Constraining the contribution of organic acids and AMS *m/z* 44 to the organic aerosol budget: On the importance of meteorology, aerosol hygroscopicity, and region

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[1]   Airborne measurements in regions of varying meteorology and pollution are used to quantify the contribution of organic acids and a mass spectral marker for oxygenated aerosols, *m/z* 44, to the total organic aerosol budget. Organic acids and *m/z* 44 separately are shown to exhibit their highest organic mass fractions in the vicinity of clouds. The contribution of such oxygenated species is shown to increase as a function of relative humidity, aerosol hygroscopicity (and decreasing organic mass fraction), and is typically greater off the California coast versus the continental atmospheres studied. Reasons include more efficient chemistry and partitioning of organic acid precursors with increasing water in the reaction medium, and high aqueous-phase processing times in boundary layers with higher cloud volume fractions. These results highlight the importance of secondary organic aerosol formation in both wet aerosols and cloud droplets. **Citation:** Sorooshian, A., S. M. Murphy, S. Hersey, R. Bahreini, H. Jonsson, R. C. Flagan, and J. H. Seinfeld (2010), Constraining the contribution of organic acids and AMS *m/z* 44 to the organic aerosol budget: On the importance of meteorology, aerosol hygroscopicity, and region, *Geophys. Res. Lett.*, *37*, L21807, doi:10.1029/2010GL044951.

1.   Introduction

[2] The chemical complexity of atmospheric aerosols poses a challenge for accurate modeling of their interactions with water vapor, radiation, and clouds. It is now well established that the organic fraction of atmospheric aerosols becomes increasingly oxidized with age, leading to species that are both less volatile and more hygroscopic [*Jimenez et al.*, 2009]. Water-soluble organic species, especially organic acids, are of interest owing to their hygroscopic properties [*Hallquist et al.*, 2009]. Oxidized organic compounds can be generated in cloud droplets as well as moist aerosols [*Volkamer et al.*, 2009; *Lim et al.*, 2010; *Ervens and Volkamer*, 2010], and increased partitioning of water-soluble organic compounds (WSOC) with increasing sub-saturated relative humidity (RH) is observed [*Hennigan et al.*, 2008, 2009]. While the concentrations of organic acids are documented in different regions [*Sorooshian et al.*, 2007a, and references therein], the extent to which such water-soluble oxygenated acids contribute to total organic aerosol levels is not well established in a variety of atmospheres [*Takegawa et al.*, 2007; *Kondo et al.*, 2007].

[3] We present an analysis of datasets from four aircraft field studies that addresses the following questions: (1) What is the contribution of organic acids and the mass spectral peak *m/z* 44 to total organic aerosol mass in a variety of clear and cloudy atmospheres?; and (2) How does the relative abundance depend on meteorology, background aerosol physicochemical properties, and reaction medium (i.e., wet aerosols versus dilute droplets)?

2.   Measurements

[4] Airborne measurements were carried out with the Center for Interdisciplinary Remotely-Piloted Aircraft Studies (CIRPAS) Twin Otter during the following campaigns: International Consortium for Atmospheric Research on Transport and Transformation (ICARTT, August 2004; Ohio River Valley), Marine Stratus/Stratocumulus Experiments (MASE I and II, in July 2005 and 2007, respectively; off the central California coast), and the Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS, August–September 2006; Southeastern Texas). Three aircraft inlets were utilized: (i) a forward-facing inlet outside of clouds [*Hegg et al.*, 2005]; (ii) a counterflow virtual impactor (CVI) inlet in clouds to isolate droplet residual particles [*Sorooshian et al.*, 2006b]; and (iii) a reverse-facing inlet in clouds to isolate interstitial aerosol particles (used only during MASE II).

[5] Particulate organic acid measurements were carried out with a particle-into-liquid sampler (PILS; Brechtel Mfg Inc.) coupled to an ion chromatograph [*Sorooshian et al.*, 2006a]. Data are presented for a suite of organic acids ions (saturated dicarboxylic acids C_2–C_9, acetic, formic, pyruvic, glyoxylic, maleic, malic, and methanesulfonic acids). Independent measurements of inorganic mass (sulfate, nitrate, ammonium) and total non-refractory organic mass were obtained with a quadropole Aerosol Mass Spectrometer (Aerodyne AMS) [*Jayne et al.*, 2000; *Bahreini et al.*, 2003] during the first experiment (ICARTT) and with a compact Time of Flight Aerosol Mass Spectrometer

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Table 1. Statistical Summary of Various Ratios Between Organic Aerosol Markers in Different Regions

	Pacific Coast[a]				Continental[b]			
	Average	STD	Slope	r^2	Average	STD	Slope	r^2
Oxalate: Organic	0.04	0.04	0.02	0.34	0.03	0.02	0.02	0.42
Organic Acid: Organic	0.06	0.06	0.02	0.32	0.04	0.04	0.02	0.45
Oxalate: m/z 44	0.27	0.23	0.17	0.45	0.18	0.15	0.16	0.47
Organic Acid: m/z 44	0.39	0.33	0.19	0.43	0.23	0.22	0.18	0.50
m/z 44: Organic	0.18	0.10	0.11	0.77	0.15	0.05	0.14	0.92
Oxalate: m/z 57	2.47	2.96	0.09	0.12	2.82	2.34	1.90	0.25
Organic Acid: m/z 57	2.72	3.37	0.10	0.08	3.17	2.64	2.00	0.24

[a]"Pacific Coast" corresponds to MASE I/II data (n = 586).
[b]"Continental" represents ICARTT/GoMACCS data (n = 384).

(Aerodyne C-ToF-AMS) [*Drewnick et al.*, 2005; *Murphy et al.*, 2009] during MASE I, MASE II, and GoMACCS. Other AMS data discussed include the organic mass represented by m/z 44 (higher fractions relative to total organic mass suggest more oxidation) and 57 (higher fractions suggest more hydrocarbon-like organics) [*Zhang et al.*, 2005; *Aiken et al.*, 2008]. As an example of the measurement agreement between the AMS and PILS, the sulfate concentrations for the data set in this study exhibit an overall correlation of r^2 = 0.90 (n = 970) and an AMS:PILS ratio of 0.98. No significant relationship was observed between the AMS:PILS sulfate ratio and variables of interest in this study including ambient RH and organic mass fraction.

[6] Sub-saturated aerosol hygroscopicity measurements were provided by a differential aerosol sizing and hygroscopicity spectrometer probe (DASH-SP; Brechtel Mfg Inc.) [*Sorooshian et al.*, 2008]. DASH-SP data are only reported for the MASE II campaign, corresponding to particles with dry diameters of either 150, 175, or 200 nm, and humidified to RHs of either 74%, 85%, or 92%.

3. Cumulative Results

[7] Cumulative statistics associated with ratios of various oxygenated organic markers relative to the total organic mass are given in Table 1, with the data categorized into "Pacific Coast" (MASE I and MASE II) and "Continental" conditions (ICARTT and GoMACCS). Note that background marine conditions often do not exist off the central coast of California owing to aged ship and continental emissions [*Murphy et al.*, 2009]. Conversely, air masses during GoMACCS (southeastern Texas) may have been marine-influenced. The term "organic acids" will henceforth refer to the sum of the species quantified by the PILS as listed above. Particular attention is placed on oxalate as it was the dominant organic acid in these field studies and has been shown to be produced in clouds [*Sorooshian et al.*, 2006b, 2007a/2007b].

[8] Total organic mass and the organic mass associated with m/z 44 are highly correlated (r^2 = 0.77–0.92), suggesting that organic aerosol production in the studied regions was linked to the formation of oxidized organic aerosol species. The average mass ratios of oxalate:organic, organic acid:organic, oxalate:m/z 44, organic acid:m/z 44, and m/z 44:organic are highest in the Pacific Coast atmosphere, indicative of a more oxidized average organic component. This is thought to be partly a result of the greater fraction of the marine boundary layer volume occupied by clouds relative to the continental atmospheres studied, allowing for longer aqueous-phase processing times

[*Feingold et al.*, 1998]. Oxalate and the cumulative organic acids accounted for a maximum of 21% and 44% of the marine organic mass, respectively. The organic acids are weakly correlated with m/z 57, suggesting that there is not a strong non-oxidized emissions source of organic acids (such as emissions from ships [*Murphy et al.*, 2009]). The correlations are higher for the organic acids versus m/z 44 as compared to organic acids versus total organics, demonstrating that m/z 44 is more closely linked to oxygenated organic acid species. As a basis for comparison, *Takegawa et al.* [2007] observed higher correlations between selected carboxylic acids and m/z 44 (r^2 = 0.85–0.94), and showed that the acids contributed 14 ± 5% to the m/z 44 mass concentration. The differences in those values may be linked to the varying measurement methods and region (those organic acid measurements involved ground-based filters in Tokyo).

[9] The relatively large standard deviations in Table 1 indicate that the ratios exhibit dependence on conditions other than region. Figure 1 summarizes the variation of chemical ratios in Table 1 as a function of location below altitudes of 5 km ("clear air" away from clouds, "below cloud", "droplet residual particles" in cloud, "interstitial aerosol" in cloud, and "above cloud"). The various ratios usually exhibit the lowest values in "clear air" and the highest values and correlation coefficients (between ratio components) in cloud droplet residual particles, owing to the effectiveness of in-cloud formation [*Sorooshian et al.*, 2006b, 2007a/2007b]. As higher values are observed in cloud droplet residual particles versus interstitial aerosols, this likely reflects some combination of more efficient chemistry and partitioning of WSOC precursors as a function of increasing volume of liquid water. This result is consistent with prior measurements of enhanced partitioning of water-soluble organic species in cloud and fog droplets relative to interstitial aerosols [*Facchini et al.*, 1999; *Blando and Turpin*, 2000; *Limbeck and Puxbaum*, 2000; *Collett et al.*, 2008].

4. Relative Humidity Effect

[10] Figure 2 shows the relationship between RH and the same organic ratios examined in Figure 1. The ratios remain relatively constant until an RH near 70%, above which the ratios increase, behavior that is remarkably similar to measurements that showed maximum partitioning of WSOC to the particle phase for RH > 70% in the Atlanta atmosphere during the summertime [*Hennigan et al.*, 2008]. There is a much wider dynamic range in the organic acid:m/z 44 ratios (Figure 2a: 0.10–0.63 from 0 to 100% RH) as compared to
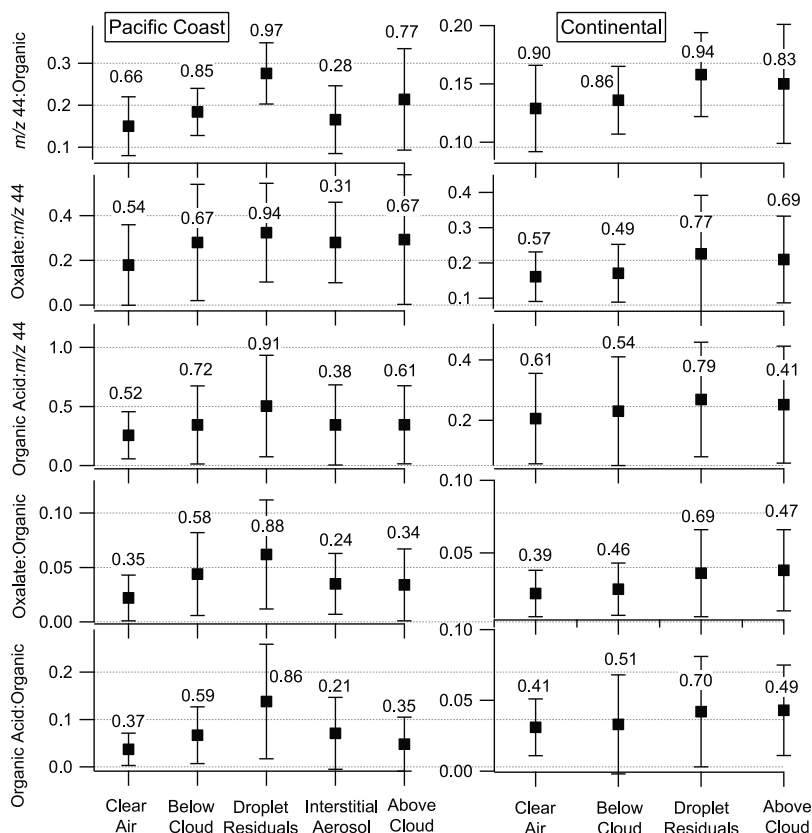
Figure 1. Relationship between ratios of organic aerosol markers and location with respect to clouds. Numbers next to markers indicate the correlation (r^2) between the two components of the ratios examined.

organic acid:organic ratios (Figure 2b: 0.02–0.08 from 0 to 100% RH), pointing to the more vigorous enrichment of organic acids relative to the oxygenated aerosol fraction represented by m/z 44. Although not shown, the organic ratios in Figure 2 exhibit the same RH-dependent qualitative behavior in each region examined, and are typically higher for the Pacific Coast across the entire RH range.

5. Aerosol Hygroscopicity Effect

[11] To further examine the role of liquid water in influencing the ratios of organic acids and oxygenated organics to the total organic mass, the relationship between aerosol hygroscopicity and these ratios is investigated in bins of ambient RH. This analysis can most directly be performed for the MASE II mission when hygroscopicity was measured. To control for the effect of ambient RH and to still do the analysis with a sufficient amount of data, the m/z 44: organic ratio is examined for measurements between RHs of 60–95%. Figure 3d shows that this ratio tends to increase as a function of the hygroscopic growth factor (GF = $D_{p,wet}/D_{p,dry}$) at the three pre-selected DASH-SP RHs (74%, 85%, 92%). This indicates that for the RH range examined, particles with a greater tendency to take up water will have an organic component that is more enriched with oxygenated species.

[12] Since hygroscopicity was not directly quantified in the other three field studies (ICARTT, GoMACCS, MASE I), the organic mass fraction of aerosols (= AMS organic mass/ AMS total mass = 1–inorganic fraction) will be used as a
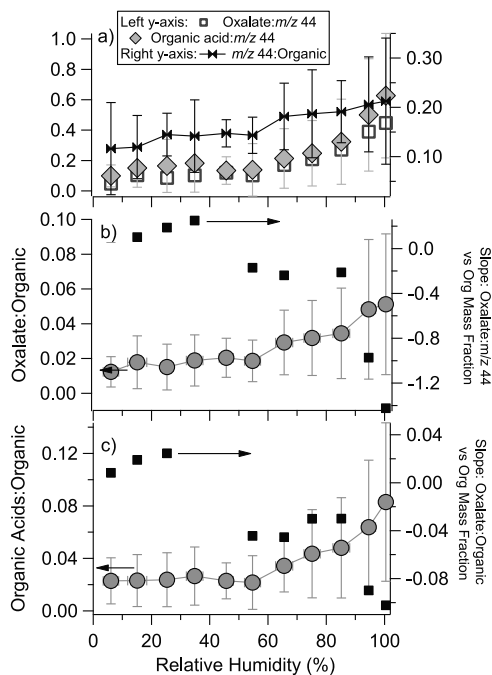

Figure 2. (a) Dependence of numerous organic ratios on RH. Data are grouped in RH bins (10% increments). (b, c) The right y-axes correspond to the slopes of "oxalate:m/z 44 vs organic mass fraction" and "oxalate:organic vs organic mass fraction" in each RH bin, where the organic mass fraction is used as a proxy for aerosol hygroscopicity. Only statistically significant slopes at 95% confidence are shown.
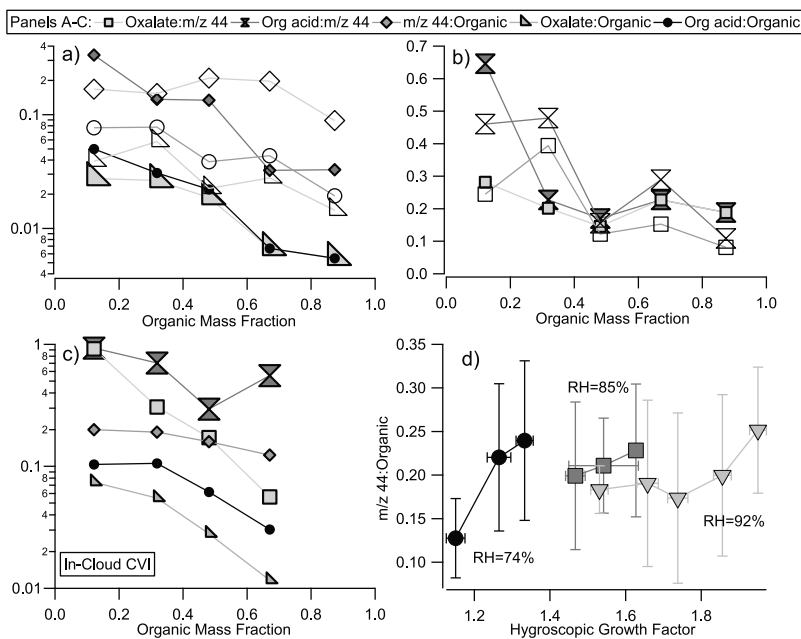
Figure 3. (a–c) Dependence of numerous organic ratios on organic mass fraction for ambient RHs between 60–95%. Data are grouped in organic mass fraction bins (0.2 increments). Open markers in Figures 3a and 3b correspond to low total aerosol mass concentrations (1–5 μg m^{-3}) and filled markers correspond to higher total aerosol mass concentrations (5–50 μg m^{-3}). (d) m/z 44:organic ratio as a function of hygroscopic growth factor at three pre-selected DASH-SP RHs (74%, 85%, 92%) for a dry diameter of 200 nm during MASE II for ambient RHs between 60–95%.

hygroscopicity proxy. At least for the MASE II region, hygroscopicity expectedly increases with decreasing organic mass fraction, as shown by *Hersey et al.* [2009], with the effect more pronounced at higher RHs. It is shown in Figures 2b and 2c that in the highest RH bins (> 50%), the enrichment of organic acids and oxalate is most pronounced at lower organic mass fractions. This is more clearly illustrated in Figures 3a and 3b where it is shown that the contribution of organic acids and m/z 44 to the total organic mass typically increases as a function of decreasing organic mass fraction for in-cloud droplet residual particles and for wet aerosols between ambient RHs of 60 to 95%. These results agree with those of MASE II in that higher aerosol hygroscopicity will result in more aerosol-laden water, and therefore the enrichment of organic acids and other oxygenated organics relative to the total organic mass.

[13] Since the amount of liquid water in particles increases as a function of higher hygroscopic aerosol mass concentrations, the effect of aerosol mass on the various ratios of organic acid and oxygenated organics to total organic mass is also examined. Out-of-cloud data are examined in Figures 3a and 3b in bins of "low" and "high" aerosol mass concentrations. It is difficult to see any enhancement in the organic acids or m/z 44 at the higher mass concentrations, except in conditions of very low organic mass fractions (< 0.2). When binning the field data by m/z 44 mass concentration, the ratios in Figures 3a and 3b still were not greater at the higher m/z 44 levels. These measurements do not exhibit as clear a signal as recent studies showing a linear relationship between SOA production and aerosol seed concentration (and water mass) [*Ervens and Volkamer*, 2010], and greater WSOC aerosol/gas partitioning ratios as a function of increasing particulate WSOC concentration

[*Hennigan et al.*, 2009]. This may be owing to the enrichment of species other than organic acids in the regions studied.

6. Conclusions

[14] From several airborne field missions, a highly water-soluble class of organics, specifically organic acids, and also a larger body of oxygenated species indicated by the m/z 44 mass spectral peak, are found to contribute to the total organic aerosol fraction, with the absolute contribution increasing as a function of RH and aerosol hygroscopicity (and decreasing organic mass fraction). The contribution of organic acids is highest in cloud droplet residuals and is larger for the Pacific Coast (up to more than 44% of the organic mass) relative to the continental atmospheres examined. The high fraction of such species in the former region is thought to be at least partly due to longer aerosol residence times in the aqueous phase owing to higher cloud volume fractions in the boundary layer. These results highlight the important dual role of both ambient RH and hygroscopicity in leading to an enrichment of oxygenated organics, especially organic acids, in ambient aerosols. More liquid water associated with aerosol particles facilitates the dissolution of organic acid precursors, such as glyoxal, and also conversion of such species to the eventual organic acids [*Blando and Turpin*, 2000].

[15] This work shows that the relative amount of organic acids (especially oxalate) to other aerosol components (e.g., organic mass, m/z 44) can be used as tracers for air parcels that have undergone aqueous-phase processing. This work strengthens a growing consensus among modeling, laboratory chamber, and ground-based field studies that liquid water content plays a key role in organic aerosol formation.

References

Aiken, A. C., et al. (2008), O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high resolution time-of-flight aerosol mass spectrometry, *Environ. Sci. Technol.*, 42, 4478–4485, doi:10.1021/es703009q.

Bahreini, R., J. L. Jimenez, J. Wang, R. C. Flagan, J. H. Seinfeld, J. T. Jayne, and D. R. Worsnop (2003), Aircraft-based aerosol size and composition measurements during ACE-Asia using an Aerodyne aerosol mass spectrometer, *J. Geophys. Res.*, 108(D23), 8645, doi:10.1029/2002JD003226.

Blando, J. D., and B. J. Turpin (2000), Secondary organic aerosol formation in cloud and fog droplets: A literature evaluation of plausibility, *Atmos. Environ.*, 34, 1623–1632, doi:10.1016/S1352-2310(99)00392-1.

Collett, J. L., P. Herckes, S. Youngster, and T. Lee (2008), Processing of atmospheric organic matter by California radiation fogs, *Atmos. Res.*, 87, 232–241, doi:10.1016/j.atmosres.2007.11.005.

Drewnick, F., et al. (2005), A new time-of-flight aerosol mass spectrometer (TOF-AMS): Instrument description and first field deployment, *Aerosol Sci. Technol.*, 39, 637–658, doi:10.1080/02786820500182040.

Ervens, B., and R. Volkamer (2010), Glyoxal processing outside clouds: Towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles, *Atmos. Chem. Phys.*, 10, 8219–8244, doi:10.5194/acp-10-8219-2010.

Ervens, B., G. Feingold, G. J. Frost, and S. M. Kreidenweis (2004), A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, *J. Geophys. Res.*, 109, D15205, doi:10.1029/2003JD004387.

Facchini, M. C., et al. (1999), Partitioning of the organic aerosol component between fog droplets and interstitial air, *J. Geophys. Res.*, 104, 26,821–26,832, doi:10.1029/1999JD900349.

Feingold, G., S. M. Kreidenweis, and Y. Zhang (1998), Stratocumulus processing of gases and cloud condensation nuclei: 1. Trajectory ensemble model, *J. Geophys. Res.*, 103, 19,527–19,542, doi:10.1029/98JD01750.

Hallquist, M., et al. (2009), The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236, doi:10.5194/acp-9-5155-2009.

Hegg, D. A., D. S. Covert, P. A. Covert, and H. Jonsson (2005), Determination of the efficiency of an aircraft aerosol inlet, *Aerosol Sci. Technol.*, 39, 966–971, doi:10.1080/02786820500377814.

Hennigan, C. J., M. H. Bergin, J. E. Dibb, and R. J. Weber (2008), Enhanced secondary organic aerosol formation due to water uptake by fine particles, *Geophys. Res. Lett.*, 35, L18801, doi:10.1029/2008GL035046.

Hennigan, C. J., M. H. Bergin, A. G. Russell, A. Nenes, and R. J. Weber (2009), Gas/particle partitioning of water-soluble organic aerosol in Atlanta, *Atmos. Chem. Phys.*, 9, 3613–3628, doi:10.5194/acp-9-3613-2009.

Hersey, S. P., A. Sorooshian, S. M. Murphy, R. C. Flagan, and J. H. Seinfeld (2009), Aerosol hygroscopicity in the marine atmosphere: A closure study using high-resolution, size-resolved AMS and multiple-RH DASH-SP data, *Atmos. Chem. Phys.*, 9, 2543–2554, doi:10.5194/acp-9-2543-2009.

Jayne, J. T., D. C. Leard, X. F. Zhang, P. Davidovits, K. A. Smith, C. E. Kolb, and D. R. Worsnop (2000), Development of an aerosol mass spectrometer for size and composition analysis of submicron particles, *Aerosol Sci. Technol.*, 33, 49–70, doi:10.1080/027868200410840.

Jimenez, J. L., et al. (2009), Evolution of organic aerosols in the atmosphere, *Science*, 326, 1525–1529, doi:10.1126/science.1180353.

Kondo, Y., Y. Miyazaki, N. Takegawa, T. Miyakawa, R. J. Weber, J. L. Jimenez, Q. Zhang, and D. R. Worsnop (2007), Oxygenated and water-soluble organic aerosols in Tokyo, *J. Geophys. Res.*, 112, D01203, doi:10.1029/2006JD007056.

Lim, H. J., Y. Tan, M. J. Perri, S. P. Seitzinger, and B. J. Turpin (2010), Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, *Atmos. Chem. Phys. Discuss.*, 10, 14,161–14,207, doi:10.5194/acpd-10-14161-2010.

Limbeck, A., and H. Puxbaum (2000), Dependence of in-cloud scavenging of polar organic aerosol compounds on the water solubility, *J. Geophys. Res.*, 105, 19,857–19,867, doi:10.1029/2000JD900123.

Murphy, S. M., et al. (2009), Comprehensive simultaneous shipboard and airborne characterization of exhaust from a modern container ship at sea, *Environ. Sci. Technol.*, 43, 4626–4640, doi:10.1021/es802413j.

Sorooshian, A., et al. (2006a), Modeling and characterization of a particle-into-liquid sampler (PILS), *Aerosol Sci. Technol.*, 40, 396–409, doi:10.1080/02786820600632282.

Sorooshian, A., et al. (2006b), Oxalic acid in clear and cloudy atmospheres: Analysis of data from International Consortium for Atmospheric Research on Transport and Transformation 2004, *J. Geophys. Res.*, 111, D23S45, doi:10.1029/2005JD006880.

Sorooshian, A., N. L. Ng, A. W. H. Chan, G. Feingold, R. C. Flagan, and J. H. Seinfeld (2007a), Particulate organic acids and overall water-soluble aerosol composition measurements from the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), *J. Geophys. Res.*, 112, D13201, doi:10.1029/2007JD008537.

Sorooshian, A., et al. (2007b), On the source of organic acid aerosol layers above clouds, *Environ. Sci. Technol.*, 41, 4647–4654, doi:10.1021/es0630442.

Sorooshian, A., S. Hersey, F. J. Brechtel, A. Corless, R. C. Flagan, and J. H. Seinfeld (2008), Rapid, size-resolved aerosol hygroscopic growth measurements: Differential aerosol sizing and hygroscopicity spectrometer probe (DASH-SP), *Aerosol Sci. Technol.*, 42, 445–464, doi:10.1080/02786820802178506.

Takegawa, N., T. Miyakawa, K. Kawamura, and Y. Kondo (2007), Contribution of selected dicarboxylic and omega-oxocarboxylic acids in ambient aerosol to the m/z 44 signal of an aerodyne aerosol mass spectrometer, *Aerosol Sci. Technol.*, 41, 418–437, doi:10.1080/02786820701203215.

Volkamer, R., P. J. Ziemann, and M. J. Molina (2009), Secondary organic aerosol formation from acetylene (C_2H_2): Seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase, *Atmos. Chem. Phys.*, 9, 1907–1928, doi:10.5194/acp-9-1907-2009.

Zhang, Q., et al. (2005), Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry, *Environ. Sci. Technol.*, 39, 4938–4952, doi:10.1021/es048568l.

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