Additional Supplemental Information to the paper

In-Cloud Oxalate Formation in the Global Troposphere: A 3D Modeling Study

S. Myriokefalitakis, et al. acpd-2010-968

Table S4. Location of stations with OXL observations, time, station classification, concentrations (in ng m^{-3}) and analytical method taken into account for the model validation in Fig. 6.

Location	Time	Station Classification	Measurements	Filters	Analytical Method	Reference
California, USA	June – September, 1984	Urban - Surface	490	Quartz	GC-MS	Kawamura et al., 1985
Monterey, CA	24 August – 3 September, 2002	Urban - Air	140±30	[#]PTFE	IC	Crahan et al., 2004
Mexico City, Mexico	17-30 March, 2006	Urban - Surface	1330± 620	Quartz	HPLC-MS/MS	Stone et al., 2010
Chicago, USA	July-August, 2002 and July, 2003	Urban - Surface	118±0	Quartz	IC	Fosco and Schmeling, 2006
Claremont, CA	11-19 September, 1985	Urban - Surface	210	Nylon-Nylon	IC	Grosjean, 1988
Sao Paulo, Brazil	July, 1996	Urban - Surface	1140±1200	PTFE	IC	Souza et al., 1999
Vienna, Austria	16-18 February, 1999	Urban - Surface	86±25	Quartz	GC/MS	Limbeck et al., 2005
Vienna, Austria	June, 1997	Urban - Surface	340	Quartz	GC-FID-MS	Limbeck and Puxbaum, 1999
Lahore, Pakistan	December, 2005 – February, 2006	Urban - Surface	600±520	PTFE	IC	Biswas et al., 2008
Baoji, China	10-15 February, 2008	Urban - Surface	816±172	Quartz	GC-MS	Wang et al., 2010
Baoji, China	1-6 April, 2008	Urban - Surface	532±247	Quartz	GC-MS	Wang et al., 2010
Tokyo, Japan	April, 1988 - February, 1989	Urban - Surface	270±190	Quartz	GC-MS	Kawamura and Ikushima, 1993
Tokyo, Japan	24-26 February, 1992	Urban - Surface	521-650	Quartz	GC-MS	Sempere and Kawamura, 1994
Tokyo, Japan	22-23 July, 1992	Urban - Surface	1352-1680	Quartz	GC-MS	Sempere and Kawamura, 1994
Helsinki, Finland	April-May, 2006	Urban - Surface	91±110	Quartz	IC	Saarnio et al., 2010
Helsinki, Finland	July and September, 2006	Urban - Surface	50±37	Quartz	IC	Saarnio et al., 2010
Chennai, India	23 -28 January, 2007	Urban - Surface	472.4±136.9	Quartz	GC-MS	Pavuluri et al., 2010

Denver, USA	July and August, 1981 and 1982	Rural - Surface	<180	PTFE	IC	Norton et al., 1993
N. Carolina, USA	July and September, 2003	Rural - Surface	10-200	PTFE	IC	Lewandowski et al., 2007
Sydney, FL	27 April - 31 May, 2002	Rural - Surface	290	Glass fiber	IC	Martinelango et al., 2006
Amazon Basin, Brazil	July-August, 1985	Rural - Air	158±59	PTFE	IC	Talbot et al., 1988
Rondonia, Brazil	8 September - 11 November, 2002	Rural - Surface	22-1340	Quartz-PTFE	IC	Falkovich et al., 2005
Rondonia, Brazil	1 September-25 October, 1999	Rural - Surface	140-1330	Quartz	IC	Graham et al., 2002
*Aveiro, Portugal	July, 2002 – June, 2004	Rural - Surface	262±117	Quartz	IC	Legand et al., 2007 / CARBOSOL consortium
*Pay de Dome, France	September 2002-September 2004	Rural - Surface	137±85	Quartz	IC	Legand et al., 2007 / CARBOSOL consortium
*Schauinland, Germany	October 2002 –September 2004	Rural - Surface	223±105	Quartz	IC	Legand et al., 2007 / CARBOSOL consortium
*K-Pustza, Hungury	July 2002 – May 2004	Rural - Surface	288±93	Quartz	IC	Legand et al., 2007 / CARBOSOL consortium
Goldlauter, Germany	7-8 and 26-27, October 2001	Rural - Surface	>104	Quartz	GC-MS	Muller et al., 2005
Fichtelgebirge, Germany	July 2002	Rural - Surface	69±19	Quartz	GC-MS	Plewka et al., 2006
Salzburg, Austria	July, 2002	Rural - Surface	153	Quartz	GC-MS	Limbeck and Puxbaum, 1999
Nylsvley, South Africa	May 1997	Rural - Surface	193	Quartz	GC-MS	Limbeck and Puxbaum, 1999
Mt. Rax, Austria	12–25 April 1999	Rural - Surface	57±32	Quartz	GC-MS	Limbeck et al., 2005
Bangui, Central Africa	November 1996	Rural - Surface	140±50	Glass fiber	IC	Ruellan et al., 1999
Valencia, Spain	11 September - 19 October, 2006	Rural - Surface	200 (100-400)	Quartz	IC	Vianna et al., 2008
Mt. Tai, China	22–28 June 2006	Rural - Surface	306.5±84.5	Quartz	GC/FID	Wang et al., 20009
Mangshan, China	15 September - 5 October, 2007	Rural - Surface	760	Quartz	GC	He and Kawamura, 2010
*Mace Head, Ireland	Apr.–Sept. 1998	Marine - Surface	101±47	Quartz	CE	Kleefeld et al., 2002
*Alert, Canada	22 January - 20 April, 1992	Marine - Surface	39±15	Quartz	GC/MS	Kawamura et al., 2005
Azores, Terceira Island	Oct. 1998–March 1999	Marine - Surface	54±27	Quartz	IC	Legand et al., 2007 / CARBOSOL consortium
*Finokalia, Greece	January - December , 2005	Marine - Surface	155±60	PTFE	IC	Mihalopoulos, N., 2011, pers. com.
*Amsterdam Island	May, 2003 - December, 2004	Marine - Surface	11.3±2.2	Quartz	IC	Sciare, J, 2011, pers. com
Syowa Station, Antarctica	19 March -29 April, 1991	Marine - Surface	1.59	Quartz	GC	Kawamura et al., 1996
Syowa Station, Antarctica	13 May – 9 June 1991	Marine - Surface	3.12	Quartz	GC	Kawamura et al., 1996

Syowa Station, Antarctica	29 August – 29 October 1991	Marine - Surface	3.26	Quartz	GC	Kawamura et al., 1996
Syowa Station, Antarctica	28 November – 31 December	Marine - Surface	10.29	Quartz	GC	Kawamura et al., 1996
Indian Ocean-Arabian Sea	February-March 1999	Marine - Ship	103±62	Quartz	GC/MS	Neussus et al., 2002
Jesu Island, Korea	13 - 29 April, 2001	Marine - Surface	430±290	PTFE	IC	Topping et al., 2004
North Atlantic Ocean	11 October – 2 November 1996	Marine - Ship	46±43	PTFE	IC	Baboukas et al., 2000
North Pacific Ocean	29 July - 19 August 2008	Marine - Ship	97±35	Quartz	GC	Miyazaki et al., 2010

[*]*Monthly means have been used for the comparison with the model results*

[#]*PTFE : poly Tetra Fluoro ether*

Table S5. ANOVA statistics for model evaluation (based on data depicted in Figures 5 and 6)

Station	**Simulation**	**Slope**	**r^2**	**N**	**a**	**F-value**	**Prob>F**
urban	S1	0.01	-0.06	18	0.05	0.07	0.793
marine	S1	0.63	0.68	49	0.05	102	2.33E-13
rural	S1	0.53	0.26	63	0.05	22	1.21E-5
rural&marine	S1	0.64	0.45	112	0.05	91	4.44E-16
Seasonality	**model**	**evaluation**					
Finokalia	S1	0.61	0.61	12	0.05	18.221	0.0016
	S2	0.65	0.63	12	0.05	20.154	0.0012
	S3	0.86	0.65	12	0.05	21.891	0.0009
	S4	0.85	0.64	12	0.05	20.416	0.0011
Amsterdam island	S1	1.35	0.53	12	0.05	13.405	0.004
	S2	1.39	0.59	12	0.05	17.075	0.002
	S3	1.46	0.56	12	0.05	15.199	0.003
	S4	1.84	0.25	12	0.05	4.641	0.057
Mace Head	S1	0.33	0.58	11	0.05	14.971	0.004
	S2	0.33	0.59	11	0.05	15.204	0.004
	S3	0.39	0.71	11	0.05	25.402	0.0001
	S4	0.54	0.73	11	0.05	28.005	0.005
Aveiro	S1	0.31	0.33	12	0.05	6.461	0.029
	S2	0.33	0.37	12	0.05	7.403	0.021
	S3	0.34	0.34	12	0.05	6.762	0.026
	S4	0.35	0.35	12	0.05	6.969	0.025
Azores	S1	0.07	-0.04	12	0.05	0.519	0.487
	S2	0.07	-0.05	12	0.05	0.384	0.502
	S3	0.06	-0.07	12	0.05	0.311	0.589
	S4	0.15	-0.01	12	0.05	0.913	0.362
Schauinsland	S1	0.39	0.72	12	0.05	29.840	0.003
	S2	0.39	0.72	12	0.05	29.664	0.003
	S3	0.24	0.23	12	0.05	4.420	0.062
	S4	0.25	0.25	12	0.05	4.724	0.055
Puy de Dome	S1	0.42	0.41	12	0.05	8.581	0.015
	S2	0.41	0.39	12	0.05	0.045	0.018
	S3	0.35	0.24	12	0.05	4.448	0.061
	S4	0.36	0.24	12	0.05	4.397	0.062
K-Pustza	S1	-0.01	-0.09	12	0.05	0.002	0.967
	S2	0.06	-0.09	12	0.05	0.054	0.821
	S3	0.20	0.01	12	0.05	1.092	0.321
	S4	0.19	-0.01	12	0.05	0.978	0.345

Supplementary Figures

Surface | 500hPa

OXL/SOA

SOAb/SOA

SOAa/SOA

MSA/SOA

Marine amine salts/SOA

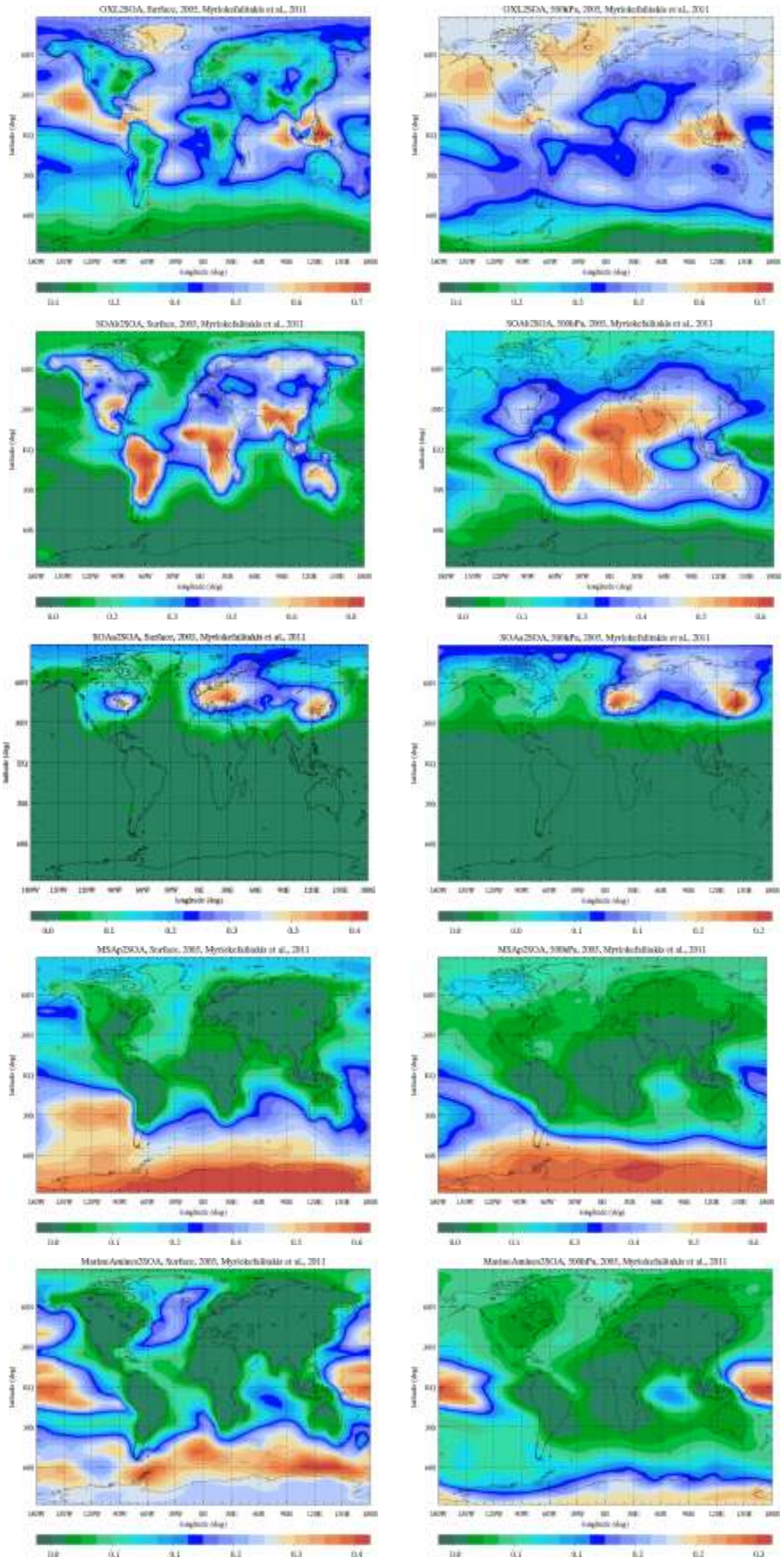

Figure S1. Specific component groups contributions to secondary organic aerosol mass as computed by the TM4-ECPL model for surface (left panels) and for 500 hPa (right panels).

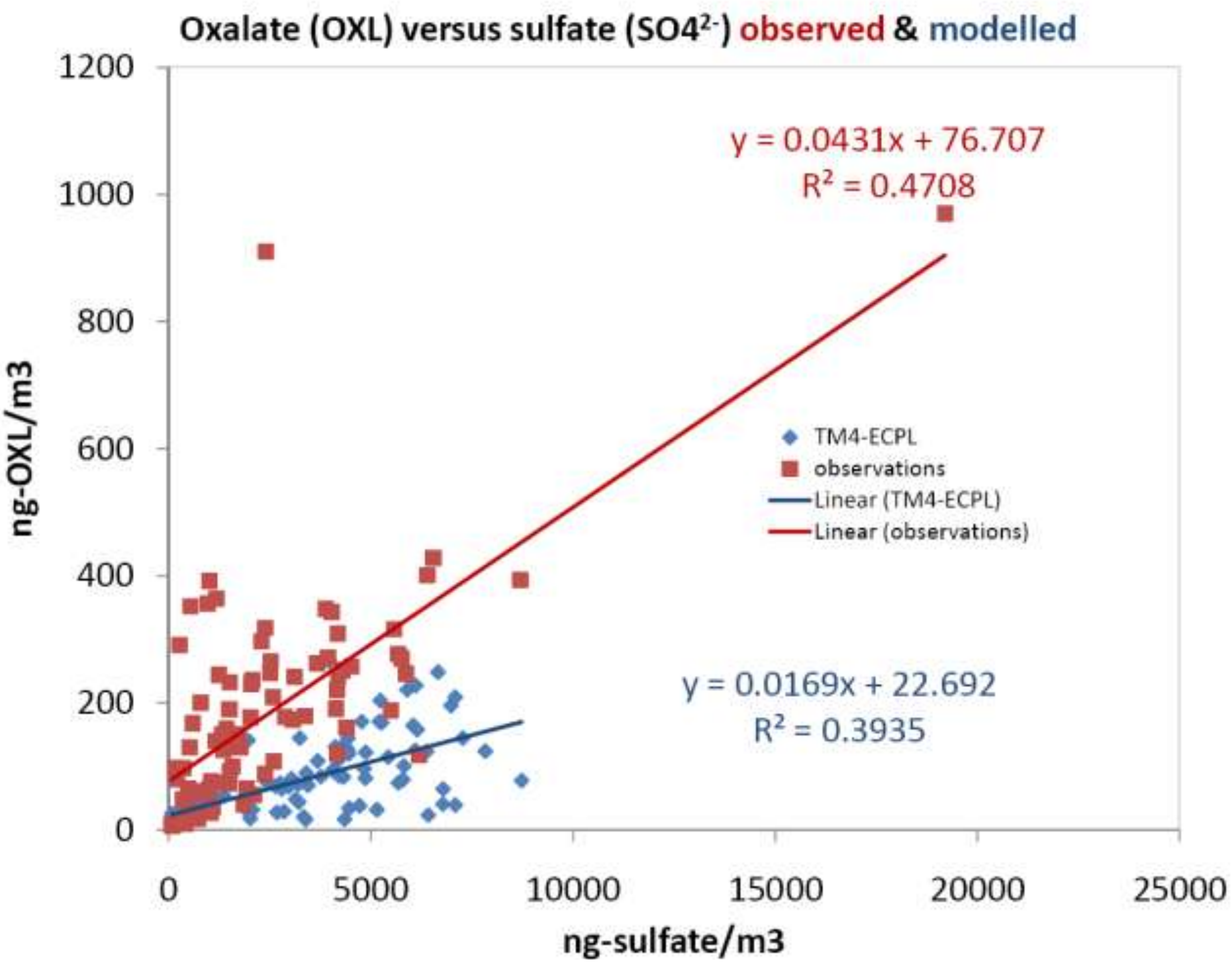

Figure S2. Oxalate (ng-OXL/m^3) as a function of $SO_4^{=}$ (ng-SO_4/m^3) mass concentrations from observations (red squares) and as calculated by the model (blue diamonds), based on monthly mean values.. Observations are taken from Crahan et al., 2004, Fosco and Schmeling, 1988; Biswas et al., 2008; Saarnio et al. 2010; Legrand et al., 2007; Koulouri et al ., 2008 ; Sciare J. unpublished data.

References

Baboukas, E.D., Kanakidou, M., Mihalopoulos, N.: Carboxylic acids in gas and particulate phase above the Atlantic Ocean, J. Geophys. Res., 105, 14459-14471, 2000.

Barth, M. C., Sillman, S., Hudman, R., Jacobson, M. Z., Kim, C.-H., Monod, A., Liang, J.: Summary of the cloud chemistry modeling intercomparison: Photochemical box model simulation, J. Geophys. Res., 108, 4214, doi:10.1029/2002JD002673, 2003.

Biswas, K.F., Ghauri, B.M., Husain, L.: Gaseous and aerosol pollutants during fog and clear episodes in South Asian urban atmosphere, Atmos. Environ., 42, 7775–7785, 2008.

Brimblecombe, P., Clegg, S.L., Khan, I.: Thermodynamic properties of carboxylic acids relevant to their solubility in aqueous solutions, J. Aeros. Sci., 23, suppl. I, S901-S904, 1992.

Carlton, A. G., Turpin, B. J., Altieri, K. E., et al.: Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, Atmos. Environ., 41, 7588–7602, 2007.

Crahan, K.K., Hegg, D., Covert, D.S., Jonsson H.: An exploration of aqueous oxalic acid production in the coastal marine atmosphere, Atmos. Environ. 38, 3757–3764, 2004.

Falkovich, A. H., Graber, E.R., Schkolnik, G., Rudich, Y., Maenhaut, W., and Artaxo, P.: Low molecular weight organic acids in aerosol particles from Rondonia, Brazil, during the biomass-burning, transition and wet periods, Atmos. Chem. Phys., 5, 781–797, 2005.

Ervens, B., Feingold, G., Frost, G.J., Kreidenweis S.M.: 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, 2004.

Ervens, B., and Volkamer, R.: 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, 2010.

Fosco, T. and Schmeling, M.: Aerosol ion concentration dependence on atmospheric conditions in Chicago, Atmos. Environ. 40, 6638–6649, 2006.

Grosjean, D.: Aldehydes, carboxylic acids and inorganic nitrate during nsmcs, Atmos. Environ., 22, 1637-1648, 1988.

He, N. and Kawamura, K.: Distributions and diurnal changes of low molecular weight organic acids and α-dicarbonyls in suburban aerosols collected at Mangshan, North China, Geochem. J., 44, e17-e22, 2010.

Herrmann, H., Ervens, B., Jacobi, H.-W., Wolke R., Nowacki P, and Zellner R.: CAPRAM2.3: A Chemical Aqueous Phase Radical Mechanism for Tropospheric Chemistry, J. Atmos. Chem.36, 231–284, 2000.

Herrmann, H.: Kinetics of Aqueous Phase Reactions Relevant for Atmospheric Chemistry, Chem. Rev. 2003, 103, 4691-4716, doi: 10.1021/cr020658q, 2003.

Ip, H. S. S., Huang, X.H.H,. Yu J.Z.: Effective Henry's law constants of glyoxal, glyoxylic acid, and glycolic acid, Geophys. Res. Lett., 36, L01802, doi:10.1029/2008GL036212, 2009.

Kawamura, K., Ng, L.-L., Kaplan, I.R.: Determination of Organic Acids (Cl-Cl0) in the Atmosphere, Motor Exhausts and Engine Oils, Environ. Sci. Tech., 19, 1082–1086, 1985.

Kawamura, K. and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, Environ. Sci. Technol., 27, 2227 – 2235, 1993.

Kawamura,K., Kasukabe, H., and Barrie, L.A.: Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, Atmos. Environ., 30, 1709–1722, 1996.

Kawamura, K., Imai, Y., Barrie L.A.: Photochemical production and loss of organic acids in high Arctic aerosols during long-range transport and polar sunrise ozone depletion events, Atmos. Environ., 39, 599–614, 2005.

Kleefeld, S., Hofferb, A., Krivacsy, Z., Jennings, S. G.: Importance of organic and black carbon in atmospheric aerosols at Mace Head, on the West Coast of Ireland (53^{o}19’N, 9^{o}54’W), Atmos. Environ., 36, 4479–4490, 2002.

Legrand, M., Preunkert, S., Oliveira, T., Pio, C., Hammer, S., Gelencser, A., Kasper-Giebl, A., Laj, P.: Origin of C2-C5 dicarboxylic acids in the European atmosphere inferred from year-round aerosol study conducted at a west-east transect, J. Geophys. Res., doi:10.1029/ 2006JD008019, 2007.

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

Lewandowski, M., Jaoui, M., Kleindienst, T.E., Offenberg, J.H., Edney, E.O.: Composition of PM2.5 during the summer of 2003 in Research Triangle Park, North Carolina, Atmos. Environ. 41, 4073–4083, 2007.

Lim, H. J., Carlton, A. G., and Turpin, B. J.: Isoprene forms secondary organic aerosol through cloud processing: Model simulations, Environ. Sci. Technol., 39, 4441–4446, 2005.

Limbeck, A., Kraxner, Y., Puxbaum, H.: Gas to particle distribution of low molecular weight dicarboxylic acids at two different sites in central Europe (Austria), Aeros. Sci. 36, 991–1005, 2005.

Limbeck, A., Puxbaum, H.: Organic acids in continental background aerosols, Atmos. Environ. 33, 1847-1852, 1999.

Martinelango, P. K., Dasgupta, P.K., Al-Horr, R.S.: Atmospheric production of oxalic acid/oxalate and nitric acid/nitrate in the Tampa Bay airshed: Parallel pathways, Atmos. Environ. 41, 4258–4269, 2007.

Miyazaki, Y., Aggarwal, S. G., Singh, K., Gupta, P. K. and Kawamura, K: Dicarboxylic acids and water-soluble organic carbon in aerosols in New Delhi, India, in winter: Characteristics and formation processes, J. Geophys. Res., 114, D19206, doi:10.1029/2009JD011790, 2009.

Muller, K., van Pinxteren, D., Plewka, A., Svrcina, B., Kramberger, H., Hofmann, D., Bachmann, K., Herrmann, H.: Aerosol characterisation at the FEBUKO upwind station Goldlauter (II): Detailed organic chemical characterization, Atmos. Environ. 39, 4219–4231, 2005.

Myriokefalitakis, S., Vrekoussis, M., Tsigaridis, K., Wittrock, F., Richter, A., Brühl, C., Volkamer, R., Burrows, J. P., Kanakidou, M.: The influence of natural and anthropogenic secondary sources on the glyoxal global distribution, Atmos. Chem. Phys., 8, 4965–4981, 2008.

Noziere, B., Dziedzic, P., Cordova, A.:, Products and Kinetics of the Liquid-Phase Reaction of Glyoxal Catalyzed by Ammonium Ions (NH_4^+), J. Phys. Chem. A., 113, 231–237, doi: 10.1021/jp8078293, 2009.

Neususs, C., Gnauk, T., Plewka, A., Herrmann, H., and Quinn, P. K.: Carbonaceous aerosol over the Indian Ocean: OC/EC fractions and selected specifications from size segregated onboard samples, J. Geophys. Res., 107, 8031, doi:10.1029/2001JD000327, 2002.

Norton, R.B., Roberts, J.M., Huebert, B.J.: Tropospheric oxalate, Geophys. Res. Lett., 10, 517–520, doi:10.1029/GL010i007p00517, 1983.

Pavuluri, C.M., Kawamura, K. and Swaminathan, T.: Water-soluble organic carbon, dicarboxylic acids, ketoacids, and a-dicarbonyls in the tropical Indian aerosols, J, geophys. Res., 115, D11302, doi:10.1029/2009JD012661, 2010.

Plewka, A., Gnauk, T., Bruggemann, E., Herrmann, H.: Biogenic contributions to the chemical composition of airborne particles in a coniferous forest in Germany, Atmos. Environ., 40, 103–115, 2006.

Ruellan, S., Cachier, H., Gaudichet, A., Masclet, P., Lacaux, J.P.: Airborne aerosols over central Africa during the experiment for regional sources and sinks of oxidants (EXPRESSO), J. Geophys. Res., 104, 30 673–30 690, 1999.

Sander, R.: Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, available at http://www.mpch-mainz.mpg.de/~sander/res/ henry.html, 1999.

Saarnio, K., Aurela, M., Timonen, H., Saarikoski S., Teinilä, K., Mäkelä, T., Sofiev, M., Koskinen, J., Aalto, P.P., Kulmala, M., Kukkonen, J., Hillamo, R.: Chemical composition of fine particles in fresh smoke plumes from boreal wild-land fires in Europe, Sci. of the Tot. Environ., 408, 2527–2542, 2010.

Schwartz, S.E.: Mass-transport considerations pertinent to aqueous phase reactions of gases on liquid water clouds, in Chemistry of Multiphase Atmospheric Systems, NATO ASI Ser., edited by W. Jaeschke, Springer, Berlin, 1986.

Sempere, R., and Kawamura, K.: Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere, Atmos. Environ. 28, 449-459, 1994.

Seinfeld J. H. and Pandis S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, A Wiley-Interscience publication, USA, 1998.

Souza, S.R., Vasconcellos, P.C., Carvalho, L.R.F.: Low molecular weight carboxylic acids in an urban atmosphere: Winter measurements in Sao Paulo City, Brazil, Atmos. Environ., 33, 2563-2574, 1999.

Stone, E.A., Hedman, C.J., Zhou, J., Mieritz, M., Schauer, J.J.: Insights into the nature of secondary organic aerosol in Mexico City during the MILAGRO experiment 2006, Atmos. Environ., 44, 312-319, 2010.

Talbot, R.W. Andreae M.O., Andreae, T.W., Harriss, R.C.: Regional aerosol chemistry of the Amazon basin during the dry season, J. Geophys. Res., 93, 1499-1508, 1988.

Topping, D., Coe, H., McFiggans, G., Burgess, R., Allan, J., Alfarra, M.R., Bower, K., Choularton, T.W. Decesari, S., Facchini, M.C.: Aerosol chemical characteristics from sampling conducted on the Island of Jeju, Korea during ACE Asia, Atmos. Environ., 38 2111–2123, 2004.

Viana, M., Lopez, J.M., Querol, X., Alastuey, A., Garcia-Gaciob, A.D., Blanco-Heras, G., Lopez-Mahia, P., Pineiro-Iglesias, M., Sanz, M.J. Sanz, F., Chi, X., Maenhaut, W.: Tracers and impact of open burning of rice straw residues on PM in Eastern Spain, Atmos. Environ., 42 1941–1957, 2008.

Wang, G., Xie, M., Hu, S., Gao, S., Tachibana, E., and Kawamura, K.: Dicarboxylic acids, metals and isotopic compositions of C and N in atmospheric aerosols from inland China: implications for dust and coal burning emission and secondary aerosol formation, Atmos. Chem. Phys., 10, 6087–6096, 2010.