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Aerosol and gas re-distribution by shallow cumulus clouds: An investigation using airborne measurements

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[1] Aircraft measurements during the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS) are used to examine the influence of shallow cumulus clouds on vertical profiles of aerosol chemical composition, size distributions, and secondary aerosol precursor gases. The data show signatures of convective transport of particles, gases and moisture from near the surface to higher altitudes, and of aqueous-phase production of aerosol mass (sulfate and organics) in cloud droplets and aerosol water. In cloudy conditions, the average aerosol volume concentration at an altitude of 2850 m, above typical cloud top levels, was found to be 34% of that at 450 m; for clear conditions, the same ratio was 13%. Both organic and sulfate mass fractions were on average constant with altitude (around 50%); however, the ratio of oxalate to organic mass increased with altitude (from 1% at 450 m to almost 9% at 3450 m), indicative of the influence of in-cloud production on the vertical abundance and characteristics of secondary organic aerosol (SOA) mass. A new metric termed “residual cloud fraction” is introduced as a way of quantifying the “cloud processing history” of an air parcel. Results of a parcel model simulating aqueous phase production of sulfate and organics reproduce observed trends and point at a potentially important role of SOA production, especially oligomers, in deliquesced aerosols. The observations emphasize the importance of shallow cumulus clouds in altering the vertical distribution of aerosol properties that influence both their direct and indirect effect on climate.

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1. Introduction

[2] Clouds and aerosols are integral components of the climate system through their role in influencing atmospheric radiative transfer. They are intimately connected through microphysical and chemical processes in which they

mutually modify each other’s properties and development in the atmosphere. Many of these interactions are still a cause of major uncertainty in model predictions of future climate. Since radiative effects of clouds and aerosols are altitude-dependent [e.g., *Haywood and Shine*, 1997, *Liao and Seinfeld*, 1998; *Collins*, 2001; *Samset and Myhre*, 2011], a detailed understanding of the vertical distribution of particle concentrations and properties is needed to quantify their effects on climate. A cloud type that can interact closely with aerosols from sources on the ground is the shallow cumulus, which is confined to the atmospheric boundary layer. Shallow cumulus fields consist of small convective clouds with clear air in between. Over land, the annual average cumulus and shallow stratocumulus cloud amounts (i.e., the fraction of the sky-hemisphere covered by the clouds) are 4.6% and 12%, respectively (<http://www.atmos.washington.edu/~ignatius/CloudMap/>) [*Warren and Hahn*, 2002]. Convective clouds have been found to re-distribute aerosols vertically, along with energy, moisture and gaseous constituents [*Thompson et al.*, 1994; *Smith and Jonas*, 1995; *Zhu and Albrecht*, 2003; *Jiménez-Escalona and Peralta*, 2010; *Langford et al.*, 2010, 2011]. The role of clouds in

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modifying trace gas budgets has been investigated in a number of studies [e.g., Yin *et al.*, 2001; Barth *et al.*, 2002, 2003; Peltier *et al.*, 2008; Kim *et al.*, 2012]. It has been suggested that non-precipitating shallow cumulus clouds can transport aerosols and gaseous pollutants from the mixed layer to the free troposphere [Ching *et al.*, 1988; Verzijlbergh *et al.*, 2009]. Convective clouds are too small to be resolved in global models, and their parameterization is an area of ongoing development [Tost *et al.*, 2006; Arakawa *et al.*, 2011]. Aerosol effects on convective clouds are often not explicitly expressed in general circulation models at all [Quaas *et al.*, 2009]. Treatment of cloud effects on aerosols, such as modification of physicochemical properties is especially weak: it is either lacking entirely or hampered by uncertainties in the parameterization of convective clouds [Tost *et al.*, 2010]. Airborne measurements of aerosol particles and associated gases in and around convective clouds can provide a better understanding of cloud effects on these constituents and can ultimately improve the treatment of cloud-aerosol interactions in atmospheric models.

[3] Aerosol particles in and around clouds do not behave as a passive tracer, but undergo a continuous physical and chemical evolution. Most fundamentally, they play a crucial role in the development of the cloud itself by acting as cloud condensation nuclei (CCN). Critical to quantifying the CCN potential of aerosol particles is knowledge of their altitude-dependent size and composition, both of which can change through cloud-processing. A number of studies have provided evidence for cloud modification of particle size distributions, composition (such as addition of sulfate mass), and optical properties [Ching *et al.*, 1988; Leitch, 1996; Isaac *et al.*, 1998; Feingold and Kreidenweis, 2000; Herrmann *et al.*, 2005; Mertes *et al.*, 2005; Peter *et al.*, 2006; Hayden *et al.*, 2008; Jiménez-Escalona and Peralta, 2010]. Hygroscopic properties of CCN have been shown to be different below and above clouds as a result of varying composition [Hersey *et al.*, 2009]. Clouds can play an important role in the modification of organic mass in aerosols. Together with inorganic compounds (such as nitrate, sulfate, ammonium, and chloride), the organic fraction of aerosol particles (“organic aerosols”), which can include thousands of organic compounds [e.g., Goldstein and Galbally, 2007], is one of the major contributors to sub-micrometer aerosol mass (20–90%) [Kanakidou *et al.*, 2005]. Organic aerosols are either emitted directly (primary organic aerosol, POA) or produced in the atmosphere from gaseous precursors by chemical and/or physical processes (secondary organic aerosol, SOA), and tend to get converted to more oxidized forms as they age [Jimenez *et al.*, 2009]. A number of field studies report elevated concentrations of organic compounds [Novakov *et al.*, 1997; Heald *et al.*, 2005, 2006] and water-soluble organic carbon (WSOC) [Duong *et al.*, 2011] in aerosols aloft. Traditional atmospheric models underestimated observed total organic aerosol [de Gouw *et al.*, 2005; Morris *et al.*, 2006; Volkamer *et al.*, 2006] and altitude-dependent WSOC levels in the boundary layer and free troposphere [Heald *et al.*, 2006; Carlton *et al.*, 2008]. The addition of processes involving semi-volatile organics leads to much better agreement in total SOA mass prediction [Hodzic *et al.*, 2010]. Aside from gas-to-particle conversion, chemical processes in the aque-

ous phase in droplets and the water in deliquesced aerosol particles (“wet aerosol”) are a source of SOA [Blando and Turpin, 2000; Chen *et al.*, 2007; Carlton *et al.*, 2008; Hennigan *et al.*, 2008, 2009]. Such processes are explored by work involving modeling [e.g., Warneck, 2003; Ervens *et al.*, 2004, 2008; Gelencsér and Varga, 2005; Lim *et al.*, 2005; Chen *et al.*, 2007; Ervens and Volkamer, 2010; Myriokefalitakis *et al.*, 2011; Liu *et al.*, 2012a] and laboratory experiments [e.g., Liggio *et al.*, 2005; Carlton *et al.*, 2006, 2007; Altieri *et al.*, 2008; Corrigan *et al.*, 2008; Perri *et al.*, 2009; Volkamer *et al.*, 2009; Sun *et al.*, 2010; Lee *et al.*, 2011; Zhao *et al.*, 2012]. Recent findings concerning multiphase processes include: (i) uptake and chemical processing of gaseous organic species by wet aerosol particles and cloud droplets, with reaction products remaining in the particle phase after evaporation of the water [El Haddad *et al.*, 2009; Ervens *et al.*, 2011; Liu *et al.*, 2012b; Ortiz-Montalvo *et al.*, 2012]; (ii) changes in SOA characteristics via direct photolytic processing in cloud water [Bateman *et al.*, 2011; Nguyen *et al.*, 2012]; (iii) formation of oligomers in evaporating cloud droplets and wet aerosols [De Haan *et al.*, 2009; Tan *et al.*, 2009; Ervens and Volkamer, 2010]; and (iv) increasing contributions of organic acids, especially oxalate, to total non-refractory organic mass with increasing relative humidity [Sorooshian *et al.*, 2010]. Based on these findings, aqueous-phase SOA sources are relevant in air masses with clouds and high relative humidity. Their overall role in the vertical distribution of organic aerosol is currently uncertain [Heald *et al.*, 2011], hampering the understanding of aerosol modification by clouds and thus the impact of the clouds on the aerosol direct and indirect effects on climate. Scaling relationships between sulfate and organic aerosol, which are used to estimate fluxes for different sources of organic aerosols [e.g., Goldstein and Galbally, 2007], may also be affected by this uncertainty.

[4] In this study, we examine the vertical distribution of aerosol physicochemical properties and selected gases in and around shallow cumulus clouds using airborne measurements from the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS) in Houston, Texas. The moist atmospheric conditions and shallow cumulus fields encountered during this campaign provide a natural laboratory to investigate the role of wet aerosol and droplet processes in shaping the vertical variability of aerosol properties. We use cumulative statistics and focused case studies to address the following topics: (i) cloud re-distribution of aerosol particles, gases, and moisture; (ii) identification of above-cloud areas and their aerosol characteristics; (iii) cloud detrainment of aerosols; and (iv) the utility of a new metric for the degree of cloud influence on aerosols in cloud-free air. Finally, measured chemical characteristics are compared to predictions from a cloud parcel model with a particular focus on the trends in predicted sulfate, oxalate and total organic masses formed in clouds and in humid air outside of clouds.

2. Study Area and Background

[5] The Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), an intensive field campaign in the framework of the Second Texas Air Quality Study (TexAQS 2006) [Parrish *et al.*, 2009], took place in Texas

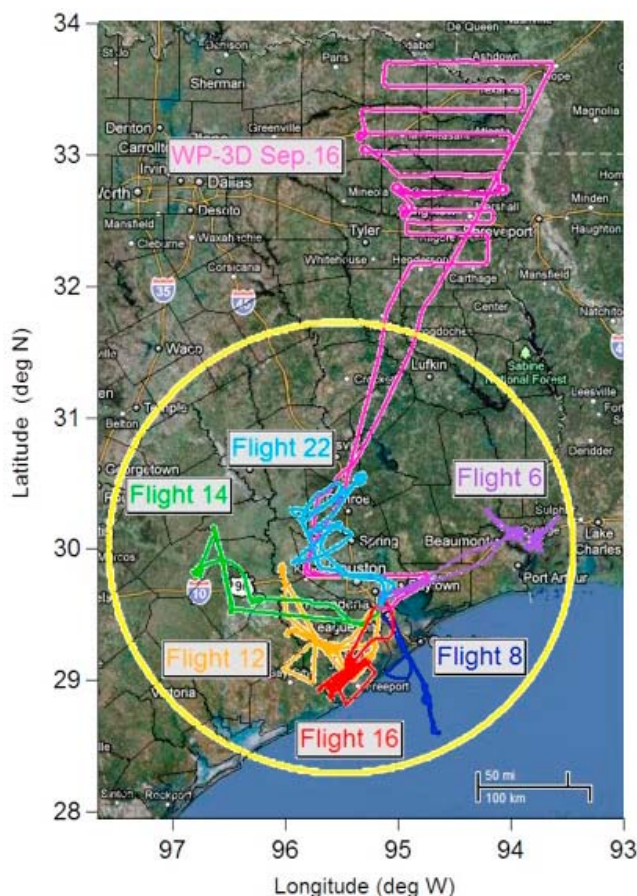


Figure 1. Map of the study area and flight tracks for flights explicitly discussed. Numbered flights refer to CIRPAS Twin Otter flights, the flight track of the NOAA WP-3D is shown in pink.

between August and October 2006. The associated aerosol-cloud flight data set, which we examine in this work, was collected in the greater Houston area in August and September of 2006. A map of the general area covered by the flights is shown in Figure 1. Houston is the fourth largest city in the United States (U.S. Census Bureau, <http://2010.census.gov/news/releases/operations/cb11-cn124.html>) and a center of the petrochemical industry. Anthropogenic pollution and photochemical smog are major issues in the region. During GoMACCS, the local sub-micrometer aerosol mass was found to consist of 66% organic matter, 20% sulfate and 14% elemental carbon, with hydrocarbon-like organic aerosol dominating organic aerosol mass in the mornings and oxygenated organic aerosols prevailing in the afternoon [Bates *et al.*, 2008]. Marine air influenced by ship emissions and Saharan dust was added to the local aerosol during periods of onshore flow [Bates *et al.*, 2008]. SOA was shown to form in urban and industrial plumes in a TexAQS 2006 study focusing on clear to partly cloudy days in early fall (ambient relative humidity mostly below 70%) [Bahreini *et al.*, 2009]. Houston's late summer climate, the time period investigated in this study, is hot and humid with shallow cumulus activity on many days and incidence of late afternoon thunderstorms. The shallow cumulus clouds encountered during GoMACCS were impacted by

anthropogenic emissions [Lu *et al.*, 2008; Small *et al.*, 2009]. Evidence of aqueous-phase processing of power plant plumes was found in a TexAQS 2006 model-measurement inter-comparison study [Zhou *et al.*, 2012] as SO_2 was rapidly removed from the plumes by clouds.

3. Data and Methods

3.1. Research Flights and Measurements

3.1.1. CIRPAS Twin Otter Aircraft

[6] During GoMACCS, twenty-two research flights (between 21 August and 15 September) were conducted by the Center for Interdisciplinary Remotely Piloted Aircraft Studies (CIRPAS) Twin Otter. Flights took place during the day. Cloudy conditions dominated the vast majority of flights and flight segments. The aircraft flight path was usually designed to profile individual clouds and cloud fields. The typical flight strategy included level flight legs below, within and above the cloud, long transit legs to and from points of interest, and slant and spiral soundings. Typically, clouds were encountered at altitudes between ~ 500 and 2500 m.

[7] Inorganic and organic acid measurements were carried out with a Particle-Into-Liquid Sampler (PILS) [Sorooshian *et al.*, 2006a]. The PILS grows sub-micrometer particles into droplets sufficiently large to be collected by inertial impaction. The collected liquid sample is then delivered to vials on a rotating carousel, and analyzed off-line with ion chromatography. The time resolution of PILS measurements was ~ 5 min. The PILS samples were analyzed for sulfate and water-soluble organic acids, a detailed listing of which is given by Sorooshian *et al.* [2007a]. The detection limits of the PILS are $0.1 \mu\text{g m}^{-3}$ for inorganic ions and $0.01 \mu\text{g m}^{-3}$ for organic acids [Sorooshian *et al.*, 2007a]. The present study focuses on oxalate, as it is ubiquitous in cloud-processed aerosol [Crahan *et al.*, 2004; Yu *et al.*, 2005; Sorooshian *et al.*, 2006b, 2007a, 2007b], is thought to have no gas-phase production mechanism [Warneck, 2003], and can serve as a tracer for aqueous-phase chemistry [Sorooshian *et al.*, 2010]. Aerosol organic and inorganic non-refractory components were measured by a compact Time-of-Flight Aerosol Mass Spectrometer (c-ToF-AMS, hereinafter "AMS") [Drewnack *et al.*, 2005] with a detection limit of $0.05 \mu\text{g m}^{-3}$ [Murphy *et al.*, 2009]. During flight legs through clouds, the PILS and the AMS periodically sampled behind a counterflow virtual impactor (CVI) inlet in order to chemically characterize droplet residual particles. A sub-isokinetic aerosol inlet was used outside of clouds. All composition measurements are reported for ambient temperature and pressure conditions.

[8] Dry particle size distributions ($d_p = 10\text{--}700$ nm) were measured with a Dual Automated Classified Aerosol Detector (DACAD) [Wang *et al.*, 2003], at an averaging time of 73 s per scan. Size distributions of larger particles (100 nm – $2.5 \mu\text{m}$) and cloud droplets ($2.55\text{--}42.7 \mu\text{m}$) were obtained every second with a Passive Cavity Aerosol Spectrometer Probe (PCASP, PMS Inc., modified by DMT Inc.) and Forward Scattering Spectrometer Probe (FSSP, PMS Inc.), respectively. Number concentrations of particles were measured by two condensation particle counters (TSI CPC 3010, $d_p > 10$ nm; TSI CPC 3025, $d_p > 3$ nm; time resolution of both: 1 s). The CPC 3010 also sampled droplet residual particles downstream of the CVI. Liquid water content

(LWC, PVM-100 probe [Gerber *et al.*, 1994]) and several other meteorological variables (temperature T , dew point T_d , relative humidity RH, wind direction and wind speed) were measured at 1 s resolution. Comprehensive lists of all instruments onboard of the Twin Otter aircraft are given by Lu *et al.* [2008] and Parrish *et al.* [2009].

3.1.2. NOAA WP-3D Aircraft

[9] The NOAA WP-3D aircraft, which flew in the vicinity of the CIRPAS Twin Otter during GoMACCS (flight days between 11 September and 12 October), provided detailed gas and aerosol measurements that are summarized by Parrish *et al.* [2009, Table A1]. In the present study, organic and sulfate concentrations measured by a c-ToF-AMS [Bahreini *et al.*, 2009] as well as gas-phase measurements of sulfur dioxide (SO₂) and the volatile organic compounds (VOCs) acetone, methacrolein (MACR), toluene and methyl vinyl ketone (MVK) are used. These VOCs are directly emitted or are oxidation products of parent hydrocarbons and are precursors to SOA. For example, MVK and MACR are oxidation products of isoprene, which react with ozone or OH to form smaller, highly water soluble species (e.g., methylglyoxal, glyoxal) that partition to the aqueous phase to generate SOA [e.g., Ervens *et al.*, 2004]. A subset of the available VOC measurements are used as input to a cloud parcel model in order to simulate the most efficient SOA formation pathways in the aqueous phase of cloud droplets and aqueous aerosol. VOC data were obtained via Proton-Transfer Reaction Mass Spectrometry (PTR-MS, Ionicon Analytik) [de Gouw and Warneke, 2007]. Sulfur dioxide measurements were carried out with a TECO 43C-TL pulsed fluorescence instrument [Ryerson *et al.*, 1998].

3.2. Satellite Imagery

[10] GOES visible and radar images (<http://www.esrl.noaa.gov/csd/metproducts/textaqs/>) were used to determine the position of the aircraft relative to cloud fields and to help interpret the flight data in a larger spatial and temporal context. Successive images (every 30 min) were used to gain insight into the pre-conditioning (high or sustained cloud development, little cloud activity, precipitation) of the atmosphere before individual flights.

3.3. Data Processing, Vertical Profiles and Composite Analysis

[11] Total AMS mass was calculated as the sum of all constituents measured by the AMS. During the research flights, sampling occurred inside and outside of clouds. The only in-cloud aerosol measurements used in this study are those of cloud droplet residual particles sampled downstream of the CVI (i.e., PILS, AMS, and CPC 3010) and will be directly identified as such in the remainder of this study. In-cloud time periods were identified based on LWC ($>0.05 \text{ g m}^{-3}$) and FSSP droplet concentration ($>2 \text{ cm}^{-3}$). For flight segments over the sea at low altitude, this last criterion had to be relaxed to FSSP droplet concentration $>7 \text{ cm}^{-3}$ to account for sea spray. In particular, particle size distributions are only used when obtained outside of clouds. This restriction is needed to ensure data quality: aerosol measurements that require the physical sampling of particles can suffer from problems, such as well-documented droplet shatter effects [Weber *et al.*, 1998], when taken within a cloud.

[12] Mission-average vertical profiles of aerosol chemical composition and meteorological variables were created by calculating the mean of all data taken within a particular altitude increment. For the high time-resolution measurements (AMS and meteorological data), the altitude increments were 100 m. Approximately 75 data points entered the average in each 100 m altitude bin. For the lower time-resolution PILS measurements, the increments were 300 m, with about 26 data points (out-of-cloud sampling) and nine (CVI sampling) data points in each altitude bin.

[13] Vertical profiles of particle size distributions averaged by cloudy and cloud-free conditions were examined for systematic differences. For this purpose, data subsets were created by distinguishing two categories: (i) “clear”: data collected outside of shallow cumulus fields; and (ii) “cloudy”: measurements conducted on cloudy days in cloud-free air above, within and below shallow cumulus fields during slant and spiral soundings. Examples of the design of these categories are shown in Figure S1.¹ Size distribution measurements and auxiliary meteorological variables falling into each category were averaged by 100 m altitude increments. The average vertical profiles of the category “cloudy” are averages over the 15 individual true vertical profiles measured during ascents and descents of the aircraft between (but not through) the individual shallow cumulus clouds. Not every vertical profile covered all altitudes and, on average, about 5 data points entered the average of each 100 m altitude bin. Ascents and descents over large altitude ranges were typically not conducted on completely cloud-free days, with the exception of Flights 8 (over the Gulf of Mexico) and 20 (over land). The statistical category “clear” therefore consists of data from completely cloud-free days as well as from flight legs through cloud-free areas (outside of shallow cumulus fields) on days that were not completely cloud-free. The number of data points entering the average in each 100 m altitude increment was variable, ranging from two to 80, with an average of nine data points per altitude bin. Figure 2 shows the average vertical temperature, dew point, and total humidity profiles for the two categories. Total humidity q , defined as the total mass of water vapor and liquid water per kilogram of moist air, was calculated from measurements of RH, ambient pressure, T and LWC. The profiles reflect the overall drier air in clear conditions and the higher RH at cloud-relevant altitudes in cloudy conditions. When comparing the T and T_d profiles for the category “cloudy” with the mission-average (“all data”), it is evident that any averages over the entire data set are more representative of cloudy than of clear conditions.

3.4. Residual Cloud Fraction

[14] The clouds investigated during GoMACCS were found to be heavily impacted by entrainment at altitudes above the first few hundred meters above cloud base [Lu *et al.*, 2008]. Air parcels in the immediate vicinity of a cloud are therefore expected to have mixed with the cloud in their recent past and thus contain cloud-processed aerosol. In order to quantify the “cloud-processing history” of an air parcel, a new metric, the residual cloud fraction (f_{RC}) is introduced. It is defined along a flight leg at constant altitude

¹Auxiliary materials are available in the HTML. doi:10.1029/2012JD018089.

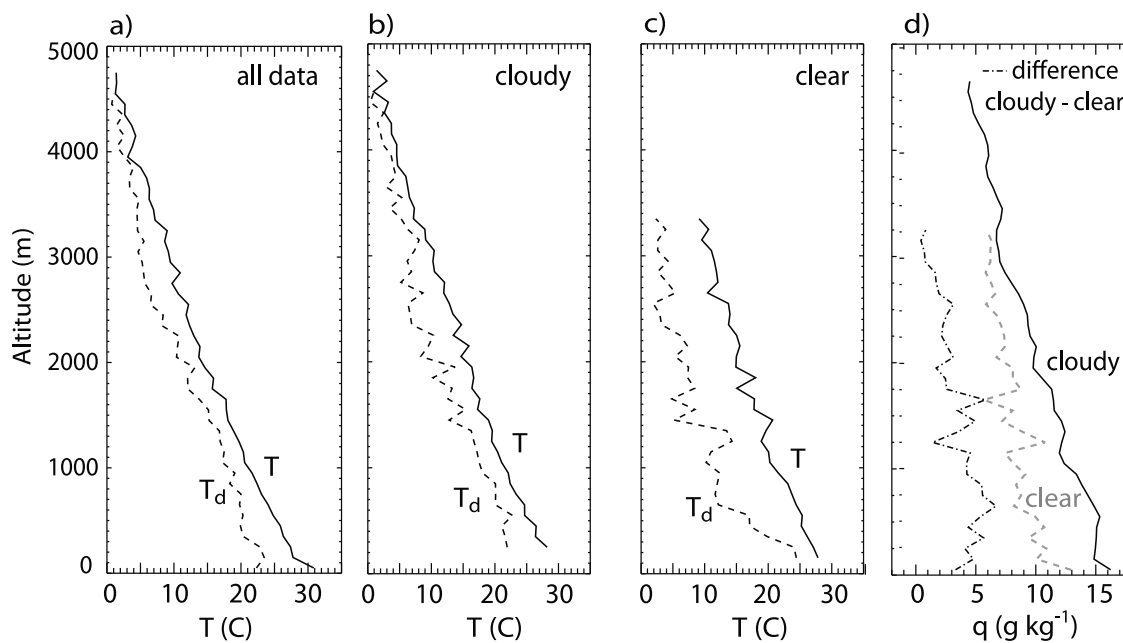


Figure 2. Vertical profiles for temperature (T), dew point (T_d) for (a) the cumulative data set (“all data”), (b) the meteorological category “cloudy,” (c) the category “clear,” and (d) total humidity (q). Averages over all data most accurately represent cloudy conditions.

through a shallow cumulus cloud field and calculated from the total humidity q . We assume that the air encountered along the level flight leg is at all times a mixture of two distinct air masses (with varying relative contributions): detrained in-cloud air and ambient, cloud-free background air. The lowest values of q found along that level flight leg are assumed to be representative of the ambient, cloud-free air, whereas the highest values of q represent the core region of the cloud at that altitude (i.e., in-cloud air). The residual cloud fraction is defined as

$$f_{RC} = (q - q_e)/(q_c - q_e) \text{ with } q_e < q < q_c \quad (1)$$

where q is the measured total humidity (g kg^{-1}), and q_e and q_c are representative total humidities for cloud-free and in-cloud air, respectively. The f_{RC} thus relates the absolute humidity encountered at a particular point during a level flight leg to the characteristic total humidity inside the nearby clouds and, as opposed to RH, is independent of T . Low values of f_{RC} in an air parcel indicate that it has not recently been part of a cloud, while higher values indicate an increased likelihood that it has undergone recent cloud processing. The reference values q_e and q_c were calculated as the 5th percentile of out-of-cloud specific humidity values and the 75th percentile of in-cloud total humidity values. This choice of statistical parameters was largely in the interest of achieving “workable” numerical values of f_{RC} . More specifically, in-cloud total humidity, defined as the sum of specific humidity and LWC, varies over a much larger range than out-of-cloud total humidity, for which LWC is negligible.

3.5. Cloud Parcel Model

[15] Simulations of chemical processing of aerosols were performed with a cloud parcel model [Feingold and

Heymsfield, 1992] in order to help interpret the observed aerosol chemical data. The model treatment of inorganic and organic multiphase chemistry is described in detail by Ervens *et al.* [2004]. Briefly, sulfate aerosol particles with a defined mass concentration size distribution are tracked on a moving size grid along trajectories passing through clouds. After activation of the particles into cloud droplets, the model explicitly describes the uptake of gaseous soluble compounds into the droplets and SOA and sulfate production in the droplets from these precursors. The model runs in this study differ from those in previous studies in the following aspects: (i) The trajectories driving the model air parcels were derived from Large Eddy Simulation (LES) of shallow cumulus fields (as opposed to stratocumulus trajectories in prior studies [Sorooshian *et al.*, 2006b]). The properties of these LES cumulus fields compared well with the cloud fields observed during GoMACCS [Jiang *et al.*, 2008]. Two-hour segments of three LES trajectories, representative of observed cloud altitudes, were selected as model input. The trajectory segments were repeated in order to simulate multiple cloud cycles; one cloud cycle per trajectory was selected for analysis. (ii) A mechanism for SOA formation in aerosol water, described by Ervens and Volkamer [2010], was added for trajectory segments in which $\text{RH} \leq 95\%$. The mechanism includes oligomer formation, which is favored in the small water volumes in deliquesced aerosol particles. At $\text{RH} > 95\%$, particles are assumed to be too dilute to allow for efficient oligomer formation. This RH limit was chosen somewhat arbitrarily; however, laboratory studies of aqueous aerosol SOA formation were performed at much higher solute concentration than encountered in the dilute particles above 95% RH. Thus, reaction parameters for this intermediate dilution regime are highly uncertain. Wet aerosol SOA formation in interstitial particles within clouds is not

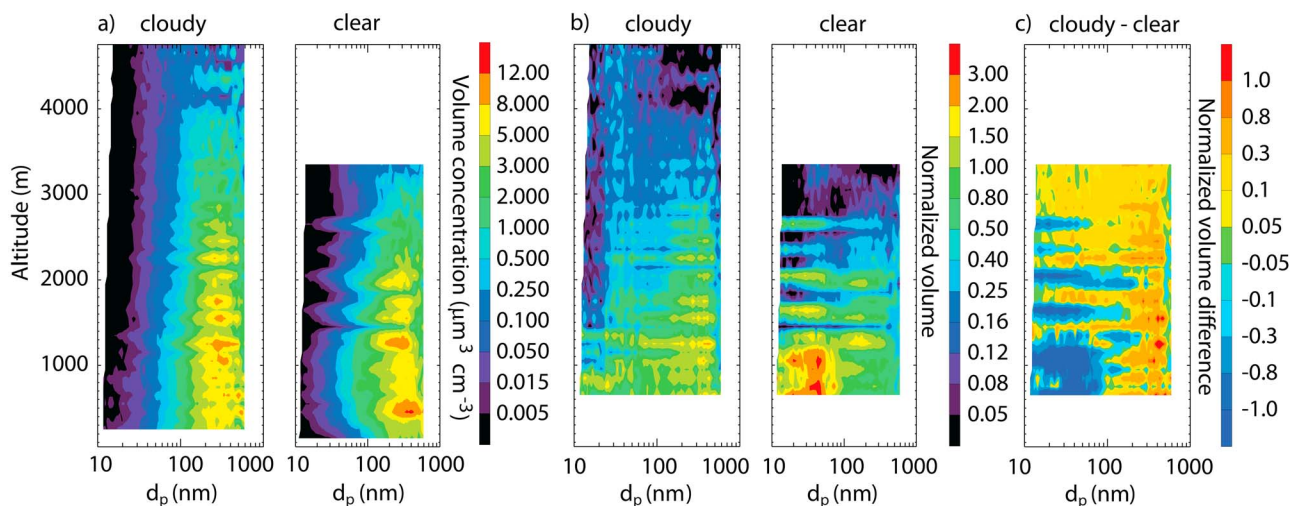


Figure 3. Average vertical profiles of aerosol volume distributions for ascents and descents in cloud-influenced air (“cloudy”) and for flights and flight legs in clear air (“clear”). Volume distributions were calculated from measured DACAD dry size distributions. (a) Aerosol volume distributions, (b) aerosol volume distributions normalized by low level (<600 m) average volume distributions, and (c) difference in normalized volume between cloudy and clear conditions. In cloud-influenced air, the aerosol volume is more evenly distributed across the altitudes.

considered since these particles contain negligible amounts of liquid water.

[16] The initial concentrations of the gaseous precursors, SO_2 , toluene and isoprene, were 1.5, 5 and 3 ppb, respectively. Initial mixing ratios of oxidants were 80 ppb for O_3 , 20 ppb for NO_x , 0.5 ppb for H_2O_2 , and 0.2 ppb for HCHO. These values are typical for ‘downtown plumes’, identified by *Bahreini et al.* [2009]. The three precursors were not replenished over the course of the simulations. The initial aerosol population consists of ammonium sulfate particles in a total concentration of $10 \mu\text{g m}^{-3}$, a fairly typical value for the region [*Sorooshian et al.*, 2007a; *Bates et al.*, 2008]. The reported sulfate refers to the sulfate that is predicted to have formed in cloud droplets upon initialization. Since sulfate formation scales with LWC, its formation in wet aerosol particles is not considered. Its contribution is expected to be negligible due to the much lower amount of water in wet aerosols than in cloud droplets. For wet aerosol SOA production, the produced species are $\sim 20\%$ oxalate and 80% oligomers, based on laboratory studies of photochemical aqueous phase processing of glyoxal [*Lim et al.*, 2010]. This ratio has not been evaluated for atmospheric conditions; however, many laboratory studies agree that the fraction of oligomers exceeds that of small monomeric dicarboxylic acids in highly concentrated solutions such as aerosol water [e.g., *Tan et al.*, 2009; *Lim et al.*, 2010]. Since the branching ratio of oligomers to monomeric dicarboxylic acids is highly uncertain, we do not draw any strong conclusions on the source strength of oxalate formation in clouds versus wet aerosol. All aqueous SOA products are assumed to be further oxidized in the aqueous phase. Aside from this chemical sink, the model does not include any aerosol loss processes (e.g., deposition, dilution). These limitations of the parcel model might lead to an overestimate of predicted masses that are formed in aqueous phase. In reality, particles might be removed within clouds, or air might be diluted by cleaner

and/or drier air, leading to decreased particle number concentrations and total mass.

4. Results and Discussion

4.1. Vertical Profile of Particle Volume

[17] Vertical profiles of dry particle volume distributions for the cloudy and clear categories are shown in Figure 3. For the ascents and descents on cloudy days, the particle volume concentration in the accumulation mode is more evenly distributed than in the “clear” category over the examined altitude range. In the “clear” category, the accumulation mode volume is high in the lowest 2000 m and drops off above that level (Figure 3a). Average sub-micrometer volume concentrations in the two categories were calculated by integrating over the average volume distributions for selected altitudes. At an altitude of 450 m, well below typical cloud base altitudes, the volume concentration for cloudy conditions was found to be $5.4 \pm 0.9 \mu\text{m}^3 \text{cm}^{-3}$; for clear conditions it was $7.3 \pm 0.8 \mu\text{m}^3 \text{cm}^{-3}$. For an altitude of 2850 m, above typical cloud top heights, the volume concentrations for cloudy and clear conditions were 1.8 ± 0.3 and $0.9 \pm 0.2 \mu\text{m}^3 \text{cm}^{-3}$, respectively. Thus, the sub-micrometer particle volume concentration aloft was found to be 34% of that close to the surface for cloudy conditions, compared to 13% for clear conditions. The “clear” category is characterized by somewhat higher overall particle concentrations, in particular at smaller sizes at lower altitudes. This is likely due to less efficient particle removal by wet deposition and scavenging than on cloudy days. Also, on clear days, gas-phase photochemistry may eventually lead to higher particle concentrations at lower altitudes not shaded by clouds. The masking effect of overall higher particle concentrations in clear conditions is removed by a normalization procedure: for each category, the average volume distributions in the individual altitude bins were

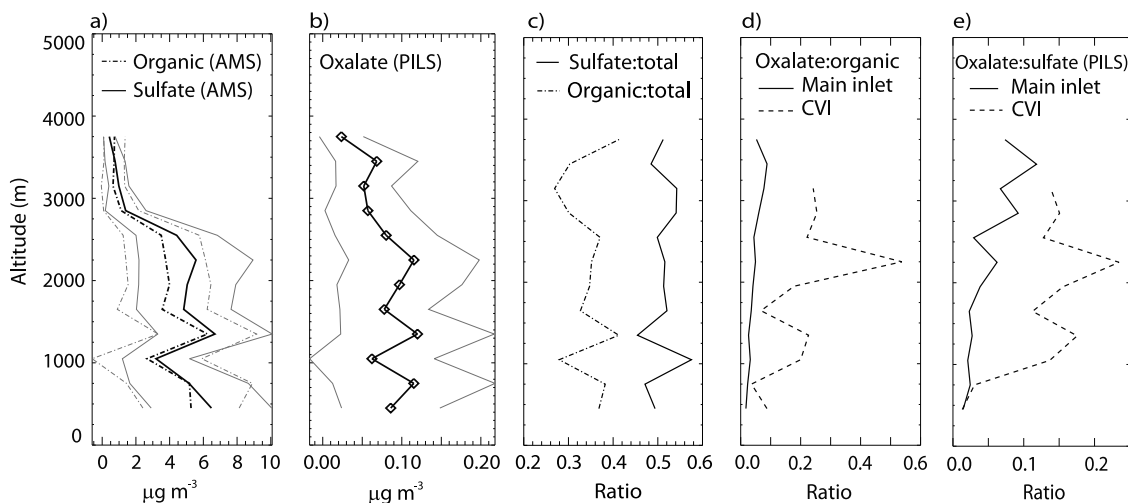


Figure 4. Average vertical profiles (mission average) of (a) AMS organic and sulfate mass concentrations, (b) PILS oxalate, and (c–e) selected ratios. Gray lines in Figures 4a and 4b represent standard deviations. While absolute concentrations decrease with altitude, organic and sulfate mass fractions remain stable and ratios of oxalate to both organic and sulfate mass increase with altitude, regardless of whether droplet residual particles (CVI) or aerosol outside of clouds (main inlet) were sampled.

divided by the respective average volume distribution for the lowest 600 m. Figure 3b shows that the bulk of the accumulation mode volume during clear conditions is concentrated in the lower parts of the atmosphere, whereas it is higher (relative to the near-surface layers) in cloudy conditions. This effect is even more obvious in the difference (cloudy - clear) of the normalized volume for the two categories, presented in Figure 3c. The normalized volume difference for the accumulation mode (Figure 3c) yields largely positive values, a clear manifestation of relatively higher abundance of aerosol volume aloft on cloudy days. Negative values occur mostly at smaller particle sizes, particularly at lower elevations, and can be explained by more effective gas-phase photochemistry in clear conditions due to the absence of cloud shading, and by a less abundant liquid phase as a sink for precursor gases. The normalized volume difference has the largest positive values for accumulation mode particles. This indicates a change in the size distribution featuring a more pronounced and larger accumulation mode relative to the surface in cloudy conditions. Cloud processing can explain this change in the size distribution as it adds mass to the droplet mode [e.g., John *et al.*, 1990; Ervens *et al.*, 2011; Hersey *et al.*, 2011]. The high accumulation mode volume concentrations aloft relative to low layers in cloudy conditions likely result from the transport of particles and precursor gases from the near-surface regions to higher levels in updrafts associated with cumulus convection and from the added particle volume through cloud and aerosol aqueous phase processing.

[18] An alternative explanation could attribute the abundance of accumulation mode particles aloft simply to advection of different air masses: the air mass history in a meteorological regime giving rise to cumulus convection could be a different one than that leading to clear conditions. In order to further explore this possibility, three-day HYSPLIT (R. R. Draxler and G. D. Rolph, HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model, 2012, <http://ready.arl.noaa.gov/HYSPLIT.php>) back-trajectories based on

three ending altitudes (500, 1000 and 3000 m) were investigated for the times and locations entering the composite averages (Figure S2). The “clear” category tends to be associated with trajectories from the continent, whereas trajectories associated with the “cloudy” category usually spend at least some time over the ocean. The effect is less pronounced at the highest elevation (3000 m), where the largest difference between the two categories is found. Air masses from the land are expected to contain more rather than less overall particle volume than those coming from the sea [Bates *et al.*, 2008]. For elevations above 2000 m, however, the observations in Figure 3 show the opposite behavior. Furthermore, on some days, the plane flew descents and ascents between clouds (the data of which entered the cloudy category) preceded or followed by flight legs outside of shallow cumulus fields (providing data for the clear category). This increases the likelihood that the presence and absence of clouds is indeed the most fundamental aspect dividing the clear and cloudy categories for the purpose of aerosol characterization. Entrainment of substantial amounts of accumulation mode aerosol from the free troposphere into the boundary layer is unlikely to explain the observations: particle concentrations in the free troposphere are too low (average sub-micrometer volume concentration for altitudes >4000 m = $0.55 \pm 0.14 \mu\text{m}^3 \text{cm}^{-3}$). Cumulus convection thus has a clear impact on the vertical distribution and higher-altitude abundance of accumulation mode particles.

4.2. Vertical Distribution of Aerosol Composition

[19] At cloud altitudes, aqueous-phase processing may influence particle concentrations and chemical composition. Vertical variability of chemical components and ratios between total non-refractory organic mass, sulfate and oxalate were examined for signs of such influences. Mission-average vertical profiles of chemical components measured behind the sub-isokinetic total aerosol inlet are shown in Figure 4. As discussed in Section 3.3 and shown in Figure 2, such averages over the entire out-of-cloud data set best

represent the aerosol particle composition in cloudy (rather than clear) conditions. The absolute concentrations of sulfate, organic and oxalate show an even distribution up to an altitude of about 2500 m and a decline above that altitude (similar to the accumulation mode volume concentrations in Figure 3a). The sulfate and organic mass fractions (sulfate:total AMS mass and organic:total AMS mass, respectively) are relatively stable across all altitudes. In contrast, the relative contribution of oxalate to the organic mass increases with altitude and reaches a maximum at 3450 m (8.8% versus 1.8% at 450 m), well above the altitude at which overall particle concentrations decrease. The ratio oxalate:sulfate shows a similar behavior, increasing from 0.01 at 450 m to 0.09 at 2850 m. In the cloud droplet residual particles measured behind the CVI, oxalate:sulfate ranges from 0.01–0.23. The ratios of oxalate:sulfate and oxalate:organic are higher than those measured downstream of the total aerosol inlet by factors of up to four and 13, respectively, showing a signature of in-cloud production of oxalate.

[20] The vertical profiles of oxalate:organic are an indicator of the influence of clouds on aerosol chemistry: the ratio is expected to be higher in the vicinity of clouds than in cloud-uninfluenced aerosol due to the addition of cloud-processed particles and due to elevated RH (both a result of detrainment), which favors SOA formation in aerosol water. The ratio is highest in cloud droplet residual particles, corroborating this interpretation. The ratio of oxalate:sulfate follows a similar behavior as oxalate:organic in spite of the fact that sulfate is produced in the aqueous phase as well. The increase of oxalate:sulfate with altitude may be explained by different time scales of production and the vertical distribution of precursor gases. While sulfate is produced in a one-step mechanism (sulfur(IV) oxidation by H_2O_2 or O_3), oxalate production requires multiple reaction steps (such as oxidation of glyoxal to glyoxylic acid, which gets further oxidized to oxalate) leading to longer formation time scales [Ervens *et al.*, 2004]. Furthermore, SO_2 is the direct precursor for sulfate whereas aqueous SOA precursors (glyoxal and methylglyoxal) are oxidation products of VOCs. The reaction mechanism for sulfate starts closer to the surface and earlier in the convective transport process than the mechanisms for aqueous SOA, whose precursors may only be available in higher layers. Sulfate formation rates, and the associated SO_2 removal may be more efficient in the lower part of the clouds compared to VOC removal associated with SOA formation. As SO_2 gets depleted with time and increasing cloud altitude, sulfate formation rates may slow down, whereas organic mass might be continuously produced over longer time and spatial scales in the cloud. These trends provide important insight into the impact of clouds on chemical composition. However, there is a need for more data especially at high altitudes (above clouds and free troposphere). Measurements at these altitudes contribute a small fraction to the total data set in this study. In particular, ratios of chemical components, which, at higher altitudes, are ratios of smaller numbers, should be better constrained in future studies by acquiring larger data sets.

4.3. Influence of Clouds on Vertical Profiles: Case Studies

[21] Individual vertical profiles from measurements – the result of ascents and descents during three flights (Flights 8,

12, and 16) allow comparisons between different locations and environmental conditions.

[22] Case study 1 (Figure 5) is an investigation of aerosol largely uninfluenced by clouds. The two vertical profiles, measured during Flight 8, correspond to an ascent over the Gulf of Mexico, and a descent partially (lower 2500 m) over land, which took place on a clear, cloud-free and calm day (low vertical wind speeds at the higher altitudes in both profiles). Profile 1 features a well-defined marine boundary layer in the lowest 400 m with constant potential temperature θ , high RH, and relatively high turbulence in the vertical wind (w) profile. Marine concentrations (profile 1) of supermicrometer particles (PCASP volume) are comparable to those measured over land (profile 2), most likely a manifestation of sea spray aerosol. In contrast, sub-micrometer particle number concentrations (CPC) and volume (DACAD) concentrations are substantially lower in the marine profile than over land (Figures 6 and 7). Concentrations of sulfate are much lower than in the other case study flights, and oxalate remained below the detection limit for the marine profile. Low concentrations of total organic acids (mostly methanesulfonic acid) are reported instead. During the descent over land, oxalate was measured at the comparatively low concentration of $0.03 \mu\text{g m}^{-3}$.

[23] Case study 2 (Flight 12, Figure 6) considers a day with high cloud activity: clouds were present in the area since sunrise and had been for the majority of the previous day (GOES visible), but precipitation was negligible (GOES radar). The structure of the boundary layer is clearly visible in the vertical profiles of θ , w , PCASP volume concentration, and q : a surface layer (high PCASP volume, turbulence, constant q and θ) reaches up to ~ 1000 m (increase of θ indicating increasing stability with a sharp decline in all other parameters), followed by a mixed layer up to ~ 2800 m, and the free troposphere above 2800 m (further sharp decline in several aerosol and meteorological parameters). Absolute concentrations of oxalate, sulfate, and organic mass are highest at typical cloud altitudes (oxalate concentrations up to $0.18 \mu\text{g m}^{-3}$). The ratio of oxalate:sulfate, oxalate:organic and organic:total AMS mass are highest in the free troposphere - oxalate:sulfate up to 0.032, and organic mass fraction up to 0.51. The ratios of oxalate:sulfate and oxalate:organic increase throughout the mixed layer, consistent with in-cloud SOA formation. The decrease of the organic fraction (organic:total AMS mass) at mid-elevations (~ 1000 – 3000 m) is most likely a function of fast in-cloud production of sulfate. The vertical profile of volume distributions shows that particle volume concentrations are high and the shape of the distribution is consistent across all altitudes until cloud top.

[24] Case study 3 (Figure 7) directly investigates oxalate-enriched particles left behind by an evaporated cloud. Flight 16 included a spiral descent through an air mass that had previously been occupied by a cloud, as confirmed both visually and by GOES satellite imagery. Particle volume concentrations in the accumulation mode are consistently high up to an altitude of about 3000 m, corresponding to cloud top altitude during the rest of the flight. Just as in case study 2, the organic fraction experiences a decrease when the sulfate fraction increases at cloud altitudes, and absolute oxalate and sulfate concentrations are highest at cloud altitudes. Oxalate concentrations reached $0.41 \mu\text{g m}^{-3}$,

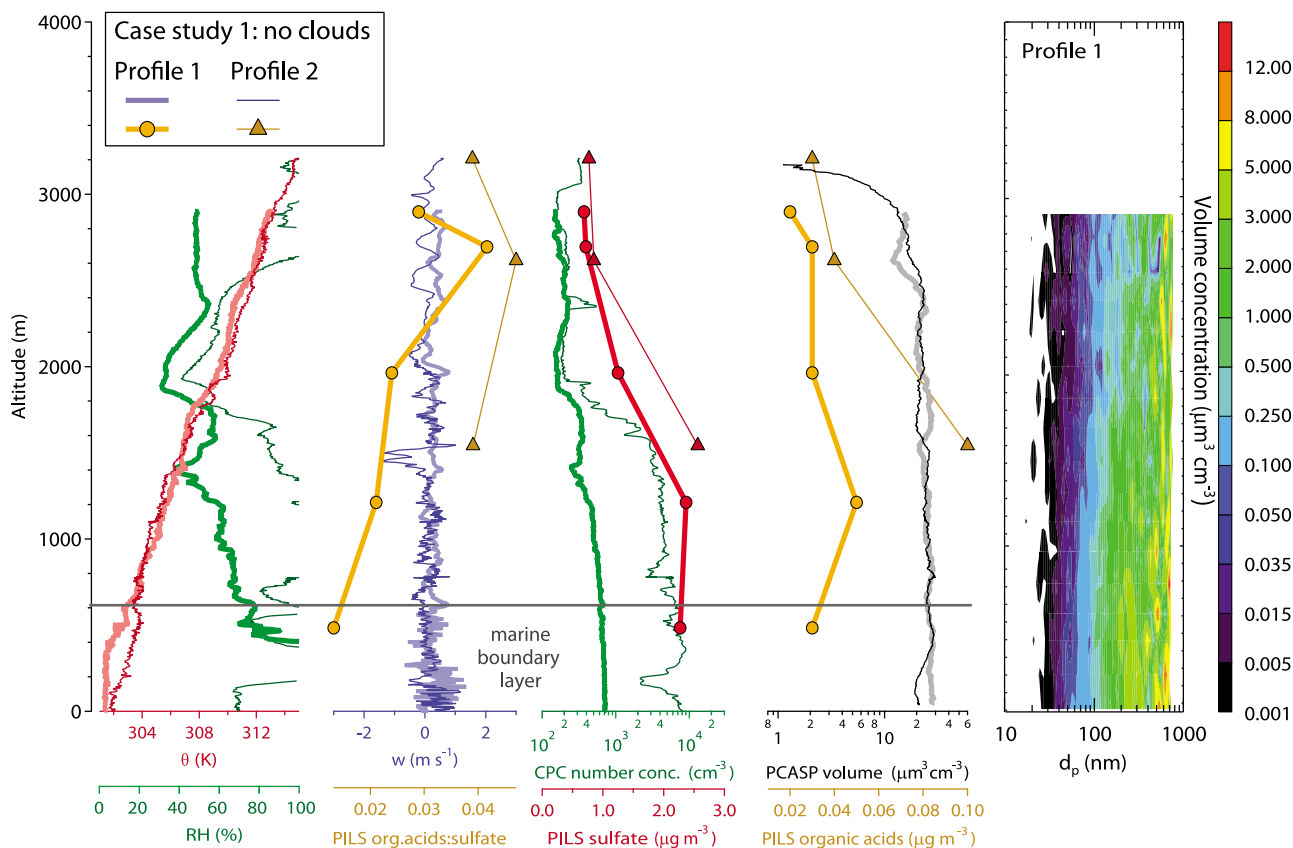


Figure 5. Vertical profiles of meteorological parameters and aerosol measurements for two descents during Flight 8. In Figures 5–8, sulfate concentrations derive from AMS measurements unless otherwise indicated. The first descent occurred over the Gulf of Mexico, the second partially over land, from an altitude of 2500 m to landing. Oxalate concentrations were below detection limit in these soundings, and total organic acid concentration is reported instead.

among the highest oxalate concentrations measured in the entire campaign, pointing at a large contribution of cloud-processed particles to the encountered ambient aerosol. During the remainder of the flight, oxalate concentrations were below $0.2 \mu\text{g m}^{-3}$. Ratios of oxalate:organic, oxalate:sulfate and the organic fraction show an increase up to an altitude of 2000 m.

[25] Three key observations in the two cloudy profiles clearly show that clouds play a large role in re-distributing overall aerosol concentrations, moisture, sulfate, and organic aerosol mass: (i) Absolute concentrations of oxalate and sulfate are high at cloud-relevant altitudes, most likely a result of aqueous-phase production in clouds or wet aerosols; (ii) accumulation mode particle concentrations are evenly distributed up to cloud top, confirming the overall vertical trend discussed in Section 4.1; and (iii) the ratio of oxalate to both organic and sulfate is highest in the free troposphere (case study 2). In an environment governed by shallow cumulus convection, this observation can be explained by detrainment of cloud-processed aerosol and potentially ongoing aging processes aloft (discounting an unknown organic aerosol source in the free troposphere itself). Convective re-distribution can transport oxidants such as ozone into higher layers [e.g., Langford *et al.*, 2010, 2011], enabling further oxidative processing of aerosols. The

possibility of cloud top detrainment is further explored in the next section.

4.4. Observations Above Cloud Top

[26] Two case studies, each examining a level flight leg above clouds, are examined for indications of cloud top detrainment of particles, gases, and moisture. Time series of particle number concentrations and chemical composition during two flight legs just above cloud top are shown in Figure 8. For both cases, the altitude of the aircraft was constant within 40 m. Liquid water content is low ($<0.015 \text{ g m}^{-3}$), assuring that the aircraft did not dip in and out of cloud tops, but was indeed at all times located above the cloud. Total humidity q was unavailable for Flight 16.

[27] Increases in sulfate, organic mass and particle number concentrations are encountered in two instances during the level leg in Flight 16. For Flight 6, similar spikes were observed in two consecutive overpasses above the same cloud top location. Nucleation events are unlikely to be the reason for these spikes: they would cause a high small particle fraction, which would show in an increased difference between the concentrations measured by the two CPCs with different lower cutoff sizes. This was not observed (Figure 8). Furthermore, there is insufficient mass in nucleation mode particles to explain the observed jumps in the

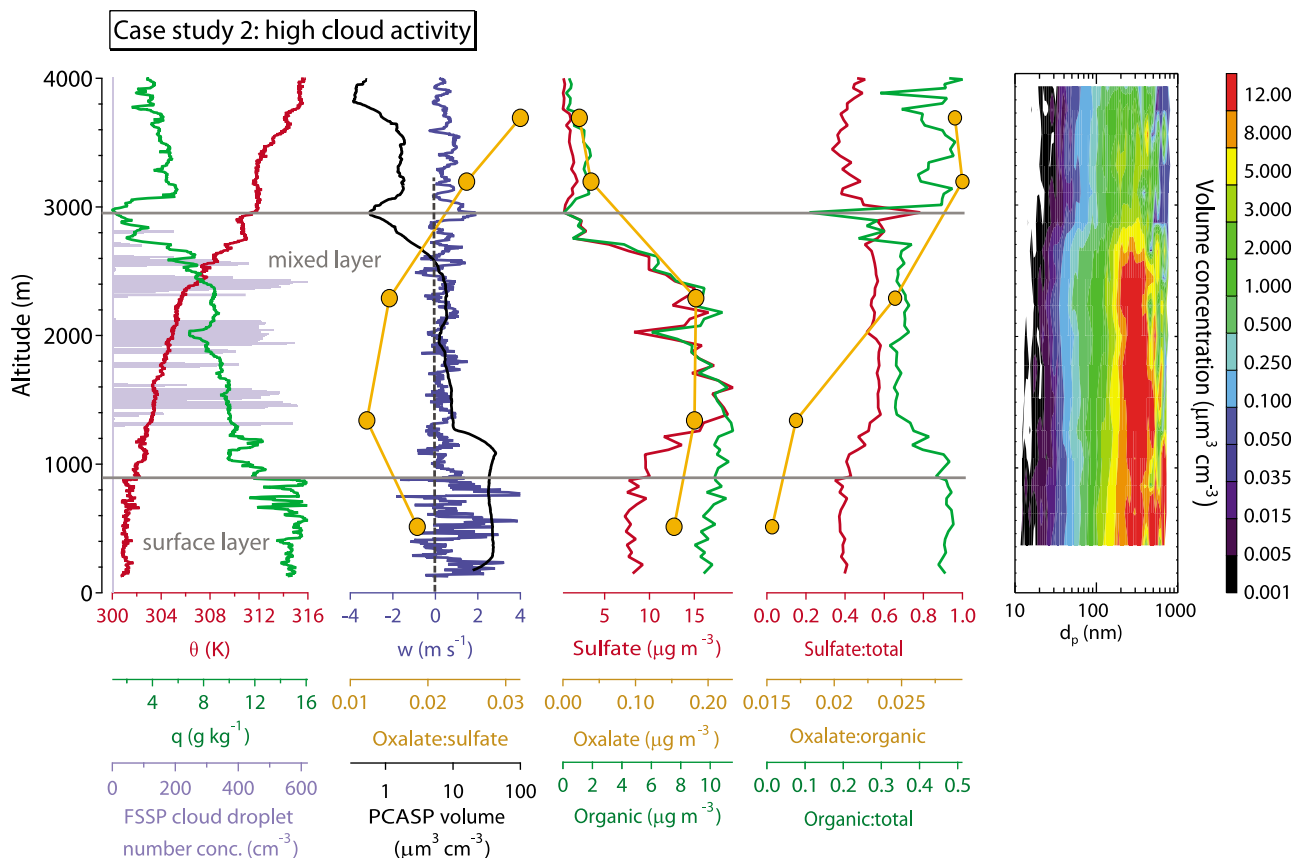


Figure 6. Vertical profiles of meteorological parameters and aerosol measurements for an ascent (11:18–11:30 LT) during Flight 12 (high cloud activity, over land). FSSP cloud droplet number concentrations are plotted for the entire flight, for the purpose of identifying the altitude range of the cloud layer, and were negligible during the actual ascent.

mass concentrations of the chemical constituents. The elevated concentrations of q (Flight 6) and sulfate indicate that these regions of high concentrations may be cloud top detrainment zones. As shown in Figure 7, the cloud top during Flight 16 is slightly over 3000 m. In the shallow cumulus regime, cloud top often marks the top of the boundary layer; therefore, the flight leg in Figure 8 shows an example of moisture and aerosol transport from the boundary layer into the free troposphere. The results of these case flights can be explained by clouds transporting aerosols and converting soluble gases to SOA and sulfate.

[28] To further explore this last possibility, the vertical abundance of gases relevant to aqueous-phase aerosol production, along with concentrations of organic and sulfate, are examined. A case study from an independent flight by the NOAA WP-3D aircraft on 16 September 2006 examines a stack of level flight legs with decreasing altitudes passing through a zone of elevated concentrations of SO_2 , acetone, toluene, and the sum of methyl vinyl ketone and methacrolein (MVK+MACR). Figure 9 clearly shows the presence of increased particulate sulfate and organic mass together with some of the precursors for their aqueous phase production. The zone extends through a vertical range of 1500 m. Convection in shallow cumulus fields, which were prevalent in the area during the time of the flight, likely caused the upward transport of the particles and precursor gases found

in this zone. SOA above clouds may have been transported there or originated from formation of gas-to-particle conversion during transport of VOC plumes such as the one shown in Figure 9. The simultaneous presence of products and precursors of aqueous-phase processes through a wide range of altitudes (Figure 9) indicates that above-cloud SOA can be a result of aqueous phase processing of the VOCs followed by particle detrainment from the cloud top or of gas-to-particle generation SOA above cloud top after detrainment of VOCs (Figure 8). These case study results provide additional support for cloud processes modifying vertical profiles of sulfate and organic aerosol, especially at cloud-relevant altitudes and higher. To assist future studies quantifying cloud effects on aerosol properties in cloud-free air, a new metric is introduced in the next section to quantify the “cloud processing history” of aerosols.

4.5. Residual Cloud Fraction and Chemical Composition

[29] The residual cloud fraction f_{RC} (equation (1)) was designed to estimate the “cloud history” of an air mass without the need to visually confirm the location of evaporated clouds. Cloud processing of aerosols should be visible as changes in chemical composition with varying f_{RC} . Five suitable flight legs from Flights 14 and 22 were chosen to test f_{RC} . Values for f_{RC} in those flight legs ranged between

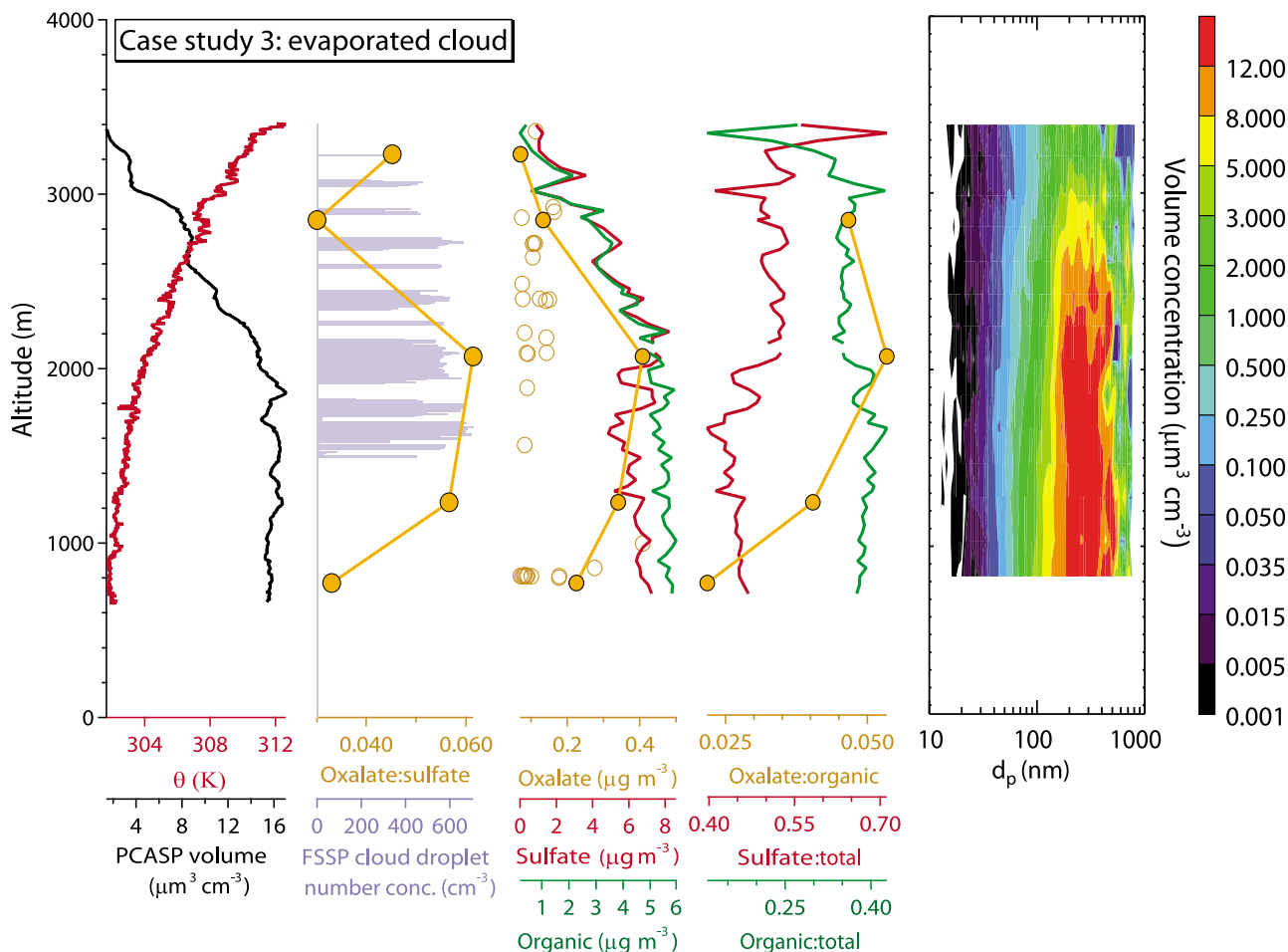


Figure 7. Vertical profiles of meteorological parameters and aerosol measurements for a descent through an evaporated cloud during Flight 16. Oxalate concentrations measured during the remainder of the flight are shown for comparison (open circles). FSSP plot as in Figure 6.

0.0 and 0.3. Figure 10 shows the behavior of organic, oxalate, and sulfate masses and selected ratios as a function of f_{RC} . Absolute concentrations of all three components (Figure 10, top) and the organic mass fraction (Figure 10, middle) increase with higher f_{RC} and are accompanied by a decrease in the sulfate mass fraction (Figure 10, middle). In as much as the basic assumption for f_{RC} – the air along a level leg through a cloud is at all times a mix of in-cloud humid and out-of-cloud drier ambient air – is applicable, the increased organic mass fraction in air parcels with higher f_{RC} can be a result of several processes: (i) higher organic mass fractions in particles detrained out of clouds, due to either in-cloud aqueous phase production or passive transport of aerosol with high organic fractions by the dynamic processes of cloud convection; (ii) production of SOA in aerosol water at high RH resulting from the detrainment of moisture from the cloud, with precursors either present in the ambient air or detrained out of the cloud; and (iii) entrainment of drier, free tropospheric aerosol (contributing to the “dry end” of f_{RC}) with a lower organic mass fraction. However, this last explanation is unlikely, since organic mass fractions are not necessarily expected to be lower in the free troposphere than in the boundary layer (e.g., Figure 6). In either of the cases (i) and (ii), the re-distribution of aerosols or precursors by

clouds is the key mechanism explaining the changes in chemical characteristics of the aerosol with f_{RC} .

[30] Similarly, discounting entrainment of free tropospheric air as argued above, the increase of absolute concentrations of organic and sulfate may be driven by (i) overall increased particle mass from upward transport of higher particle concentrations from atmospheric layers closer to the surface in the cloud convection, or (ii) aqueous phase production of sulfate and SOA. The increase of oxalate with f_{RC} suggests that aqueous-phase production of aerosol mass is at least partly responsible for the increase in sulfate and organic concentrations and organic mass fractions. The decreasing trend in the sulfate mass fraction and the increase of oxalate:sulfate with f_{RC} are likely a result of the different time scales of aqueous-phase production processes as discussed in section 4.2. Figure 10 (bottom) shows the corresponding increase of organic mass relative to sulfate, in addition to an increase in oxalate:sulfate. Thus, f_{RC} is shown to be a useful tool to leverage in future work to study the degree of influence of cloud processing and cloud transport in shaping aerosol properties in clear air. This first investigation of f_{RC} is somewhat limited by the constraint on the flight path, most importantly the condition that the plane reach a pocket of relatively dry background air along the

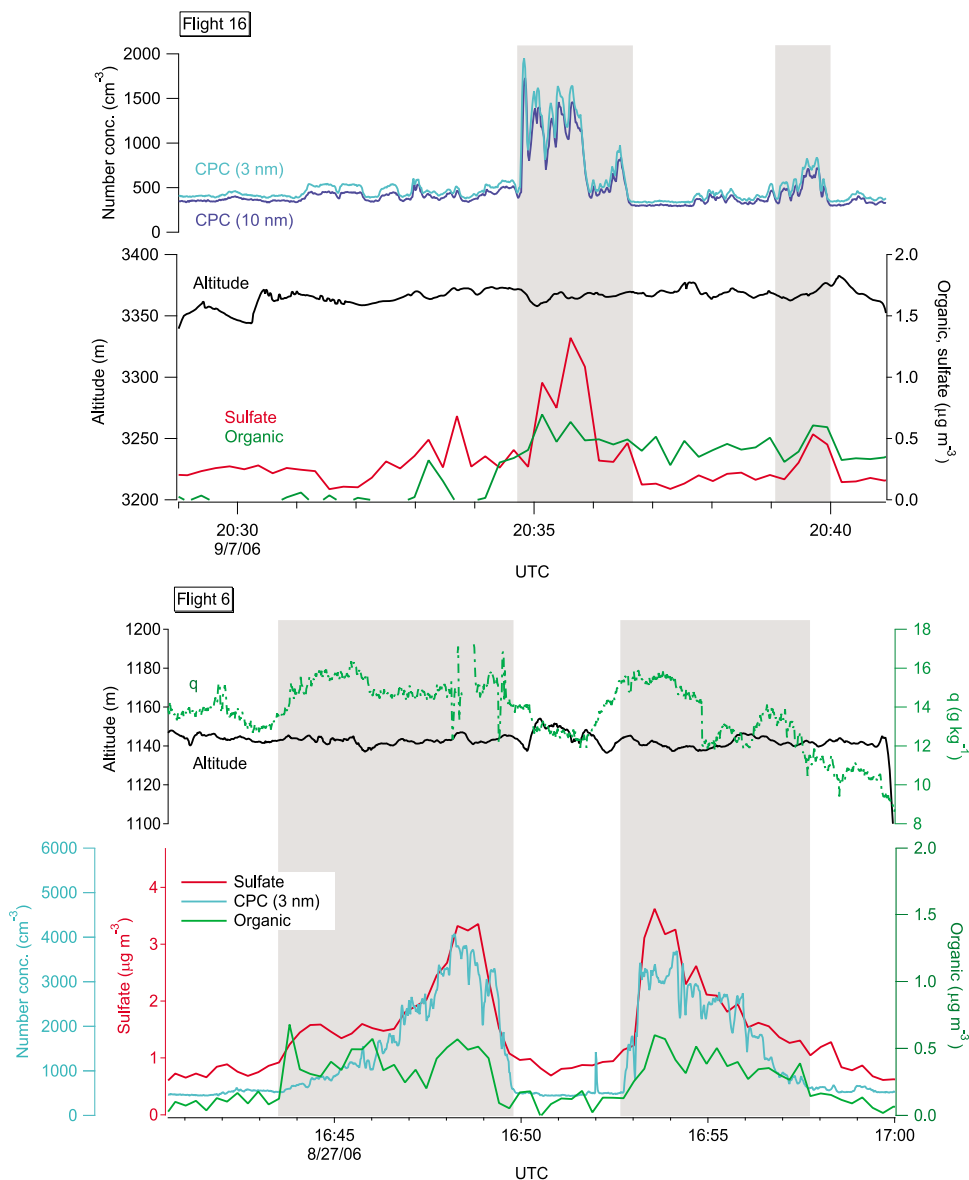


Figure 8. In above-cloud level legs, potential detrainment zones (shaded areas) are visible as large jumps in CPC particle concentrations, sulfate and organic concentrations, and, in the case of flight 16, total humidity q (q was unavailable for flight 6).

same level leg that went through a cloud. Further investigations are warranted to build a greater inventory of data across a wider range of conditions.

4.6. Model Predictions of Wet Aerosol and Droplet Chemistry

[31] The cloud parcel model was used to gain insight into the chemical signature of aqueous phase production of sulfate and oxalate. Despite great uncertainties regarding chemical mechanisms of SOA formation in aerosol water, our results point to an important role of such processes in the vicinity of clouds where RH is high. Since the model results suggest that SOA production in aerosol water can be at least as efficient as in-cloud SOA production (despite the much smaller liquid water contents) due to different chemical pathways that favor oligomer formation [Ervens *et al.*,

2011], these air masses may be a relevant source of SOA [Tan *et al.*, 2009; Lim *et al.*, 2010; Tan *et al.*, 2010, 2012]. SOA mass produced in clouds is predicted to be composed of $\sim 80\%$ oxalate and $\sim 20\%$ pyruvate. A similar ratio was found in model simulations with different initial conditions and thus might be regarded as a typical branching ratio for a wide range of conditions [Ervens *et al.*, 2004]. Figure 11 presents the model results for the second and third cloud cycles of three representative air parcel trajectories. For the actual southeastern Texas environment, it is unknown how many cloud cycles the aerosols experienced prior to sampling; but given the frequent and continuous formation of shallow cumulus clouds, it was presumably more than one. The altitudes reached by the model air parcels in the three representative trajectories are 1938 m (Trajectory 1), 1981 m (Trajectory 2) and 2820 m (Trajectory 3). Only a minor

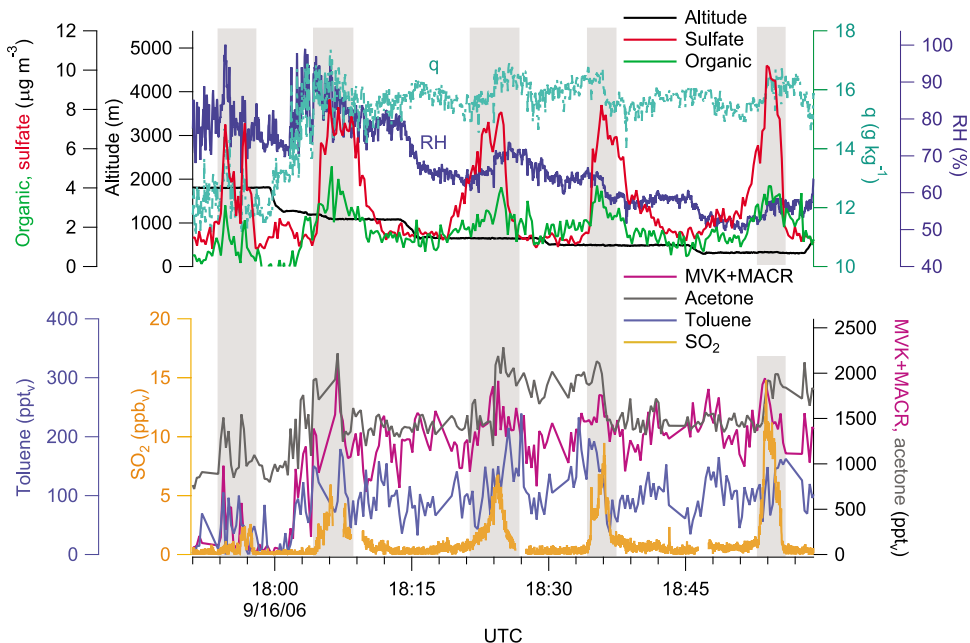


Figure 9. Concentrations of volatile organic compounds, AMS organic, and AMS sulfate from the NOAA WP-3D flight (16 September 2006) on a stack of level flight legs. A zone of elevated concentrations is observed at cloud-relevant altitudes.

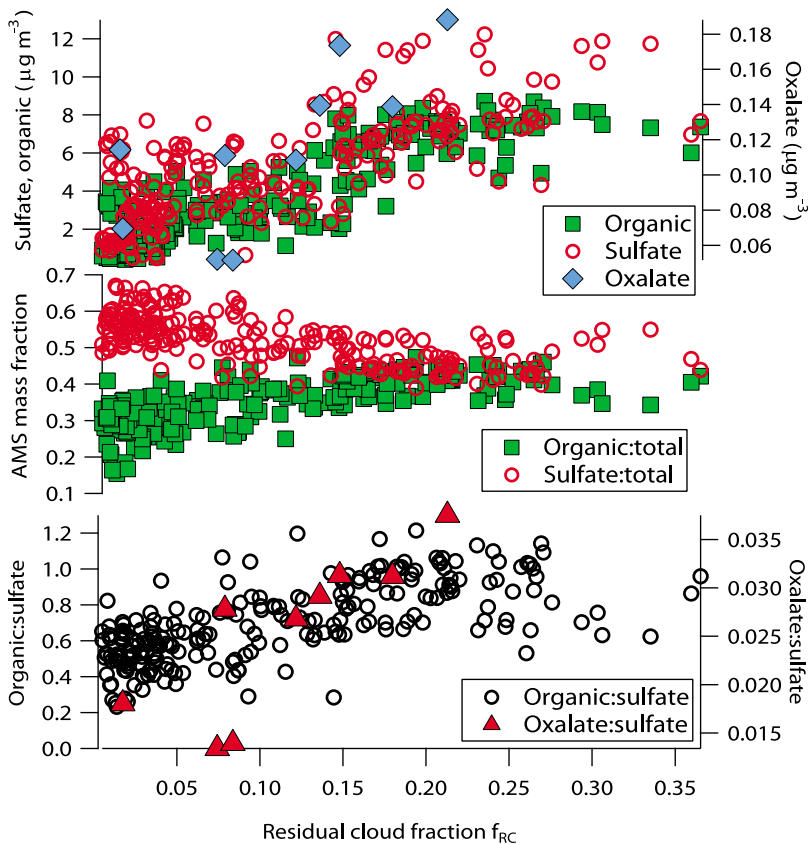


Figure 10. Increase of organic, sulfate, and oxalate as well as selected fractions with increasing “cloud history” of the aerosol, indicated by increasing values of residual cloud fraction f_{RC} . The presence of oxalate is a signature of aqueous phase processing of the aerosol in cloud-influenced air. Increases in organic mass fractions may originate from aqueous-phase processing in both cloud drops and wet aerosols.

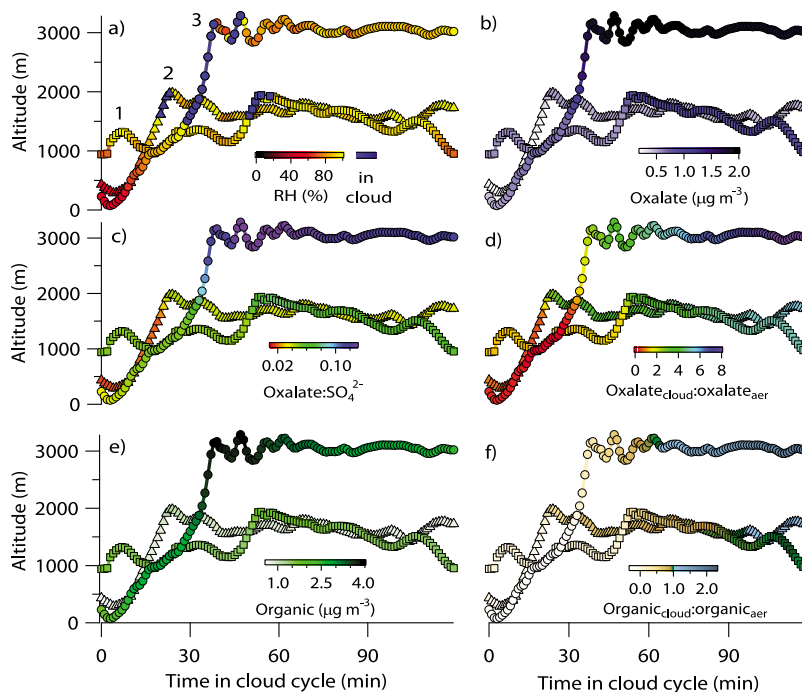


Figure 11. Parcel model predictions of aqueous phase production of sulfate (in clouds) and SOA mass (in clouds and wet aerosol) along typical trajectories for cumulus convection. “Organic” and “Sulfate” refer to the aerosol masses formed in the aqueous phase. For Trajectories 1 and 2, the third cloud cycle is shown, for Trajectory 3, the second cloud cycle is shown. Products of in-cloud (subscript “cloud”) and wet aerosol (subscript “aer”) chemistry accumulate with time spent in the cloud cycle. In-cloud production dominates for oxalate, but not for other organic species.

fraction of the two-hour cycle is spent in clouds (7, 3 and 12 min for Trajectories 1, 2, and 3, respectively; Figure 11a); thus, wet aerosol chemistry is at work for a much longer time than processes in cloud water. Absolute concentrations of oxalate only increase substantially during in-cloud sections and range between 0.5 and $2 \mu\text{g m}^{-3}$ for the three trajectories at the end of their cycles (Figure 11b). The ratio of oxalate:sulfate shows a similar behavior and reaches maximum values of 0.035–0.12 for the end of the cloud cycle. The increase of this ratio is the result of the longer formation time of oxalate relative to that of sulfate. The ratio approaches a constant value as the precursors for both species get depleted. Model predictions of altitude-dependent oxalate:sulfate (~ 0.12 at 3000 m, Figure 11c) are in agreement with the measurements (~ 0.09 at 2800 m outside of clouds, up to ~ 0.2 in cloud droplet residual particles, Figure 4e). The model overpredicts absolute oxalate concentrations by about an order of magnitude (up to $2.1 \mu\text{g m}^{-3}$) versus measured concentrations of up to $0.41 \mu\text{g m}^{-3}$ in the evaporated cloud of case study 3 (Section 4.3). This is due to the many physical loss mechanisms and exchange processes between the cloud and the ambient aerosol, which are not taken into account in the model. In addition, chemical oxalate sinks, such as the photolysis of iron-oxalate-complexes [Faust and Zepp, 1993], which might also cause a decrease of oxalate, are not included in the model.

[32] In this model study we imply that the findings from laboratory studies [Tan et al., 2009; Lim et al., 2010; Tan et al., 2010, 2012], in which a clear predominance of oligomer formation over oxalate formation in concentrated

solutions (aerosol water) was observed, can be extrapolated to atmospheric conditions. The model predicts only minor formation of oxalate outside of clouds, supporting the use of oxalate as a cloud-processing tracer (Figure 11d). However, for total aqueous phase SOA (mostly oligomers), the model suggests that production in wet aerosol in the vicinity of clouds is more important in terms of mass production. Before the air parcel enters the cloud, organic concentrations reach as high as $2.8 \mu\text{g m}^{-3}$ (Trajectory 3), as a result of wet aerosol processing (Figure 11e). During transit through the cloud, the production of total organic mass (a 30% increase after cloud processing) is dominated by oxalate formation (increase by a factor of 2). In-cloud produced organic mass starts to dominate over wet-aerosol organic mass in the later parts of the cycle (Figure 11f). This may partly be a result of further oxidation of oligomers in wet aerosols in the out-of-cloud time periods, acting as a sink for SOA. Oxalate and pyruvate, produced in cloud droplets, are also subject to further oxidation while dissolved in a cloud droplet, but not in wet aerosols, where they are likely present as salts. Since the in-cloud periods are much shorter than the out-of-cloud periods, further oxidation as a sink for oxalate and pyruvate is not very efficient. Note that SOA processing in wet aerosol is associated with large uncertainties since (i) kinetic data for oligomer oxidation are not readily available and (ii) it is assumed that oxalate forms salts in wet aerosol particles and is not further processed.

[33] The model predictions show that cloud processing can strongly alter the chemical composition and mass of the organic fraction in aerosols, which consequently alters the

particle size distribution. The increase of oxalate mass after transit through the model cloud is in agreement with the measured high oxalate concentrations in the evaporated cloud (Figure 7) and the increased contribution of oxalate to the organic fraction in cloud-droplet residual particles (Figure 4). The increasing trend of oxalate:sulfate with ongoing cloud processing in the model mirrors the increasing ratio of oxalate:sulfate as a function of altitude (Figures 4 and 6), in cloud droplet residual particles (Figure 4), and as a function of residual cloud fraction (Figure 10). This corroborates that both the vertical profiles and the high values of this ratio above cloud top are best explained by aqueous-phase processing in cloud droplets. Furthermore, the model prediction of substantial SOA production in wet aerosols also points at a crucial role of shallow cumulus convection in the organic budget in the southeastern Texas atmosphere: the re-distribution of bulk aerosol (Figure 3, 6 and 7) and precursor gases (Figure 9) to cloud-relevant altitudes exposes these “ingredients” to high RH in and around the shallow cumulus clouds. In the ensuing hygroscopic growth, oligomer formation (as predicted by the model) can add organic mass to the particles. The continuing cycle of convection and formation of shallow, non-precipitating clouds, which are soon subject to (partial) evaporation, leaves ample time and opportunity for this process to take its course. While the understanding of this SOA source is still in its infancy, our study compares for the first time the possible relative contributions of SOA formation in clouds versus aerosol particles on a process level. The findings suggest that the vertical profiles of oxalate are dominated by in-cloud processing, and that the overall organic profile may be heavily influenced by SOA formation in wet aerosols.

5. Conclusions

[34] We investigated the role of shallow cumulus convection in aerosol re-distribution, aerosol and gas transport from the boundary layer into the free troposphere, and aqueous-phase sulfate and SOA formation, using in situ aircraft measurements and cloud model predictions. Composite average vertical profiles of measured accumulation mode particle volume in cloudy and clear conditions were compared. In cloudy conditions, particle volume distributions showed a more even vertical distribution than in clear conditions. Averaged sub-micrometer particle volume in cloudy conditions showed a decrease by 66% from near surface layers (below 450 m) to typical cloud top altitudes (2850 m) as opposed to a decrease by 87% in clear conditions. Both averages and case studies of vertical profiles of aerosol chemistry showed that while absolute concentrations of the chemical components generally decrease with altitude, organic and sulfate mass fractions remained largely constant throughout the altitudes. However, the ratios of the aqueous chemistry tracer oxalate to both sulfate and organic increased with altitude. This indicates that it is important to consider changes in organic functionality of particles as a function of altitude, which may influence their overall hygroscopic and radiative properties. Zones of possible cloud top detrainment of moisture, aerosols and gaseous precursors of aerosols were identified. The presence of sulfate and SOA precursor gases at cloud-relevant altitudes was confirmed, pointing to the important role that clouds play in

promoting secondary aerosol formation in and above cloud tops and in the free troposphere. The residual cloud fraction was introduced as a metric for the extent to which an air mass has been influenced by nearby clouds. Organic mass fractions increased together with oxalate:organic and oxalate:sulfate as a function of residual cloud fraction. A cloud parcel model was used to gain insight into the importance of in-cloud sulfate and SOA formation and wet aerosol aqueous SOA production. The predictions of the cloud parcel model are in good agreement with observed trends of the ratio oxalate:sulfate in cloud droplet residual particles. The model results raise confidence in aqueous SOA formation being the best explanation for the observations. The comparison of model trends with observations indicate that in the Houston atmosphere, vertical profiles of oxalate are governed by in-cloud formation. The model further suggests that in addition to oxalate formation, which is only a small contribution to overall organic mass, oligomer formation in wet aerosols may contribute substantial amounts of aqueous SOA and heavily influence the vertical distribution of organics.

[35] This study has shown that shallow cumulus clouds are instrumental in shaping the vertical profiles of aerosol chemical composition and size distributions, SO₂ and SOA precursor gases. While each individual observation presented in this paper may be explicable by processes other than those connected to shallow cumulus convection, the combination of the observations is most easily explained by transport of aerosols to higher altitudes and into the free troposphere by shallow cumulus convection and production of SOA and sulfate mass in cloud droplets and wet aerosols.

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