F. Dentener, C. George and P. Mirabel, CAPRAM2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application, in preparation. (See also CAPRAM webpage via www.tropos.de.

Exner, M., H. Herrmann and R. Zellner, Laser-based studies of reactions of the nitrate radical in aqueous solution, *Ber. Bunsenges. Phys. Chem.*, **96**, 470-477, 1992.

Facchini, M.C., M. Mircea, S. Fuzzi and R.J. Charlson, Cloud albedo enhancement by surface-active organic solutes in growing droplets, *Nature*, **401**, 257-259, 1999b.

Facchini, M.C., S. Decesari, M. Mircea, S. Fuzzi and G. Loglio, Surface tension of atmospheric wet aerosol and cloud / fog droplets in relation to their organic carbon content and chemical composition, *Atmos. Environ.*, **34**, 4853-4857, 2000.

Facchini, M.C**.**, S. Fuzzi, J.A. Lind, H. Fierlinger-Oberlinninger, M. Kalina, H. Puxbaum, W. Winiwarter, B.G. Arends, W. Wobrock, W. Jaeschke, A. Berner and C. Kruisz, Phase-partitioning and chemical reactions of low molecular weight organic compounds in fog, *Tellus*, **44B**, 533-544, 1992.

Facchini, M.C., S. Fuzzi, S. Zappoli, A. Andracchio, A. Gelencser, G. Kiss, Z. Krivacsy, E. Meszaros, H.C. Hansson, T. Alsberg and Y. Zebuhr, Partitioning of the organic aerosol component between fog droplets and interstitial air, *J. Geophys. Res.*, **104**, 26821-26832, 1999a.

Feingold, G., S.M. Kreidenweis, B. Stevens, and W.R. Cotton, Numerical simulations of stratocumulus processing of cloud condensation nuclei through collision-coalescence, *J. Geophys. Res.*, **101**, 21,391-21,402, 1996.

Ferek, R.J., T. Garrett, P.V. Hobbs, S. Strader, D. Johnson, J.P. Taylor, K. Nielsen, A.S. Ackerman, Y. Kogan, Q.F. Liu, B.A. Albrecht, and D. Babb, Drizzle suppression in ship tracks, *J. Atmos. Sci.*, **57**, 2707-2728, 2000.

Fitzgerald, J., J.J. Martin, W.A. Hoppel, G.M. Frick, and J. Gelbard, A one-dimensional sectional model to simulate multi-component aerosol dynamics in the marine boundary layer, 2, Modeling application, *J. Geophys. Res.*, **103**, 16,103-16,117, 1998.

Flossmann, A., W.D. Hall, and H.R. Pruppacher, A theoretical study of the wet removal of atmospheric pollutants, I, The redistribution of aerosol particles captured through nucleation and impaction scavenging by growing cloud drops, *J. Atmos. Sci.*, **42**, 583-606, 1985.

Flossmann, A. I., H.R. Pruppacher, and J.H. Topolian, A theoretical study of the wet removal of atmospheric pollutants, II, The uptake and redistribution of $(NH_4)_2SO_4$ particles and SO_2 gas simultaneously scavenged by growing cloud drops, *J. Atmos. Sci.*, **44**, 2912-2923, 1987.

Frick, G.M., and W.A. Hoppel, Airship measurements of aerosol size distribution, cloud droplet spectra, and trace gas concentrations in the marine boundary layer, *Bull. Amer. Meteor. Soc.*, **74**, 2195-2202, 1993.

Gieray, R., P. Wieser, T. Englehardt, E. Swietlicki, H.C. Hansson, B. Mentes, D. Orsini, B. Martinsson, B. Svenningsson, K.J. Noone, and J. Heintzenberg, Phase partitioning of aerosol constituents in cloud based on single-particle and bulk analysis, *Atmos. Environ.*, **31**, 2491-2502, 1997.

Gill, P.S., T.E. Graedel, and C.J. Weschler, Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops, and snowflakes, *Rev. Geophys. Space Phys.*, 21, 903-920, 1983.

Graedel, T. E. and C. J. Weschler, Chemistry within aqueous atmospheric aerosols and raindrops, *Rev. Geophys. Space Phys.*, **19**, 505-539, 1981.

Graedel, T. E., M. L. Mandich and C. J. Weschler, Kinetic model studies of atmosheric droplet chemistry 2. Homogeneous transition metal chemistry in raindrops, *J. Geophys. Res.*, **91**, 5205-5221, 1986.

Grosjean, D. and B. Wright, Carbonyls in urban fog, ice fog, cloud water and rain water, *Atmos. Environ.*, ***17***, 2093-2096, 1983.

Hallberg, A., J.A. Ogren, K.J. Noone, J. Heintzenberg, A. Berner, I. Solly, C. Kruisz, G. Reischl, S. Fuzzi, M.C. Facchini, H.C. Hansson, A. Wiedensohler, and I.B. Svenningsson, Phase partitioning for different aerosol species in fog, *Tellus*, **44B**, 545-554, 1992.

Hansson, H.-C., M.J. Rood, S. Koloutsou-Vakakkis, K. Hameri, D. Orsini and A. Wiedensohler, NaCl aerosol particle hygroscopicity dependence on mixing with organic compounds, *J. Atmos. Chem.*, **31**, 321-346, 1998.

Havers, N., P. Burba, J. Lambert and D. Klockow, Spectroscopic characterization of humic-like substances in airborne particulate matter, *J. Atmos. Chem.*, **29**, 45-54, 1998.

Hegg D.A., S.A. Rutledge, and P.V. Hobbs, A numerical model for sulfur chemistry in warm-frontal rainbands, *J. Geophys. Res.*, **89**, 7133-7147, 1984.

Hegg, D. A., P.V. Hobbs, and L.F. Radke, Observations of the modification of cloud condensation nuclei in wave clouds, *J. Rech. Atmos.*, **14**, 217-222, 1980.

Hegg, D.A., and T.W. Larson, The effects of microphysical parametrization on model predictions of sulfate production in clouds, *Tellus*, **42B**, 272-284, 1990.

Hegg, D.A., Heterogeneous production of cloud condensation nuclei I the marine atmosphere, *Geophys. Res. Lett.*, **17**, 2165-2168, 1990.

Hegg, D.A., L.F. Radke, and P.V. Hobbs, Particle production associated with marine clouds, *J. Geophys. Res.*, **95**, 917-926, 1990.

Hegg, D.A., P.-F. Yuen, and T.V. Larson, Modeling the effects of heterogeneous cloud chemistry on the marine particle size distribution, *J. Geophys. Res.*, **97**, 12,927-12,933, 1992.

Hegg, D.A., S.A. Rutledge, P.V. Hobbs, M.C. Barth, and O. Hertzman, The chemistry of a mesoscale rainband, *Q. J. R. Meteorol. Soc.*, **115**, 867-886, 1989.

Herrmann, H., B. Ervens , H.-W. Jacobi, R. Wolke, P. Nowacki and R. Zellner, CAPRAM 2.3: A chemical aqueous phase radical mechanism for tropospheric chemistry, *J. Atmos. Chem.*, **36,** 231-284, 2000.

Herrmann, H., M. Exner and R. Zellner, A laser photolysis study of reactions of the carbonate radical anion (CO_3^-) in aqueous solution, in Air Pollution Research Report 33: Atmospheric Oxidation Processes, edited by K.H.Becker, pp. 134-138, CEC, Brussels, 1991.

Hoffmann, M.R., On the kinetics and mechanism of oxidation of aquated sulfur dioxide by ozone, *Atmos. Environ*., **20**, 1145-1154, 1986.

Hoigné, J., Y. Zuo, M. von Piechowski, R. Bühler and D. Sedlak, The role of iron and copper species for reactions of photooxidants and photochemical reactions in atmospheric waters, in Air Pollution Research Report 45: Chemical Mechanisms Describing Tropospheric Processes, edited by J. Peeters, pp. 5-16, CEC, Brussels, 1993.

Hoppel, W.A., G.M. Frick, J.W. Fitzgerald, and B.J. Wattle, A cloud chamber study of the effect that nonprecipitating water clouds have on the aerosol size distribution, *Aerosol Sci. and Technol.*, **20**, 1-30, 1994.

Hoppel, W.A., J.W. Fitzgerald, G.M. Frick, R.E. Larson, and E.J. Mack, Aerosol size distributions and optical properties found in the marine boundary layer over the Atlantic Ocean, *J. Geophys. Res.*, **95**, 3659-3686, 1990.

Hudson, J.G., and P.R. Frisbie, Cloud condensation nuclei near marine stratus, *J. Geophys. Res.*, **96**, 20,795-20,808, 1991.

Huie, R. E. and P. Neta, Rate constants for some oxidations of S(IV) by radicals in aqueous solutions, *Atmos. Environ*., **21**, 1743-1447, 1987.

Huie, R.E., Free radical chemistry of the atmospheric aqueous phase, in Progress and Problems in Atmospheric Chemistry, edited by J.R. Barker, pp. 374-419, World Scientific: Singapore, 1995.

Jacob D.J. and M.R. Hoffmann, A dymamic model for the production of H^+, NO_3^- and SO_4^{2-} in urban fog, *J. Geophys. Res*., **88**, 6611-6621, 1983.

Jacob, D.J., Heterogeneous chemistry and tropospheric ozone, *Atmos. Environ*., **34**, 2131-2159, 2000.

Jacob, D.J., E.W. Gottlieb and M.J. Prather, Chemistry of a polluted cloud boundary layer, *J. Geophys. Res*., **94**, 12975-13002, 1989.

Jacob, D.J., Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate, *J. Geophys. Res*., **91**, 9807-9826, 1986.

Jacobson, M.C., H.C Hansson, K.J. Noone and R.J. Charlson, Organic atmospheric aerosols: Review and state of the science, *Rev. Geophys*., **38**, 267-294, 2000.

Junge, C.E., Air Chemistry and Radioactivity, Academic Press, New York, 1963.

Junge, C.E., and T.G. Ryan, Study of the SO_2 oxidation in solution and its role in atmospheric chemistry, *Q. J. R. Meteorol. Soc.*, **84**, 46-55, 1958.

Kaufman, Y.J., and D. Tanre, Effect of variations in supersaturation on the formation of cloud condensation nuclei, *Nature*, **369**, 45-48, 1994.

Khain, A., A. Pokrovsky, and I. Sednev, Some effects of cloud-aerosol interaction on cloud microphysics structure and precipitation formation: Numerical experiments with a spectral microphysics cloud ensemble model, *Atmos. Res.*, **52**, 195-220, 1999.

King, M.D., L.F. Radke, and P.V. Hobbs, Optical properties of marine stratocumulus clouds modified by ships, *J. Geophys. Res.*, ***98***, 2729-2739, 1993.

Kiss, G., B. Varga, A. Gelencser, Z. Krivanscy, A. Molnar, T. Alsberg, l. Persson, H.-C. Hansson and M.C. Facchini, Characterization of polar organic compounds in fog water, *Atmos. Environ*., **35**, 2193-2200, 2001.

Kleinman, L.I., and P.H. Daum, Vertical distribution of aerosol particles, water vapor, and insoluble trace gases in convectively mixed air, *J. Geophys. Res.*, **96**, 991-1005, 1991.

Kogan, Y.L., P.K. Lilly, Z.N. Kogan, and V.V. Filyushkin, The effect of CCN regeneration on the evolution of stratocumulus cloud layers, *Atmos. Res.*, **33**, 137-150, 1994.

Köhler, H., The nucleus in the growth of hygroscopic droplets, *Trans. Faraday Soc*., **32**, 1152-1161, 1936.

Kutz, S., and R. Dubois, Balloon-borne aerosol measurements in the planetary boundary layer: particle production associated with a continental stratiform cloud, *Contrib. Atmos. Phys.*, **70**, 109-116, 1997.

Laaksonen, A., P. Korhonen, M. Kulmala and R.J. Charlson, Modification of the Köhler equation to include soluble trace gases and slightly soluble substances, *J. Atmos. Sci*., **55**, 853-862, 1998.

Laj, P., S. Fuzzi, A. Lazzari, L. Ricci, G. Orsi, A. Berner, D. Schell, A. Günther, M. Wendisch, W. Wobrock, G. Frank, B. Martinsson, and R. Hillamo, The size-dependent chemical composition of fog drops, *Contrib. Atmos. Phys.*, **71**, 115-130, 1998.

Langner, J., and H. Rodhe, A global three-dimensional model of the tropospheric sulfur cycle, *J. Atmos. Chem*., **13**, 255-263, 1991.

Lary, D.J., D.E. Shallcross and R. Toumi, Carbonaceous aerosols and their potential role in atmospheric chemistry, *J. Geophys. Res*., **104**, 15929-15940, 1999.

Leaitch, W.R., Observations pertaining to the effect of chemical transformation in cloud on the anthropogenic aerosol size distribution, *Aerosol Sci. and Technol.*, **25**, 157-173, 1996.

Lelieveld J., P.J. Crutzen and H. Rodhe, Zonal average cloud characteristics for global atmospheric chemistry modelling. Report CM-76, Department of Meteorology, University of Stockholm, 1989.

Lelieveld, J., and J. Heintzenberg, Sulfate cooling effect on climate through in-cloud oxidation of anthropogenic SO_2, *Science*, **258**, 117-120, 1992.

Lelieveld, J., and P.J. Crutzen, The role of clouds in tropospheric photochemistry, *J. Atmos. Chem*., **12**, 229-267, 1991.

Lelieveld, J., and P.J. Crutzen, Influences of cloud photochemical processes on tropospheric ozone, *Nature*, **343**, 227-233, 1990.

Liang, J., and D.J. Jacob, Effect of aqueous-phase cloud chemistry on tropospheric ozone, *J. Geophys. Res*., **102**, 5993-6001, 1997.

Likens, G.E., E.S. Edgerton and J.N. Galloway, The composition and deposition of organic carbon in precipitation, *Tellus*, **35B**, 16-24, 1983.

Lohmann, U., and J. Feichter, Can the direct and semi-direct aerosol effect compete with the indirect effect on a global scale?, *Geophys. Res. Lett.*, **28**, 159-161, 2000.

Lüttke J., V. Scheer, K. Levsen, G. Wünsch, J. N. Cape, K. Hargreaves, R.L. Storeton-West, K. Acker, W. Wieprecht and B. Jones, Occurrence and formation of nitrated phenols in and out of cloud, *Atmos. Environ*., **31**, 2637-2648, 1997.

Martinsson, B.G., *et al*., Droplet nucleation and growth in orographic clouds in relation to the aerosol population, *Atmos. Res.*, **50**, 289-315, 1999.

Mayol-Bracero, O.L., P. Guyon, B. Graham, M.O. Andreae, S. Decesari, M.C. Facchini, S. Fuzzi and P. Artaxo, Black carbon, organic carbon and water-soluble organic compounds in biomass smoke particles over the Amazon Basin, *J. Geophys. Res*. [submitted], 2001.

Mircea, M., M.C. Facchini, S. Decesari, S. Fuzzi and R.J. Charlson, The influence of the organic aerosol component on CCN supersaturation spectra for different aerosol types, *Tellus*, in press, 2001.

Mitra, S.K., J. Brinkmann, and H.R. Pruppacher, A wind tunnel study on the drop-to-particle conversion, *J. Aerosol Sci.*, **23**, 245-256, 1992.

Mukai, A and Y. Ambe, Characterization of humic acid-like brown substance in airborne particulate matter and tentative identification of its origin, *Atmos. Environ*., **20**, 813-819, 1986.

Munger, J.W., D.J. Jacob and M.R. Hoffmann, The occurrence of bisulfithe-aldehyde addiction products in fog and cloud water, *J. Atmos. Chem*., **1**, 335-350, 1984.

Noone, K.J., J.A. Ogren, A. Holberg, J. Heintzenberg, J. Ström, H.C. Hansson, B. Svenningsson, A. Wiedensohler, S. Fuzzi, M.C. Facchini, B.G. Arends, and A. Berner, Changes in aerosol size- and phase distributions due to physical and chemical processes in fog, *Tellus*, **44B**, 489-504, 1992.

Noone, K.J., R.J. Charlson, D.S. Covert, J.A. Ogren, and J. Heintzenberg, Cloud droplets: Solute concentration is size dependent, *J. Geophys. Res.*, **93**, 9477-9482, 1988.

Novakov, T. and C.E. Corrigan, Cloud condensation nucleus activity of the organic component of biomass smoke particles, *Geophys. Res. Lett.*, ***23***, 2141-2144, 1996.

Novakov, T. and J.E. Penner, Large contribution of organic aerosols to cloud-condensation-nuclei concentrations, *Nature*, **365**, 823-826, 1993.

Ogren, J.A. and R.J. Charlson, Implications for models and measurements of chemical inhomogeneities among cloud droplets, *Tellus*, **44B**, 208-225, 1992.

Olson, T. M. and M.R. Hoffmann, Hydroxyalkylsulfonate formation: Its role as a S(IV) reservoir in atmospheric water droplets, *Atmos. Environ*., **23**, 985-997, 1989.

Pandis, S.N., J.H. Seinfeld and C Pilinis, Chemical composition differences in fog and cloud droplets of different sizes, *Atmos. Environ.*, **24A**, 1954-1969, 1990.

Pehkonen, S.O., R. Siefert, S. Webb, Y. Erel, and M.R. Hoffmann, Simultaneous spectrophometric measurement of Fe(II) and Fe(III) in atmospheric water, *Environ. Sci. Technol*., **26**, 1731-1736, 1992.

Pehkonen, S.O., R. Siefert, Y. Erel, S. Webb and M.R. Hoffmann, Photoreduction of iron oxyhydroxides in the presence of important atmospheric organic compounds, *Environ. Sci. Technol*., **27**, 2056-2062, 1993.

Peng, C. and C.K. Chan, The water cycle of water-soluble organic salts of atmospheric importance, *Atmos. Environ*., 35, 1183-1192, 2001.

Penner, J.E., C.C. Chuang and C. Liousse, The contribution of carbonaceous aerosol to climate change: The Fourtheenth International Conference of Nucleation and Atmospheric Aerosols, Helsinki, Finland, 1996.

Perry, K.D., and P.V. Hobbs, Further evidence for particle nucleation in clear air adjacent to marine cumulus clouds, *J. Geophys. Res.*, **99**,22,803-22,818, 1994.

Pruppacher, H.R. and J.D. Klett, Microphysics of Clouds and Precipitation, 2nd ed., Kluwer Acad. Publications, Dordrecht, 1997.

Pruppacher, H.R., and R. Jaenicke, The processing of water vapor and aerosols by atmospheric clouds, a global estimate, *Atmos. Res*., **38**, 283-295, 1995.

Rabani, J., D. Klug-Roth and J. Lilie, Pulse radiiolytic investigations of the catalyste diproportionation of peroxy radicals. Aqueous cupric ions, *J. Phys. Chem*., **77**, 1169-1173, 1973.

Radke, L.F., and D.A. Hegg, The shattering of saline droplets upon crystallization, *J. Rech. Atmos.*, **6**, 447-455, 1972.

Radke, L.F., J.A. Coakley, and M.D. King, Direct and remote sensing observations of the effects of ships on clouds, *Science*, *246*, 1146-1149, 1989.

Respondek, P.S., R.R. Alheit and H.R. Pruppacher, A theoretical study of the wet removal of atmospheric pollutants, V, The uptake, redistribution, and deposition of $(NH_4)_2SO_4$ by a convective cloud containing ice, *J. Atmos. Sci.*, **52**, 2121-2132, 1995.

Rivera-Carpio, C.A., C.E. Corrigan, T. Novakov, J.E. Penner, C.F. Rogers and J.C Chow, Derivation of contributions of sulfate and carbonaceous aerosols to cloud condensation nuclei from mass size distributions, *J. Geophys. Res*., **101**, 19483-19493, 1996.

Rodhe, H., Precipitation scavenging and tropospheric mixing, in Precipitation Scavenging, Dry Deposition and Resuspension, edited by H.R. Pruppacher, R.G. Semonin and W.G.N. Slinn, pp. 719-730, Elsevier, New York, 1983.

Roelofs, G.J.H., A cloud chemistry sensitivity study and comparison of explicit and bulk cloud model performance, *Atmos. Environ.*, **27A**, 2255-2264, 1993.

Rogge, W.F., M.A. Mazurek, L.M. Hildemann and G.R. Cass, Quantification of urban organic aerosol at a molecular level: Identification, abundance and seasonal variation, *Atmos. Environ*., **27A**, 1309-1330, 1993.

Rosenfeld, D., Suppression of rain and snow by urban and industrial air pollution, *Science*, **287**, 1793-1796, 2000.

Rudich, Y., I. Benjamin, R. Naaman, E. Thomas, S. Trakhtenberg and R. Ussyshkon, Wetting of hydrophobic organic surfaces and its implications to organic aerosols in the atmosphere, *J. Phys. Chem*., **104**, 5238-5245, 2000.

Saxena, P. and L.M. Hildemann, Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem*., **24**, 57-109, 1996.

Saxena, P., L.M. Hildemann, P.H. McMurry and J.H Seinfeld, Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res*., **100**, 18755-18770, 1995.

Saxena, V.K., and J.D. Grovenstein, The role of clouds in the enhancement of cloud condensation nuclei concentrations, *Atmos. Res.*, **31**, 71-89, 1994.

Saxena, V.K., Bursts of cloud condensation nuclei (CCN) by dissipating clouds at Palmer Station, Antarctica, *Geophys. Res. Lett.*, **23**, 69-72, 1996.

Saxena, V.K., J.N. Burford, and J.M. Kassner Jr., Operation of a thermal diffusion chamber for measurements on cloud condensation nuclei, *J. Atmos. Sci.*, **27**, 73-80, 1970.

Schell, D., W. Wobrock, R. Maser, M. Preiss, W. Jaeschke, H.W. Georgii, M.W. Gallagher, K.N. Bower, K.M. Beswick, S. Pahl, M.C. Facchini, S. Fuzzi, A. Wiedensohler, H-C. Hansson, and M. Wendisch, The size-dependent chemical composition of cloud droplets, *Atmos. Environ*., **31**, 2561-2576, 1997.

Schumann, U., H. Schlager, F. Arnold, J. Ovarlez, H. Kelder, O. Hov, G. Hayman, I.S.A. Isaksen, J. Staehelin, and P.D. Whitefield, Pollution from aircraft emissions in the North Atlantic flight corridor: Overview on the POLINAT projects, *J. Geophys. Res-Atmos.*, **105**, 3605-3631, 2000.

Sciare, J., E. Baboukas, R. Hancy, N. Mihalopoulos and B.C. Nguyen, Seasonal variation of dimethylsulfoxide in rainwater at Amsterdam Island in the southern Indian Ocean: Implications on the biogenic sulfur cycle, *J. Atmos. Chem*., **30**, 229-240, 1998.

Sedlak, D. L. and J. Hoigné, The Role of copper and oxalate in the redox cycling of iron in atmospheric waters, *Atmos. Environ*., **27A**, 2173-2185, 1993.

Sehested, K. and J. Holcman, A pulse radiolysis study of the OH radical induced autoxidation of methanesulfinic acid, *Radiat. Phys. Chem*., **47**, 357-360, 1996.

Seinfeld, J.H. and S. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley and Sons, New York, 1998.

Shaw, G., Production of condensation nuclei in clean air by nucleation of H_2SO_4, *Atmos. Environ.*, **23**, 2841-2846, 1989.

Shulman, M.L., M.C. Jacobson, R.J. Charlson, R.E. Synovec and T.E. Young, Dissolution behavior and surface tension effects of organic compounds in nucleating cloud droplets, *Geophys. Res. Lett*., **23**, 277-280, 1996.

SMIC, Inadvertent Climate Modification, MIT Press, Cambridge, 1971.

Song, N., and D. Lamb, Experimental investigation of ice in supercooled clouds, II, Scavenging of an insoluble aerosol, *J. Atmos. Sci.*, **51**, 104-116, 1994.

Ström, J., and S. Ohlsson, *In situ* measurements of enhanced crystal number densities in cirrus clouds caused by aircraft exhaust, *J. Geophys. Res.*, **103**, 11,355-11,361, 1998.

Stumm W. and J.J. Morgan, Aquatic Chemistry. John Wiley & Sons: New York, 1981.

Svenningsson, B., H.C. Hansson, B. Martinsson, A. Wiedensohler, E. Swietlicki, S.I. Cederfelt, M. Wendisch, K.N. Bower, T.W. Choularton, and R.N. Colvile, Cloud droplet nucleation scavenging in relation to the size and hygroscopic behavior of aerosol particles, *Atmos. Environ.*, **31**, 2463-2475, 1997.

Toon, O.B. and R.C. Miake-Lye, Subsonic Aircraft: Contrail and Cloud Effects Special Study (SUCCESS), *Geophys. Res. Lett.*, **25**, 1109-1112, 1998.

Twomey, S., Atmospheric Aerosols, Elsevier Scientific: Amsterdam, 302pp, 1977a.

Twomey, S., H.B. Howell, and T.A. Wojciechowski, Comments on "Anomalous cloud lines", *J. Atmos. Sci.*, ***25***, 333-334, 1968.

Twomey, S., Pollution and the planetary albedo, *Atmos. Env.*, **8**, 1251-1256, 1974.

Twomey, S., The Influence of Pollution on the Shortwave Albedo of Clouds, *J. Atmos. Sci.*, **34**, 1149-1152, 1977b.

van Eldik, R.N. Coichev, K. Bal Reddy and A. Gerhard, Metal ion catalyzed autoxidation of sulfur(IV)-oxides: Redox cycling of metal ions induced by sulfite, *Ber. Bunsenges. Phys. Chem*., **96**, 478-485, 1992.

Walcek, C.J., H.H. Yuan and W.R. Stockwell, The influence of aqueous-phase chemical reactions on ozone formation in polluted and nonpolluted clouds, *Atmos. Environ.*, **31**, 1221-1237, 1997.

Warneck, P., Chemistry and photochemistry in atmospheric water drops, *Ber. Bunsenges. Phys. Chem*., **96**, 454-460, 1992.

Warneck, P., HALIPP annual report 1992, In Annual EUROTRAC Report 1992, Part 6, *GCE/HALIPP*, Garmisch- Partenkirchen, 9-16, 1993.

Warneck, P., The relative importance of various pathways for the oxidation of sulfur dioxide and nitrogen dioxide in sunlit continental fair weather clouds, *Phys. Chem. Chem. Phys*., **1**, 5471-5483, 1999.

Warneck, P., Chemical reactions in clouds. *Fresenius J. Anal. Chem.*, **340**, 585-590, 1991.

Warneck, P., P. Mirabel, G.A. Salmon, R. van Eldik, C. Vinckier, K.J. Wannowius and C. Zetzsch, Review of the Activities and Achievements of the EUROTRAC subproject HALIPP, in Heterogeneous and Liquid-Phase Processes, edited by P. Warneck, pp. 7-74, Springer, Berlin, 1996a.

Warneck, P., H.-J. Benkelberg, U. Deister, M. Fischer, A. Schäfer and J. Ziajka, Chain Oxidation of S(IV) in Aqueous Solution: Application of Radical Scavenger Techniques, in Heterogeneous and Liquid-Phase Processes, edited by P. Warneck, pp. 140-145, Springer: Berlin, 1996b.

Warner, J., A reduction in rainfall associated with smoke from sugarcane fires: An inadvertent weather modification?, *J. Appl. Meteor.*, **7**, 247-251, 1968.

Weber, R.J., P.H. McMurry, F.L. Eisele, and D.J. Tanner, Measurement of expected nucleation precursor species and 3-500 nm diameter particles at Mauna Loa Observatory, Hawaii, *J. Atmos. Sci.*, **52**, 2242-2257, 1995.

Weschler, C. J., M. L. Mandich and T. E. Graedel, Speciation, photosensitivity and reactions of transition metal ions in atmospheric droplets, *J. Geophys. Res*., **91**, 5189-5204, 1986.

Wiedensohler, A., *et al*., Night-time formation and occurrence of new particles associated with orographic clouds, *Atmos. Environ.*, **31**, 2545-2560, 1997.

Winiwarter, W., H. Puxbaum, S. Fuzzi, M.C. Facchini, G. Orsi, N. Beltz, K. Enderle and W. Jaeschke, Organic acid gas and liquid phase measurements in Po Valley fall-winter conditions in the presence of fog, *Tellus*, **40B**, 348-357, 1988.

Yuen, P.-F., D.A. Hegg, and T.V. Larson, The effects of in-cloud sulfate production on light-scattering properties of continental aerosol, *J. Appl. Meteor.*, **33**, 848-854, 1994.

Zappoli, S., A. Andracchio, S. Fuzzi, M.C. Facchini, A. Gelencsér, G. Kiss, Z. Krivácsy, Á. Molnár, E. Mészáros, H-C. Hansson, K. Rosman and Y. Zebühr, Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility, *Atmos. Environ*., **33**, 2733-2743, 1999.

Zellner, R. and H. Herrmann, Free Radical Chemistry of the Aqueous Atmospheric Phase, in Advances in Spectroscopy, Vol. 24, Spectroscopy in Environmental Science, edited by R.J.H. Clark and R.E. Hester, pp. 381-451, Wiley, London.

Zellner, R., M. Exner and H. Herrmann, Absolute OH quantum yields in the laser photolysis of nitrate, nitrite and dissolved H_2O_2 at 308 and 351 nm in the temperature range of 278-353 K, *J. Atmos. Chem*., **10**, 411-425, 1990.

Zhang, Y., S.M. Kreidenweis, and G. Feingold, Stratocumulus processing of gases and cloud condensation nuclei, 2, Chemistry sensitivity analysis, *J. Geophys. Res.*, **104**, 16,061-16,080, 1999.

Ziajka, J, F. Beer and P. Warneck, Chain Oxidation of S(IV) in aqueous solution: application of radical scavenger techniques, in Annual EUROTRAC Report 1992, Part 6, *GCE/HALIPP*, pp. 64-69, Garmisch-Partenkirchen, 1993.

Ziajka, J., F. Beer, and P. Warneck, Iron-catalysed oxidation of bisulphite aqueous solution: Evidence for a free radical chain mechanism, *Atmos. Environ*., **28**, 2549-2552, 1994.

Editor's note: We would like to thank Sandro Fuzzi for coordinating this group of articles on clouds in the troposphere.

Please help us keep our mailing list up to date*:*

_____ Please note my new address

_____ Please also send IGAC*tivities* to my colleague

_____ Please remove me from your mailing list

Please return to the
IGAC Core Project Office
by mail or email (igac@mit.edu)

Name: ______________________________ Organization: ______________________________

Street address: ____

City: __________________State:______________ Zip:__________ Country: __________________

Telephone: __________________Fax:__________________ E-mail:_________________________

Announcements

Atmospheric Chemistry in the Earth System:
From Regional Pollution to Global Climate Change

18-25 September 2002
Kalimera Kriti Hotel
Crete, GREECE

10th Scientific Conference of the
International Association of Meteorology of
Atmospheric Sciences (IAMAS),
Commission for Atmospheric Chemistry and
Global Pollution (CACGP)
and
7th Scientific Conference of the International
Global Atmospheric Chemistry Project (IGAC)

The Symposium is divided in 5 major scientific sessions:

- Observing our changing atmosphere.
- Drivers of atmospheric composition change.
- Processes and mechanisms.
- Major campaigns with regional focus.
- Impacts.

For further information, contact:
igac2002@chemistry.uch.gr.

http://atlas.chemistry.uch.gr/IGAC2002/

Challenges of a Changing Earth

A Global Change
Open Science Conference
Amsterdam, The Netherlands
10-13 July 2001

International Geosphere-Biosphere
Programme (IGBP), International
Human Dimensions Programme on
Global Environmental Change (IHDP),
World Climate Research Programme
(WCRP)

Tel. +46-8-16-64-48; Fax 64-05
http://www.sciconf.igbp.kva.se/

A Changing Atmosphere

8th European Symposium on the Physico-Chemical Bevahiour of Atmospheric Pollutants

Torino, Italy
17-20 September 2001

European Commission; DG Research;
Joint Research Centre;

Tel. +39 0332 789958; Fax 785704
Further information: frank.raes@jrc.it
http://www.ei.jrc.it/ap/events/torino2001/

Non-CO_2 Greenhouse Gases (NCGG-3)

3rd International Symposium

Maastricht, The Netherlands
21-23 January 2002

Netherlands Association of
Environmental Professionals–
VVM Section for Clean Air
in The Netherlands (CLAN)

Tel. +31-73-621 5985; Fax 621 6985
Further information: vvm@wxs.nl
http://www.vvm.to/ncgg-3.htm

IGAC*tivities* Newsletter

Editor, Alex Pszenny
Layout and proofreading, Ed Carlevale
IGAC logo, Linda Kubrick

Published by The IGAC Core Project Office, MIT,
Room 24-409, Cambridge, MA 02139-4307, USA

Tel: (+1-617) 253-9887, Fax: (+1-617) 253-9886
E-mail: igac@mit.edu; http://web.mit.edu/igac/www/

IGAC was initiated by the Commission on Atmospheric Chemistry and Global Pollution (CACGP) and is a Core Project of the International Geosphere-Biosphere Programme (IGBP). The IGAC Core Project Office is currently supported by the National Science Foundation (NSF), National Aeronautics and Space Administration, and National Oceanic and Atmosphere Administration of the United States of America through NSF Grant No. ATM 99-08980. Any opinions, findings and conclusions, or recommendations expressed in this newsletter are those of the individual author(s) and do not necessarily reflect the views of the NSF or other agencies.

NON-PROFIT ORG:
U.S. POSTAGE
PAID
Cambridge, MA
Permit No. 54016

IGAC*tivities* Newsletter

IGAC Core Project Office
MIT Bldg. 24-409
77 Masachusetts Avenue
Cambridge, MA 02139-4307
USA

Printed on Recycled Paper
Please Recycle after Use!