

CONCENTRATIONS OF WATER SOLUBLE ORGANIC AEROSOLS AT Mt. LEMMON IN ARIZONA

*Masahiro Hori*¹

*Sachio Ohta*²

*Naoto Murao*³

*Sadamu Yamagata*⁴

Abstract

Concentrations of low molecular weight dicarboxylic acids, organics and sulfate in aerosols were measured at the summit of Mt. Lemmon (2971 m), Arizona, from October 1994 to September 1996. Oxalic acid was most abundant (4.4 ~ 62.0 ng m⁻³) among the measured dicarboxylic acids and accounted for 50% of the total dicarboxylic acid mass concentration. Monthly mean concentrations of other dicarboxylic acid components were 0.0 ~ 11.3 ng m⁻³ for malonic acid, 0.6 ~ 19.9 ng m⁻³ for malic acid, and 0.0 ~ 5.4 ng m⁻³ for succinic acid together with 148.5 ~ 1015.8 ng m⁻³ organics and 113.9 ~ 1962.2 ng m⁻³ sulfate. The concentrations of these water soluble components increased from late spring to autumn, particularly in summer, as the top of the mixing layer rose above the summit of Mt. Lemmon due to the strong solar radiation. The annual time variations in dicarboxylic acid, organics and sulfate concentrations implied that the photochemical production of malic acid and malonic acid and the dissociation of organics and oxalic acid occur in the atmosphere in middle and late of summer. The concentration ratio of total dicarboxylic acid was 2 ~ 13% of that of sulfate and highest in summer.

Changes in the stratus cloud top albedo and solar radiation net flux at the tropopause due to increases in number concentration of water soluble aerosols were calculated under three different scenarios of number concentrations. The calculations indicated that the indirect radiative effect caused by increases in number concentration of water soluble aerosols was large and a doubling in the number concentration of water soluble aerosols decreases the solar radiation net flux at the tropopause by up to 20 Wm⁻², although this occurs within a local cloudy area.

KEYWORDS: *dicarboxylic acids, sulfate, aerosol, cloud condensation nuclei, indirect radiative effect*

1 D.Eng., Invited Researcher, National Space Development Agency of Japan, Roppongi, Minato-ku, Tokyo 106-0032
2 D.Sci., Prof., Div. of Environ. Resource Eng., Graduate School of Eng., Hokkaido Univ.
3 D.Eng., Associate Prof., Div. of Environ. Resource Eng., Graduate School of Eng., Hokkaido Univ.
4 D.Eng., Instructor, Div. of Environ. Resource Eng., Graduate School of Eng., Hokkaido Univ.

1. Introduction

Atmospheric aerosols affect the global climate through two processes. One is a direct effect through a modification of the solar radiation budget due to scattering and absorption of solar radiation caused by increases in the number concentrations of aerosols, and the other is an indirect effect caused by increases in the number concentrations of cloud droplets activated from water soluble components in aerosols (Twomey, 1991). The latter process appears to affect the climate to a larger extent, because cloud droplets have larger cross sections than aerosol particles and can thus reflect more solar radiation to space than aerosols. However the indirect effect has not been estimated accurately due to a lack of information of the chemical components of aerosols which can be activated to cloud droplets, and also of the relation between number concentration of aerosols and that of activated cloud droplets in cloud processes. These inaccuracies introduce uncertainties in predictions of future surface temperatures (IPCC, 1996).

Water soluble components in aerosols are activated into cloud droplets when the humidity exceeds the critical supersaturation. Aerosols with critical supersaturations of 0.1~0.4 % are called cloud condensation nuclei (CCN). The critical supersaturation depends on the chemical component and particle size of the particular water soluble component. To estimate the magnitude of the indirect effect for each chemical component the number concentration as well as its critical supersaturation as a function of particle size must be determined.

The major chemical components which may contribute to the CCN number had been considered to be sulfate (Pruppacher and Klett, 1980), because the mass and number concentration of sulfate in aerosols was found to be high all over the world. Therefore most studies have treated the indirect forcing caused only by sulfate in aerosols (Charlson et al., 1992, Kiehl and Briegleb, 1993). However water soluble organics in aerosols must also be considered CCN, as recent studies have shown that the mass concentration of total organics in aerosols is equal to that of sulfate (Ohta et al., 1996 and 1998) and water soluble organics in aerosols account for 50 % of total organic aerosols (Sempere and Kawamura, 1994). Novakov and Penner (1993) compares mass concentrations of organics and sulfate in aerosols with number concentrations of CCN and finds that organics may account for most of the CCN fraction. Further, experimental studies have shown that some dicarboxylic acids such as glutaric acid and ammonium oxalate, which are major components of water soluble organics in aerosols, have low critical supersaturations (Cruz and Pandis, 1997; Hori, 1998). Hori determined that critical supersaturation of ammonium oxalate is comparable to that of ammonium sulfate. These results show that it is possible for some water soluble organics in aerosols to activate cloud droplets. Thus it is important to monitor the concentration of water soluble organics in aerosols and examine their contribution to indirect radiative forcing caused by sulfate, to estimate the total indirect effect caused by aerosols and to predict future surface temperatures. Observational studies of concentrations of water soluble organic aerosols are limited and no measurements at cloud forming height has been carried out.

In this study the concentration of low molecular weight dicarboxylic acids in aerosols as well as sulfate were measured at cloud forming height at the summit of a mountain, and the time variations in the concentration of each component and concentration ratio of dicarboxylic acids to sulfate are discussed (chapter 2). To estimate the magnitude of the change of solar radiation net flux at the tropopause due to increases in the number concentration of water soluble aerosols, the stratus cloud top albedo and solar radiation net flux at the tropopause were calculated for three scenarios of number concentrations of water soluble aerosols (chapter 3).

2. Observation

2.1 Sampling method

(1) Location and sampling period

Aerosol sampling was carried out in a room of the Cosmic Ray Observatory at Mt. Lemmon, Arizona, U.S.A from October 1994 to September 1996. Figure 1 shows the location of the Mt. Lemmon. The observatory is located at the top of the mountain (2791m above sea level), 25km northeast of Tucson (population 500,000) and 150km southeast of Phoenix (population 2,200,000). Each sample was collected over one month (about 30 days), and 24 samples were obtained during the 2 years.

(2) Apparatus

Aerosol particles were collected on both teflon (Sumitomo electric corp. AF07P, 47mm in diameter) and quartz fiber filters (Pallflex, 2500QAST-UP, 47mm in diameter) at a flow rate of 20 l min^{-1} . By using a cyclone separator particles smaller than $2 \mu\text{m}$ in diameter were sampled. Both filters were packed with aluminum foil and kept in a vinyl pack before and after the sampling. Before sampling, the quartz fiber filter was heated at $830 \text{ }^\circ\text{C}$ for 1 hour to remove contaminating organics from the filter.

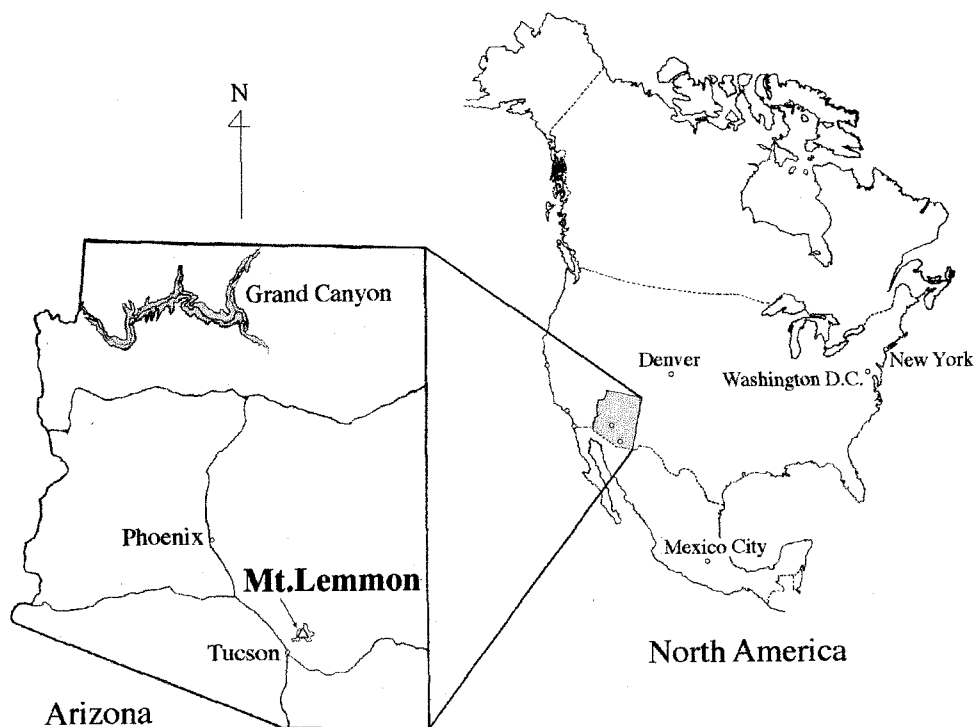


Figure 1. Location of the aerosol sampling site (Mt. Lemmon). The sampling facility is located at the summit of Mt. Lemmon (2791m above sea level).

2.2 Chemical analysis

(1) Water soluble components

After the sampling, water soluble components were ultrasonically extracted from the teflon filter into distilled-deionized water. Then low molecular weight dicarboxylic acids and sulfate were analyzed by two ion chromatographs: Dionex DX-100 with an IonPac ICE-AS1 column for analysis of dicarboxylic acids other than oxalic and phthalic acids, and a Yokogawa IC-7000 with an Excelpack ICS-A23 column for analysis of oxalic acid, phthalic acid, and sulfate.

(2) Carbonaceous components

The mass concentration of total organics in aerosols was measured to compare with the dicarboxylic acid concentrations. The concentration of organics was determined from quartz fiber filters as follows. The quartz fiber filter was cut into two, one used for total carbon (T.C) analysis and the other for elemental carbon (E.C). Before the analysis for E.C, the quartz fiber filter piece was heated at 300 °C for 30 minutes in air to remove organic carbon. Then both filter pieces were analyzed by an NC-analyzer (SUMIGRAPH NC-80) to determine the carbon content as T.C and E.C on the filter (Ohta and Okita, 1984). The difference between T.C and E.C was defined as the organic carbon (O.C), and the organics concentration was defined as 1.2 times the organic carbon concentration (Countess et al., 1980) as

$$\text{O.C} = \text{T.C} - \text{E.C} \quad (1)$$

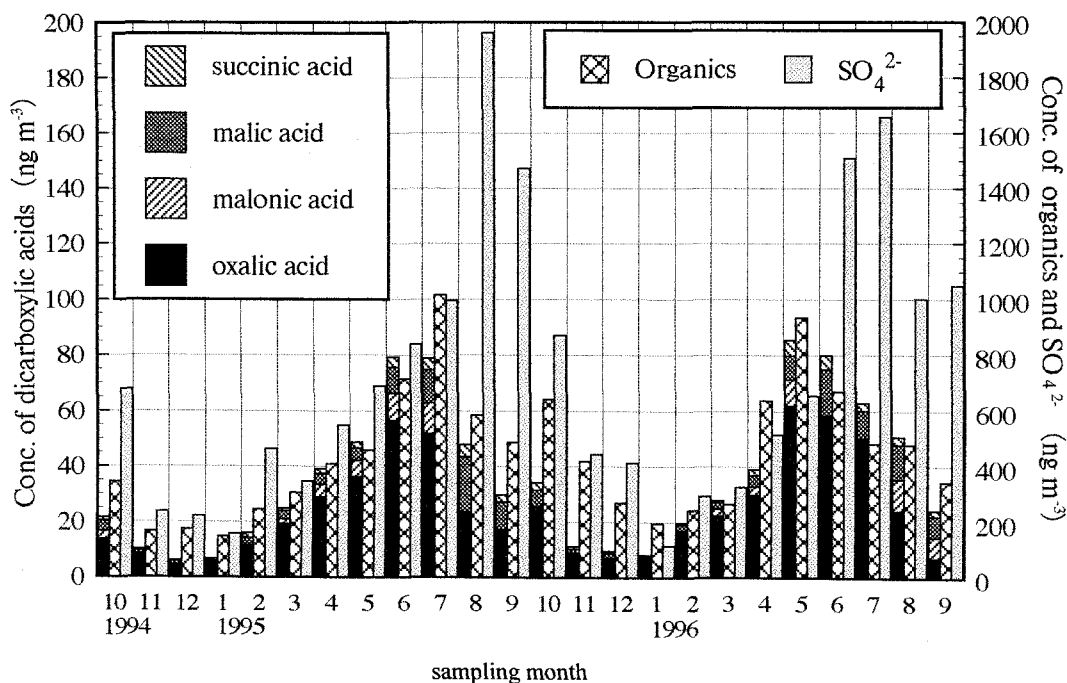


Figure 2. Monthly mean concentrations of low molecular weight dicarboxylic acids, organics, and sulfate in aerosols at Mt. Lemmon, Arizona.

and

$$\text{Organics} = 1.2 \times \text{O.C.} \quad (2)$$

2.3 Concentration of each chemical species at Mt. Lemmon

Figure 2 shows the monthly mean concentrations of dicarboxylic acids (left ordinate), organics and sulfate (right ordinate) in the aerosols. The concentrations of each component are also listed in Table 1. Oxalic acid ((COOH)₂), malonic acid (HOOCCH₂COOH), succinic acid (HOOC(CH₂)₂COOH), and malic acid (HOOC(OH)CH₂COOH) were detected as dicarboxylic acid by the ion chromatography. Malonic acid could not be quantified in some samples ('95.8 ~ 10, '96.6 ~ 7) despite the malonic acid peak in the chromatogram being high enough to indicate its existence in these samples, as the malonic acid peak in the chromatogram overlapped with a peak of unknown components. The retention times of malonic and maleic acids (HOOC(CH)₂COOH) are similar with the IonPac ICE-AS1 column. Kawamura and Ikushima (1993) found that in summer maleic acid is produced due to photochemical oxidation of benzene in urban atmospheres. Thus it may be that the quantification problems for malonic acid in the summer periods ('95.8 ~ 10, '96.6 ~ 7) were due to maleic acid in the samples, which indicates that in these periods air from the urban areas flow up to the sampling location, as will be discussed later.

Among the four dicarboxylic acid components, the concentration of oxalic acid was the highest (4.4 ~ 62 ng m⁻³) and accounted for about 50 % of the total dicarboxylic acid. Malonic acid (0.0 ~ 11.3 ng m⁻³) and malic acid (0.6 ~ 19.9 ng m⁻³) were the next most abundant and succinic acid (0.0 ~ 5.4 ng m⁻³) was the least common. Both sulfate (113.9 ~ 1962.2 ng m⁻³) and organics (148.5 ~ 1015.8 ng m⁻³) were the major chemical components in aerosols in all seasons. The concentrations of each of the dicarboxylic acids, sulfate, and organics in the aerosols increased from late spring to autumn, and particularly in summer. According to radio sonde measurements of the temperature profile at Tucson, the mixing layer in summer is thicker than in winter, due to enhancement of vertical convection caused by the strong solar radiation. The top of the layer is above 2.8 km, the height of Mt. Lemmon. At such times polluted air in the mixing layer was lifted from the ground to higher altitudes, causing the variations in the concentrations of all substances in the aerosols. However, the time when the concentration was highest was slightly different for sulfate and organic components. During the two years the concentration of organics were highest in the first year in early summer ('95.7) and in the second in late spring ('96.5) and the concentration of sulfate became the highest after that in late ('95.8) and middle ('96.7) summer. This time difference in the highest concentrations of organics and sulfate is considered to be caused by the following: According to results of back trajectory analysis of air masses from the top of Mt. Lemmon (Hoshi, 1997), the spring and early summer air masses are transported by strong westerly wind flows into the sampling site area, here the sampled aerosols are transported from distant areas in a short time. After the middle of summer, wind velocities become lower and the air mass around the sampling site tends to be stationary for a few months. Thus aerosols originating from the urban areas near Mt. Lemmon for a few months in and after the middle of summer are transported slowly to the sampling site while being oxidized photochemically. A large part of the organic aerosols may dissociate photochemically during this period. Sulfate aerosols are also produced by photochemical oxidation of sulfur dioxide but do not dissociate photochemically. Figure 2 shows a clear decrease in organic concentrations around '95. 8, 9 and '96. 6~ 9. Except in this period, concentrations of organics are almost the same as those of sulfate. The time variation in the concentration of oxalic acid was similar to that of organics. Thus oxalic acid may also dissociate during this period. The concentrations of malic and malonic acids appear to follow the time variations of sulfate. Succinic acid concentrations change similar to both organics and sulfate. These variations in the concentration of dicarboxylic acids imply that the production and dissociation rates of oxalic acid and of malic and malonic acids are subject to different seasonal influences. It may be considered that the production rate of malic and malonic acids are higher than the dissociation rates during the above period and

thus the concentration of these acids increased in the stationary air masses. The molecular structure of malic acid is similar to that of succinic acid except that malic acid has one hydroxyl group instead of hydrogen. Thus malic acid may be considered to be produced partly from succinic acid, which may lead to the unceasing time variations in the concentration of succinic acid. Other dicarboxylic acids such as maleic acid, which may cause quantification problems for malonic acid for some samples as described above, may also be produced in the stationary air masses, although their concentrations could not be quantified. According to Kawamura and Kaplan (1987), dicarboxylic acid components are mainly emitted as primary particles or precursors from automobiles and precursors such as cyclo-olefins are oxidized to dicarboxylic acids due to photochemical reactions in the atmosphere. The study here shows that dicarboxylic acid concentrations vary, and that the concentrations are very sensitive to meteorological conditions.

Figure 3 shows seasonal variations in the monthly mean concentration ratios of the dicarboxylic acid to sulfate ratio. The ratio of dicarboxylic acid to sulfate was 2.0 ~ 13 % and concentrations of other water soluble inorganic species (not shown in this paper) were also low. The mass concentration of nitrate was as high as that of oxalic acid, and chloride was lower than oxalate. Matsumoto et al. (1998) revealed that oxalate and sulfate are

Table 1. Monthly mean mass concentrations of organic aerosol components analyzed by NC-analyzer, and dicarboxylic acids and sulfate in aerosols by ion chromatography at Mt. Lemmon, Arizona. NM denotes components which could not be quantified.

Period	Organics ng m ⁻³	Dicarboxylic acid, ng m ⁻³					SO ₄ ²⁻ ng m ⁻³	Dicarboxylic acid/Org. Dicarboxylic acid/SO ₄ ²⁻	
		oxalic acid	malonic acid	malic acid	succinic acid	total		%	%
1994.10	344.6	13.6	2.9	3.8	1.2	21.5	679.0	6.2	3.2
11	165.0	8.3	0.0	1.2	0.5	10.0	236.6	6.0	4.2
12	173.3	4.4	0.0	1.3	0.4	6.0	222.0	3.5	2.7
1995.1	148.5	5.8	0.0	0.8	0.0	6.6	157.2	4.5	4.2
2	244.2	10.9	0.7	2.6	1.8	15.9	462.7	6.5	3.4
3	306.9	19.2	1.8	2.8	1.0	24.8	345.6	8.1	7.2
4	407.3	29.0	4.6	3.8	1.7	39.1	547.6	9.6	7.1
5	457.5	36.2	6.0	4.4	2.1	48.6	689.1	10.6	7.0
6	715.8	56.6	9.7	9.3	3.6	79.2	839.2	11.1	9.4
7	1015.8	51.8	11.1	11.7	4.2	78.9	995.9	7.8	7.9
8	585.2	23.6	NM	19.9	4.5	47.9	1962.2	8.2	2.4
9	486.6	17.4	NM	10.0	2.5	29.9	1471.7	6.1	2.0
10	642.4	25.6	NM	6.0	2.7	34.3	870.9	5.3	3.9
11	419.6	8.8	0.0	1.4	1.0	11.2	445.2	2.7	2.5
12	269.6	6.9	0.0	1.8	0.7	9.4	414.2	3.5	2.3
1996.1	194.5	7.1	0.0	0.6	0.1	7.9	113.9	4.0	6.9
2	242.1	17.0	0.0	2.1	0.8	19.9	294.0	8.2	6.8
3	266.2	22.4	2.5	2.3	0.6	27.8	327.3	10.5	8.5
4	638.5	29.8	3.2	3.9	2.2	39.1	515.2	6.1	7.6
5	934.4	62.0	9.3	8.6	5.4	85.3	655.8	9.1	13.0
6	671.4	58.6	NM	16.4	5.0	79.9	1509.5	11.9	5.3
7	482.8	50.4	NM	9.9	2.8	63.0	1658.0	13.1	3.8
8	478.3	24.1	11.3	12.4	2.9	50.8	1003.2	10.6	5.1
9	343.5	6.9	7.8	7.4	2.1	24.2	1049.5	7.0	2.3

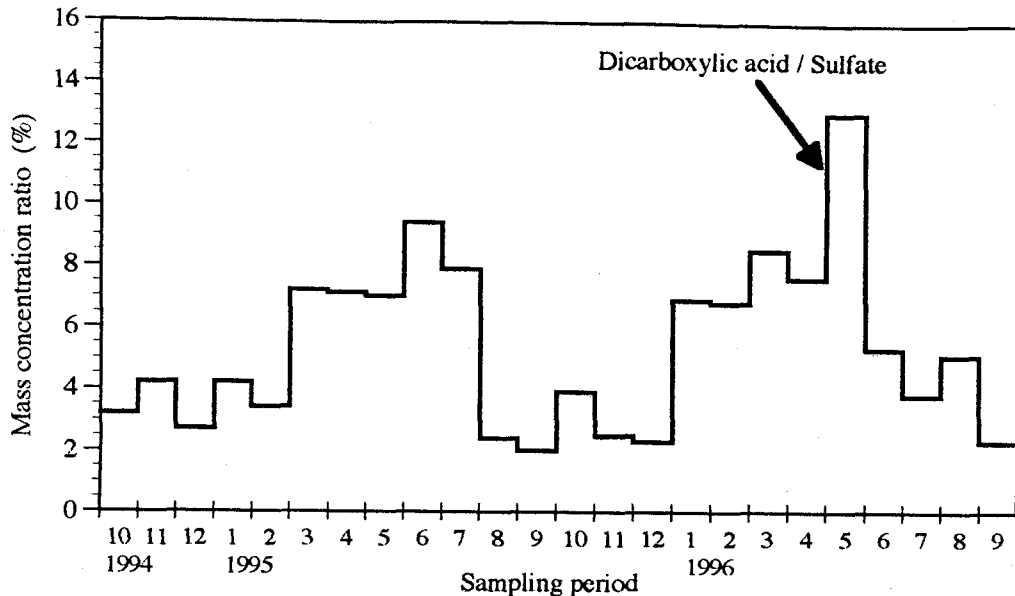


Figure 3. Monthly mean concentration ratio of dicarboxylic acid to sulfate.

mainly contained in fine particles ($d < 1.1 \mu\text{m}$) and Hori (1998) confirmed that critical supersaturation of some dicarboxylic acids is low and comparable to sulfate. Thus dicarboxylic acids in aerosols may account for at most 10 % of the number concentration of CCN. In addition Matsumoto et al. found that water soluble organic carbon is also contained in the fine particles, and a significant portion is in particles smaller than $0.2 \mu\text{m}$. The chemical components of each water soluble organic component is not fully identified at the molecular level. The result in Matsumoto et al. indicates that water soluble organic carbon may comprise a large part of the number concentration of CCN. Organic carbon is emitted from internal combustion engines, and emissions of organic carbon will continue or even increase in the future due to increases in the number of automobiles in developing countries. Sulfate may be reduced if desulfurization should come into wider use and as a result the amount of sulfate emitted into the atmosphere could be cut. Therefore the trends in concentrations of water soluble organic carbon as well as sulfate must be monitored. Further research is also necessary on the chemical characterization of the water soluble organic carbon and on its critical supersaturation.

The next chapter reports a numerical simulation to estimate changes of solar radiation net flux at the tropopause due to increases in water soluble aerosols, taking account of three different scenarios of aerosol number concentration.

3. Numerical simulation

3.1 Scenarios

In this simulation the effects of increases in water soluble aerosol concentrations in the boundary layer on the optical properties of maritime clouds was examined. Cloud droplet size distribution, volume extinction coefficient, single scattering albedo, cloud top albedo and solar radiation net flux at the tropopause were

calculated under three scenarios of number concentrations of 300 cm^{-3} (scenario : N300), 330 cm^{-3} (N330) and 600 cm^{-3} (N600). Aerosol number concentrations for each scenario were set based on the background and assumptions detailed below.

In general aerosol concentrations over oceans without air pollution are low. Less than $0.5 \mu\text{g m}^{-3}$ of ammonium sulfate is commonly observed over the central Pacific ocean (Savoie et al., 1994). However once polluted air flows from continental areas out over oceans the concentration of sulfate aerosol may increase to over $1 \mu\text{g m}^{-3}$ and oxalate has been found to comprise up to 10% of the sulfate concentration (Matsumoto et al., 1998, Kawamura and Usukura, 1993). On the assumption that the size distribution of fine particles such as sulfate and oxalate can be expressed as a log-normal distribution with the geometric mean radius $r_{\text{gN}}=0.035 \mu\text{m}$ and geometric standard deviation $\delta_{\text{g}}=2.03$ (Finlayson-Pitts and Pitts, 1986), a mass concentration of $1 \mu\text{g m}^{-3}$ corresponds to a concentration of $300 \text{ particles cm}^{-3}$. Thus in this simulation concentrations of 300 cm^{-3} represents current polluted conditions over oceans considering only sulfate aerosol, 600 cm^{-3} represents a heavily polluted condition and 330 cm^{-3} corresponds to current polluted conditions considering both sulfate and the maximum (10% of sulfate) oxalate concentration. As described in section 1, experimental study has shown that critical supersaturation of ammonium oxalate which can be considered the major component of dicarboxylic acid is comparable to that of ammonium sulfate (Hori, 1998). This simulation study of water soluble aerosols assumed only ammonium sulfate aerosol.

The simulation was assumed stratus clouds to exist over the Pacific Ocean. Stratus clouds are one of the most common cloud types. Cumulus clouds are also common, but the concentration of droplets in cumulus clouds is affected by the initial CCN concentration and by entrainment of outside air into the cloud as well as by coagulation and collision of droplets due to cloud processes. The latter effects make simulation of condensation process of droplets in cumulus clouds difficult. Stratus clouds are also affected by this, but to a lesser degree. Confining the simulation to ideal conditions where only the initial CCN concentration affects the droplet concentration, the condensation process of droplets in stratus clouds can be simulated. The assumption of ideal conditions would be valid for young and thin stratus clouds, however, in the calculations this assumption was adopted to examine the indirect effect of only water soluble aerosol increases.

3.2 Model

(1) Condensation growth model

The condensation growth model here calculates the number size distribution of cloud droplets activated from aerosol assuming the three aerosol scenarios as described above (section 3.1). It uses the one dimensional cloud model developed by Jensen and Charlson (1984) based on the condensation growth equation (Fukuta and Walter, 1970). Conditions of the calculations were: cloud-base height 1000 m, cloud-base temperature $5 \text{ }^\circ\text{C}$, cloud-base relative humidity 100 %, updraft speed 20 cm sec^{-1} , and calculation time 1500 s (corresponding to a final altitude 300m above the cloud-base). The model does not consider entrainment processes, the inflow and outflow of water vapor and aerosol through cloud boundaries. The van't Hoff factor, i , for ammonium sulfate solution during condensation growth processes is 3 and the surface tension, σ , is 75.3 dyn cm^{-1} (corresponding to water at $5 \text{ }^\circ\text{C}$). It is assumed that each solute is completely dissolved and forms small solution droplets at the cloud base before the condensation growth starts in a cloud.

(2) Mie scattering

The model calculates optical properties of cloud droplets such as the volume extinction coefficient (σ_{ext}), volume scattering coefficient (σ_{scat}), single scattering albedo ($\omega = \sigma_{\text{scat}} / \sigma_{\text{ext}}$), and phase function (P) based on Mie scattering theory. Input parameters in the model was the number size distribution of cloud droplets i.e. the output of the condensation growth model. A complex refractive index for water was used for the cloud

Table 2. Atmospheric model and input parameters for the radiative transfer calculation.

Atmospheric model	Plane parallel, 3 layer (Stratosphere, Free troposphere, Boundary layer)	
Solar constant	1376 W m ⁻²	
Solar spectral irradiance	0.3 ~ 4.5 μ m (Houghton, 1986)	
Radiative transfer calculation	35 wavelengths	
Solar zenith angle (θ ₀)	cos θ ₀ = 0.55	
Aerosol or cloud optical properties of each layer		
Mie optical depth	Stratosphere	Toon and Pollack (1976)
	Free troposphere	Toon and Pollack (1976)
	Boundary layer	output of the Mie calculations for stratus clouds (geometrical depth of cloud 500m)
Size distribution	Stratosphere	Wang et al. (1989)
	Free troposphere	Wang et al. (1989)
	Boundary layer	output of condensation growth calculations
Refractive index	Stratosphere	sulfate (m=1.55-0.0001i for all wavelengths)
	Free troposphere	Hayasaka (1987)
	Boundary layer	water (for stratus clouds)
Rayleigh optical depth	Elterman (1964) and Valley (1965)	
Gas absorption		
H ₂ O	Absorption coefficient	ESFT method (Asano and Uchiyama, 1987)
	Amount for each layer	Stratosphere: 0.000959 g cm ⁻² ,
		Free troposphere: 0.991 g cm ⁻² ,
O ₃	Absorption coefficient	Boundary layer: 2.0 g cm ⁻² (Valley, 1965)
		Goody and Yung (1989)
	Column amount	0.35 atm-cm
Surface albedo	0.06 (Payne, 1972)	

droplets in this calculation.

(3) Radiative transfer equation

To estimate the indirect effect of water soluble components in aerosols on the radiation process, the cloud top albedo and downward net radiation flux at the tropopause were calculated by solving the radiative transfer equation based on the delta-M method (Wiscombe, 1977) and P3 approximation (Ohta and Tanaka, 1984). The radiative transfer equation is:

$$\mu \frac{dI(\tau, \mu)}{d\tau} = I(\tau, \mu) - \frac{1}{2} \int_{-1}^1 P(\tau, \mu, \mu') I(\tau, \mu') d\mu' - \frac{1}{4} F_0 P(\tau, \mu, -\mu_0) e^{-\frac{\tau}{\mu_0}}, \quad (3)$$

where μ : cosine of zenith angle for diffused radiation
 μ_0 : cosine of solar zenith angle
 I : intensity of diffuse radiation
 τ : optical depth measured from the top of the atmosphere
 P : phase function independent of the azimuthal angle
 F_0 : solar radiation flux at the top of the atmosphere.

The atmospheric model and input parameters are listed in table 2. Solving the above equation, yields the cloud top albedo (A), and the upward (UF) and downward (DF) solar radiation flux at the tropopause. The solar radiation net flux (N) at the tropopause for each scenario was obtained as,

$$NF(\tau_{tp}) = DF(\tau_{tp}) - UF(\tau_{tp}). \quad (4)$$

In this study the differences of $NF(\tau_{tp})$ between the "N300" scenario and the other scenarios were calculated to estimate the indirect radiative effect caused by water soluble aerosols.

$$\Delta NF_{XXX}(\tau_{tp}) = NF_{XXX}(\tau_{tp}) - NF_{N300}(\tau_{tp}), \quad (5)$$

where XXX (N300, N330, or N600) stands for the name of the aerosol scenario.

3.3. Result and discussion

(1) Size distribution of cloud droplets

Figure 4 shows the number size distributions of cloud droplets calculated for the three scenarios of water soluble aerosols. With increases in the aerosol concentration, the mode radius of the droplet size distribution decreased and the shape of the distributions widened. Because the increase in aerosol numbers causes a shortage of water vapor needed for droplet growth, droplets at higher concentrations cannot grow larger and faster than droplets at lower concentrations. As a result, the initial wide size distribution of aerosols ($\sigma_g=2.03$) is reflected in the size distribution of the higher concentration scenarios. The droplet number concentration of cloud droplets activated from 300cm^{-3} , 330cm^{-3} and 600cm^{-3} water soluble aerosol concentrations were 180cm^{-3} , 192cm^{-3} and 275cm^{-3} . Comparing the aerosol concentrations with the activated droplet concentration, it is clear that droplet numbers did not increase in proportion to aerosol concentration. For example, the aerosol number concentrations are 1.1 times (N330) and 2 times (N600) the N300 scenario, but the droplet numbers increased only 1.07 times (N330) and 1.53 times (N600) over the N300 scenario. This non-linear increase results from a lowering of the maximum supersaturation in the updraft in clouds due to the shortage of water vapor stated above.

(2) Extinction coefficient and single scattering albedo of cloud droplets

Figure 5 shows volume extinction coefficients of stratus clouds calculated by Mie theory. As the number concentration of aerosol increased, the extinction coefficient increased at all wavelengths because the total extinction cross section of cloud droplets increased.

There were no differences in the single scattering albedo between the three scenarios. The single scattering albedo of cloud droplets in all scenarios was close to 1.0 in the visible region (wavelength of $0.3\text{-}0.8\ \mu\text{m}$). This shows that the extinction of solar radiation by cloud droplets was primarily caused by scattering.

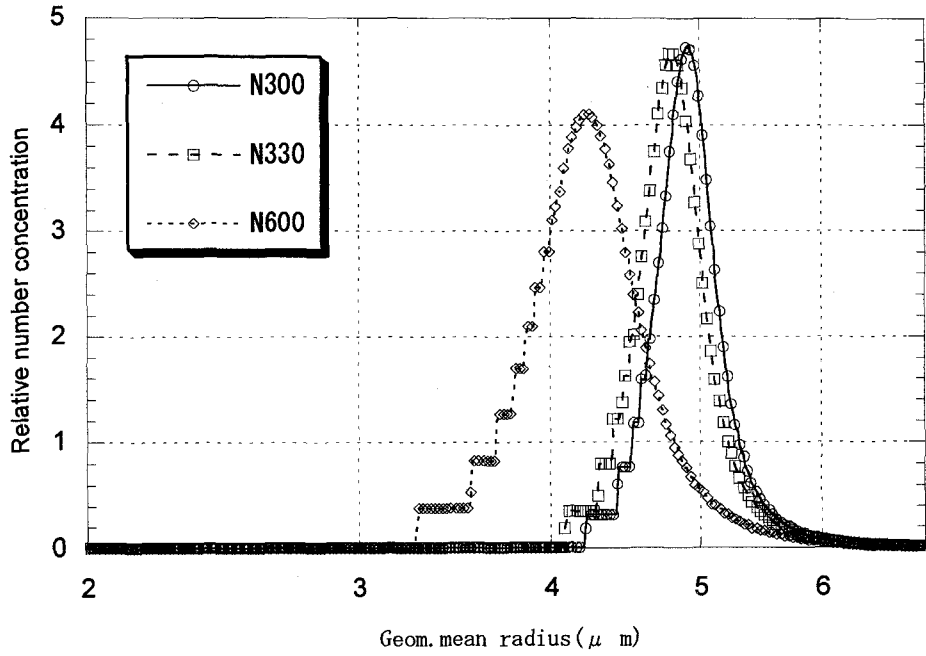


Figure 4. Calculated number size distributions of stratus cloud droplets for the three aerosol scenarios.

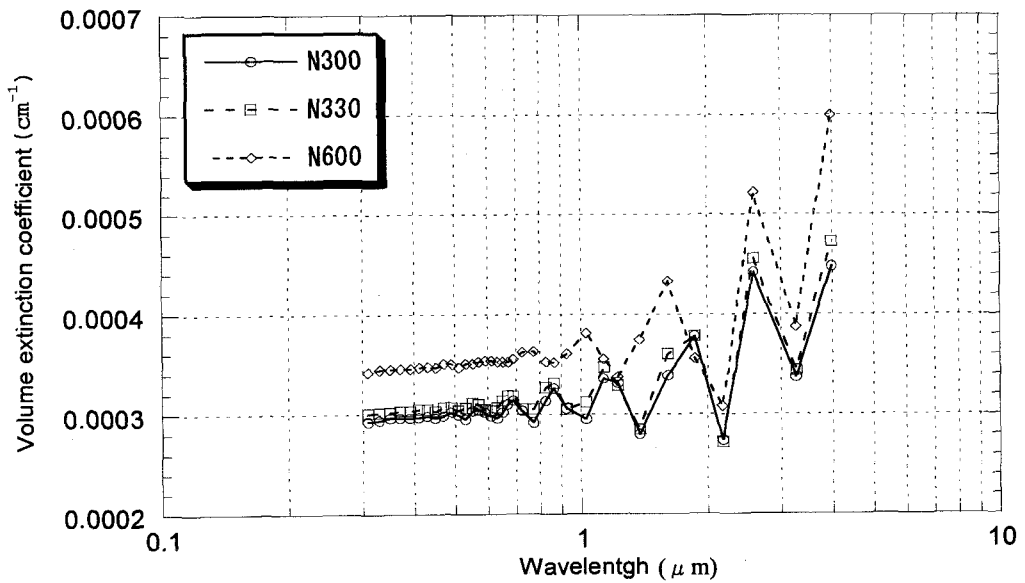


Figure 5. Calculated volume extinction coefficient of stratus cloud for the three aerosol scenarios.

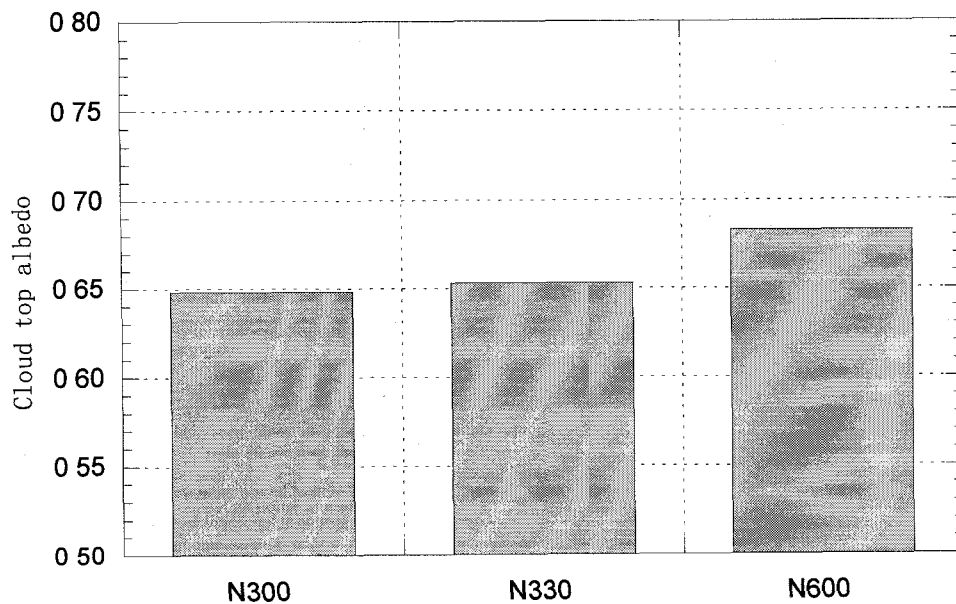


Figure 6a. Calculated stratus cloud top albedo for the three aerosol scenarios.

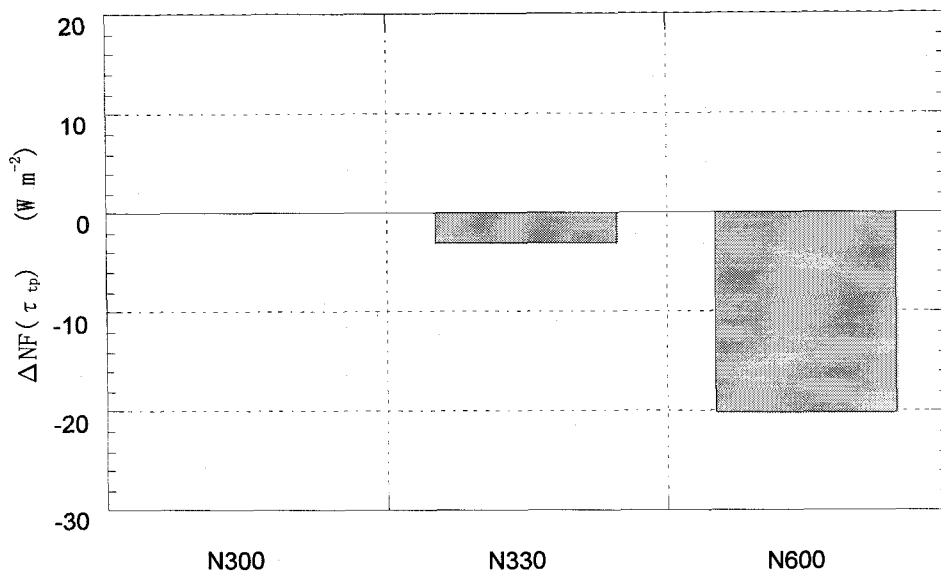


Figure 6b. Calculated differences in solar radiation net radiation flux at the tropopause between N300 and other scenarios.

(3) Cloud top albedo and net solar radiation flux at the tropopause

Figure 6a shows the calculated cloud top albedos, and figure 6b shows the calculated differences in net solar radiation flux at the tropopause from the number concentration of the 300 cm^{-3} scenario. The cloud top albedo for each scenario was 64.8 % (N300), 65.3% (N330), and 68.3 % (N600). When compared with the N300 scenario these increases in cloud top albedo lead to differences in the net solar radiation flux at the tropopause of -3.1 W m^{-2} (N330), -20.1 W m^{-2} (N600). Dicarboxylic acids cause the decrease in the net flux of not more than a few W m^{-2} . Comparing the global average radiative forcing of $+2.5 \text{ W m}^{-2}$ due to increases in greenhouse gases since the Industrial Revolution (IPCC, 1996), the changes in net solar radiation flux due to increases in water soluble aerosols are large and negative. However the changes in net flux due to water soluble aerosols do not occur globally but in stratus cloud areas. Averaged globally, the changes would be smaller. Still, these changes are large and may have a considerable effect on radiative and local meteorological processes, because the concentration of greenhouse gases is uniform worldwide as is the radiative forcing. Concentrations of atmospheric aerosols are highly changeable and non-uniform: 10 ~ 100 times increases or decreases in concentrations of aerosols are common and may occur within days. Thus the radiative effects are non-uniform over ocean and land depending on the number concentration of water soluble aerosols. It is possible that this non-uniformity may result in unusual vertical air convection and precipitation patterns. Thus the indirect radiative effect due to water soluble aerosols cannot be neglected even if only on a local scale. Many countries in Eastern Asia, particularly China, emits large amounts of photochemical pollutants due to industrialization and motorization. Even with reductions in emissions of sulfate by desulfurization equipment, the indirect effect will not be small without reductions in the emissions of water soluble organic aerosols such as ammonium oxalate.

4. Conclusions

Measurements of dicarboxylic acids and sulfate in aerosols were carried out at the summit of Mt. Lemmon, Arizona, U.S.A 2791 m above sea level, to investigate the concentration and seasonal variations in water soluble aerosols which are considered to act as CCN. Sulfate was the most abundant component, oxalic acid was the most abundant among dicarboxylic acids and accounted for about 50 % of the measured dicarboxylic acids. Other dicarboxylic acid components were malonic acid, succinic acid, and malic acid. The sum of the measured dicarboxylic acids was at most 10 % of the sulfate. The concentrations of both dicarboxylic acids and sulfate increased to a maximum in summer. Thus it is possible that the number concentration of CCN at cloud forming heights also increases to a maximum in summer.

The size distribution of cloud droplets, volume extinction coefficients, single scattering albedos, cloud top albedos, and net solar radiation flux were calculated for three scenarios differing in the concentration of water soluble aerosols, to estimate the indirect radiative effect of water soluble aerosols. The calculations showed that water soluble aerosols can have a large effect on a local scale and that doubling in the number concentration of water soluble aerosols decreases the net solar radiation flux at the tropopause by up to 20 W m^{-2} .

The concentration of dicarboxylic acids in aerosols are always less than that of sulfate in the present data. However, it is possible that the dicarboxylic acids to sulfate concentration ratio will increase. Dicarboxylic acids are mainly emitted from fossil fuel combustion engines as primary particles or precursor gases. Sulfate is also emitted from the same sources. Even with decreases in the amount of sulfate emitted into the atmosphere by desulfurization equipment, the contribution of dicarboxylic acids to indirect forcing will not decrease without reductions in emissions of the dicarboxylic acids. Thus it is also necessary to monitor the concentration and seasonal behavior of dicarboxylic acid and sulfate.

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