

Chapter 4

The potential flux of oxygenated volatile organic compounds from organic aerosol oxidation³

³ Adapted from Kwan, A. J., Crouse, J. D., Clarke, A. D., Shinozuka, Y., Anderson, B. E., Crawford, J. H., Avery, M. A., McNaughton, C. S., Brune, W. H., Singh, H. B., and Wennberg, P. O.: On the flux of oxygenated volatile organic compounds from organic aerosol oxidation, *Geophysical Research Letters*, 33, L15815, 10.1029/2006gl026144, 2006.

Abstract

Previous laboratory and field studies suggest that oxidation of organic aerosols can be a source of oxygenated volatile organic compounds (OVOC). Using measurements of atmospheric oxidants and aerosol size distributions performed on the NASA DC-8 during the INTEX-NA campaign, we estimate the potential magnitude of the continental summertime OVOC flux from organic aerosol oxidation by OH to be as large as 70 pptv C/day in the free troposphere. Contributions from O₃, H₂O₂, and photolysis may increase this estimate. These processes may provide a large, diffuse source of OVOC that has not been included in current atmospheric models, and thus have a significant impact on our understanding of organic aerosol, OVOC, PAN, and HO_x chemistry.

4.1 Introduction

Oxygenated volatile organic compounds (OVOC) comprise a large number of the species whose transport to the remote troposphere can impact radical budgets and sequester NO_x in the form of nitrates (Singh et al., 1995; Wennberg et al., 1998; Muller and Brasseur, 1999). In addition, they play a role in the formation of organic aerosols (OA) (Kanakidou et al., 2005, and references therein). Field campaigns have noted large concentrations of OVOC throughout the troposphere, but their budgets are poorly understood (Singh et al., 2001, 2004; Wisthaler et al., 2002).

Ellison et al. (1999) suggest that oxidation of OA may provide an OVOC source to the remote troposphere. Field campaigns have established the ubiquity of OA throughout the troposphere (Murphy et al., 1998; Kanakidou et al., 2005). Most aerosols

contain both organic and inorganic components, though significantly, the organic fraction tends to be found on aerosol surfaces (Tervahattu et al., 2002ab, 2005, and references therein).

Laboratory studies have demonstrated that organic surfaces can be oxidized by OH and O₃ (Rudich, 2003, and references therein; Thornberry and Abbatt, 2004; Molina et al., 2004). Several of these studies have shown volatilization of OVOC resulting from organic surface oxidation. Molina et al. (2004), for example, report the full volatilization of a C₁₈ alkane monolayer following heterogeneous loss of 2-3 OH radicals to the surface, with many (though not exclusively) OVOC products. Evidence for such chemistry in the ambient environment include the demonstration by Grannas et al. (2004) that photooxidation of snow phase organic matter may explain the daytime flux of lightweight OVOC from snowpack to the boundary layer, and field observations that atmospheric OA becomes more oxidized with greater ozone exposure and/or age (Gogou et al., 1996; de Gouw et al., 2005; Quinn et al., 2005; McFiggans et al., 2005).

Here, we use data collected on the NASA DC-8 during the INTEX-NA campaign over North America in the summer of 2004 to place constraints on OA oxidation's potential contribution to continental summertime OVOC budgets.

4.2 Method

Aerosol size distributions for particles 10 nm to 3 μm in diameter were measured on the DC-8 using a differential mobility analyzer (DMA) and an optical particle counter (OPC) (Clarke et al., 2004). Comparison of the DMA and OPC data to measurements of larger and ultrafine particles indicates that these instruments generally capture >90% of

the total aerosol surface area except in a few select plumes. The aerosol size is quantified in conditions that are often dryer than the ambient atmosphere, so the aerosols may lose water (and thus mass) prior to measurement. Correcting for this effect is non-trivial, particularly for submicron particles, so we neglect it in our calculations. We believe this may lead to an underestimate of the total ambient surface area of less than 30%. OH measurements were made by laser induced fluorescence (Faloona et al., 2004), ozone by chemiluminescence (Avery et al., 2006), and H₂O₂ by chemical ionization mass spectrometry (Crouse et al., 2006).

The collision rate of an oxidant with aerosol along the flight track was estimated using 1-minute averages of the aerosol surface area and oxidant mixing ratios:

$$\text{collisions} = \frac{1}{4} \times (8RT/\pi M)^{1/2} \times S \times [O_x] \times f(D)$$

where the factor of 1/4 converts aerosol surface area to cross sectional area, $(8RT/\pi M)^{1/2}$ is the thermal speed of the oxidant (R is the universal gas constant, T is temperature, M is the oxidant molar mass), S the aerosol surface area, [O_x] the concentration of oxidant (converted to a 24-hour average in the case of OH), and f(D) the correction applied due to gas-phase diffusion limitations to large particles (for OH only) (Fuchs and Sutugin, 1971).

For each point along the DC-8 flight track, we obtain a 24-hour average [OH] by scaling the observed [OH] by the ratio of the diurnally-averaged to instantaneous [OH] calculated from a highly constrained box model (NASA LaRC photochemical box model (Crawford et al., 1999)). Cloud effects on actinic flux, which affect [OH], are assumed to

be constant throughout the day, though they are generally transient. We expect that our large dataset sufficiently captures the variability of cloud effects such that they will not significantly bias our estimate.

Following the studies of Bertram et al. (2001) and Molina et al. (2004) we assume that each OH collision is reactive ($\gamma=1$) and volatilizes 6 organic carbons. Although the alkane used in the Molina et al. (2004) study is not representative of all OA surfaces, long chain fatty acids may comprise a significant fraction (Tervahattu et al., 2002ab, 2005). These parameters represent by far the largest uncertainties in our analysis. Because our assumptions imply a unity accommodation coefficient ($\alpha=1$), we account for diffusion limitations in calculating the OH collision rate.

Estimating the OVOC flux from aerosol collisions with O_3 and H_2O_2 is significantly more difficult. While OH is highly reactive with many classes of organic compounds, O_3 reactivity and product yield are very substrate dependent (Rudich, 2003; Thornberry and Abbatt, 2004). Also, unlike for OH (Molina et al., 2004), O_3 reactivity with solid organic surfaces may depend on relative humidity (Poschl et al., 2001). For H_2O_2 , we found no experimental studies allowing us to constrain γ or the product yield. For these oxidants, though, estimating the collision rate with aerosols is a first step for assessing their potential contributions to OVOC flux. We expect that the accommodation coefficients for these two oxidants are significantly less than unity – Berkowitz et al. (2001), for example, estimate $\alpha_{O_3} \sim 10^{-3}$ – and thus do not consider diffusion limitations for their collision rates.

4.3 Results and Discussion

Calculated 24-hour average collision rates are plotted as a function of elevation in Figure 4.1. For OH (Figure 4.1a) and O₃ (Figure 4.1b), most of the variability is driven by the (dry) aerosol surface area, whose elevation bin means range from ~10 μm²/cc in the upper troposphere to ~150 μm²/cc in the lowest elevation bin. For OH, we estimate the upper tropospheric collision rate to be ~1x10³ collisions/cc/sec. Our assumption of carbon volatilization from Molina et al. (2004) thus yields an estimated OVOC source of ~70 pptv C/day in the upper troposphere. A significantly larger source would exist in the lower troposphere (~500 pptv C/day in the lowest 2 km), but the contribution of this mechanism to OVOC concentrations will be less significant because of the much larger OVOC sources from gas phase oxidation of larger hydrocarbons in this region.

Assuming a product yield for O₃ similar to that of OH, the ratio of OH to O₃ collisions gives a value of $\gamma_{O_3} \sim 10^{-6}$ necessary for the OVOC flux from O₃ to equal that from OH. Achieving this value would require only ~0.1% surface coverage by typical alkene liquids ($\gamma \sim 10^{-3}$) (de Gouw and Lovejoy, 1998; Rudich, 2003). Thus, it is plausible that for certain aerosols reaction with O₃ can be a significant oxidation mechanism. This is particularly true in the lower troposphere, where most primary (i.e., more unsaturated) OA is expected to reside. For H₂O₂ (Figure 1c), the equivalent $\gamma_{H_2O_2}$ ranges from ~10⁻⁵ in the lower troposphere to ~10⁻² in the upper troposphere, so H₂O₂'s contribution to OVOC flux is likely confined to the lower troposphere or in cloud. Because of clouds' high aerosol surface area, increased actinic flux, and potential for aqueous phase chemistry, aerosol oxidation in clouds may warrant particular attention.

Photolysis can, in principle, also lead to the decomposition of OA (Kieber et al., 1990). To be competitive with the OH chemistry, however, photolysis rates would have

to be relatively fast ($J \sim 10^{-6}$), as it is likely less efficient at degrading organic molecules in the condensed phase than in the gas phase: caging effects can stabilize the intermediates and aid their recombination or polymerization so that they remain in the bulk phase.

4.4 Implications

A dispersed and previously unconsidered source of OVOC from aerosol oxidation may have important implications for tropospheric photochemistry. For example, measurements of acetaldehyde (CH_3CHO) have routinely exceeded model predictions (Singh et al., 2001, 2004; Wisthaler et al., 2002); this was also true during INTEX-NA (Figure 4.2a). For each acetaldehyde measurement, we divide the difference between measured and box model-predicted mixing ratios by the photochemical lifetime to estimate the flux necessary to reconcile the difference. We find that a source of ~ 90 pptv/day (~ 180 pptv C/day) is required to sustain the observed acetaldehyde concentrations in the upper troposphere. INTEX-NA also marked the first extensive airborne measurements of peroxyacetic acid ($\text{CH}_3\text{C}(\text{O})\text{OOH}$, PAA), which significantly exceeded model-predicted values in the upper troposphere as well (Figure 4.2b); a similar analysis for PAA yields an estimated missing source of ~ 20 -200 pptv C/day (Crouse et al., in preparation). Even considering only acetaldehyde, oxidation by OH alone is likely too small to explain the upper tropospheric discrepancies between OVOC measurements and models; other oxidation mechanisms or alternative explanations should be explored.

A significant flux of OVOC from aerosol would have consequent impacts on HO_x and peroxyacyl nitrates. In fact, if the observations and our understanding of the subsequent chemistry of acetaldehyde are correct, peroxyacetyl nitrate (PAN) formation

is very fast in the upper troposphere. Observations of PAN are not, however, consistent with those of acetaldehyde, based on current understanding of the chemistry that links these compounds (Staudt et al., 2003).

A large OVOC flux from aerosol is also incompatible with current OA budgets. The IPCC (2001) estimate of OA flux is ~ 150 Tg “organic matter”/year, or ~ 100 Tg C/year. If our estimated OA oxidation rate from OH were representative of the entire atmosphere, the global flux of organic carbon from aerosol would be as large as ~ 150 Tg C/yr (integrating with bin median collision rates, ~ 100 TgC/yr; interquartile range, ~ 50 – 200 Tg C/yr). This is clearly an upper limit due to the assumptions of unity γ and that the continental summertime conditions of INTEX-NA are representative. Nonetheless, even a fraction of this large flux would imply that oxidation may need to be included in models, which currently consider only wet depositional loss. From our carbon flux (and assuming an aerosol density of 1 g/cc and an organic carbon fraction of 0.5), we estimate the median lifetime of aerosol organic carbon to be ~ 10 days; thus, oxidation may be an important sink, particularly in the upper troposphere and regions with minimal precipitation.

Consideration of an additional significant sink would dramatically increase top-down estimates of OA flux based on aerosol measurements and inferences about loss processes. Bottom-up estimates, deduced from emission inventories and secondary organic aerosol (SOA) yields for precursor gases, may also be too low: Holzinger et al. (2005), for example, demonstrate that many biogenic SOA precursors are too short-lived to have been previously measured, and thus have been omitted from emission inventories. Furthermore, because of the diversity of SOA precursor gases, the photochemistry and

SOA yield of only a few model compounds have been extensively studied. Even for relatively well studied compounds, such as isoprene, estimates of SOA yields are undergoing significant revision upwards (Limbeck et al, 2003; Claeys et al., 2004ab; Kanakidou et al., 2005; Kroll et al., 2005). In addition, our understanding of other aspects of OA chemistry is poor. For example, Heald et al. (2005), considering only wet depositional loss, underpredict OA mass in the free troposphere 1-2 orders of magnitude, which they cannot attribute merely to OA flux underestimates.

4.5 Conclusions and recommendations

Our estimate of the OVOC source and its atmospheric impact are highly uncertain due to the complexity of the processes involved and the paucity of laboratory and field data for quantifying key parameters. Continued identification of OA constituents and study of oxidant interactions with a wider range of substrates is necessary to better constrain OVOC flux from atmospheric aerosols. Of particular concern is that much of the OA in the atmosphere may actually consist of highly oxidized humic like substances (HULIS) (Limbeck et al., 2003; Claeys et al., 2004a); whether HULIS can be volatilized in a similar fashion as the aliphatic compounds studied in the laboratory must be investigated. De Gouw and Lovejoy (1998) find that ozone reacts with liquid aldehydes and ketones ($\gamma \sim 10^{-4}$), but do not determine if any gas phase products form. An additional difficulty in applying laboratory studies is that they have utilized reaction parameters, such as low pressures and $[O_2]$, and high $[O_3]$ and $[OH]$, that are not representative of the real atmosphere. Moise and Rudich (2000) find, for example, that γ_{O_3} drops when O_2 instead of He is used as a carrier gas in their

experiments; also, Molina et al. (2004) propose that the carbon volatilization in their experiments would be reduced at atmospheric $[O_2]$. Laboratory studies on OA particles, rather than surface coatings on glassware, show that γ_{O_3} is also a function of aerosol size due to diffusion limitations in the bulk (Smith et al., 2002; Morris et al., 2002), which should be further investigated. Other oxidants, such as NO_3 , may also play an important role in aerosol oxidation. Finally, our analysis assumes that all aerosols are completely covered with organic films; accurate parameterizations of surface coverage are impossible without more field studies of aerosol surface coatings.

Acknowledgments

We thank Jonathan Abbatt (U. Toronto) for reviewing a draft of this manuscript, Steven Howell (U. Hawaii) for helpful discussions, Clyde Brown (NASA LaRC) for preparing merged data files, and the NASA Tropospheric Chemistry Program office for support of the INTEX-NA campaign. This material is based upon work supported under an NSF Graduate Research Fellowship (AJK) and EPA STAR Fellowship (JDC).

References

- Ammann, M., Poschl, U., and Rudich, Y.: Effects of reversible adsorption and Langmuir-Hinshelwood surface reactions on gas uptake by atmospheric particles, *Physical Chemistry Chemical Physics*, 5, 351-356, 10.1039/b208708a, 2003.
- Berkowitz, C. M., Zaveri, R. A., Bian, X. D., Zhong, S. Y., Disselkamp, R. S., Laulainen, N. S., and Chapman, E. G.: Aircraft observations of aerosols, O_3 and NO_y in a nighttime urban plume, *Atmospheric Environment*, 35, 2395-2404, 2001.

Bertram, A. K., Ivanov, A. V., Hunter, M., Molina, L. T., and Molina, M. J.: The reaction probability of OH on organic surfaces of tropospheric interest, *Journal of Physical Chemistry A*, 105, 9415-9421, 10.1021/jp0114034, 2001.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, *Science*, 303, 1173-1176, 2004a.

Claeys, M., Wang, W., Ion, A. C., Kourtchev, I., Gelencser, A., and Maenhaut, W.: Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, *Atmospheric Environment*, 38, 4093-4098, 10.1016/j.atmosenv.2004.06.001, 2004b.

Clarke, A. D., Shinozuka, Y., Kapustin, V. N., Howell, S., Huebert, B., Doherty, S., Anderson, T., Covert, D., Anderson, J., Hua, X., Moore, K. G., McNaughton, C., Carmichael, G., and Weber, R.: Size distributions and mixtures of dust and black carbon aerosol in Asian outflow: Physiochemistry and optical properties, *Journal of Geophysical Research-Atmospheres*, 109, D15s09, 10.1029/2003jd004378, 2004.

Crawford, J., Davis, D., Olson, J., Chen, G., Liu, S., Gregory, G., Barrick, J., Sachse, G., Sandholm, S., Heikes, B., Singh, H., and Blake, D.: Assessment of upper tropospheric HOx sources over the tropical Pacific based on NASA GTE/PEM data: Net effect on HOx and other photochemical parameters, *Journal of Geophysical Research-Atmospheres*, 104, 16255-16273, 1999.

de Gouw, J. A., and Lovejoy, E. R.: Reactive uptake of ozone by liquid organic compounds, *Geophysical Research Letters*, 25, 931-934, 1998.

de Gouw, J. A., Middlebrook, A. M., Warneke, C., Goldan, P. D., Kuster, W. C., Roberts, J. M., Fehsenfeld, F. C., Worsnop, D. R., Canagaratna, M. R., Pszenny, A. A. P., Keene, W. C., Marchewka, M., Bertman, S. B., and Bates, T. S.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *Journal of Geophysical Research-Atmospheres*, 110, D16305, 10.1029/2004jd005623, 2005.

Ellison, G. B., Tuck, A. F., and Vaida, V.: Atmospheric processing of organic aerosols, *Journal of Geophysical Research-Atmospheres*, 104, 11633-11641, 1999.

Faloona, I. C., Tan, D., Leshner, R. L., Hazen, N. L., Frame, C. L., Simpas, J. B., Harder, H., Martinez, M., Di Carlo, P., Ren, X. R., and Brune, W. H.: A laser-induced fluorescence instrument for detecting tropospheric OH and HO₂: Characteristics and calibration, *Journal of Atmospheric Chemistry*, 47, 139-167, 2004.

Fuchs, N. A., and Sutugin, A. G.: Highly-dispersed aerosols, in: *Topics in Current Aerosol Research, Part 2*, edited by: Hidy, G. M., and Block, J. R., Elsevier, New York, 1971.

Gogou, A., Stephanou, E. G., Stratigakis, N., Grimalt, J. O., Simo, R., Aceves, M., and Albaiges, J.: Differences in lipid and organic salt constituents of aerosols from eastern

and western Mediterranean coastal cities, *Atmospheric Environment*, 28, 1301-1310, 1994.

Grannas, A. M., Shepson, P. B., and Filley, T. R.: Photochemistry and nature of organic matter in Arctic and Antarctic snow, *Global Biogeochemical Cycles*, 18, Gb1006, 10.1029/2003gb002133, 2004.

Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H., and Weber, R. J.: A large organic aerosol source in the free troposphere missing from current models, *Geophysical Research Letters*, 32, L18809, 10.1029/2005gl023831, 2005.

Holzinger, R., Lee, A., Paw, K. T., and Goldstein, A. H.: Observations of oxidation products above a forest imply biogenic emissions of very reactive compounds, *Atmospheric Chemistry and Physics*, 5, 67-75, 2005.

I.P.C.C.: *Climate Change 2001: The Scientific Basis -- Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, New York, 2001.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L.,

Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmospheric Chemistry and Physics*, 5, 1053-1123, 2005.

Kieber, R. J., Zhou, X., and Mopper, M.: Formation of carbonyl compounds from UV-induced photodegradation of humic substances in natural waters: Fate of riverine carbon in the sea, *Limnology Oceanography*, 35, 1503-1515, 1990.

Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation under high-NO_x conditions, *Geophysical Research Letters*, 32, L18808, 10.1029/2005gl023637, 2005.

Limbeck, A., Kulmala, M., and Puxbaum, H.: Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles, *Geophysical Research Letters*, 30, 1996, 10.1029/2003gl017738, 2003.

McFiggans, G., Alfarra, M. R., Allan, J., Bower, K., Coe, H., Cubison, M., Topping, D., Williams, P., Decesari, S., Facchini, C., and Fuzzi, S.: Simplification of the representation of the organic component of atmospheric particulates, *Faraday Discussions*, 130, 341-362, 10.1039/b419435g, 2005.

Moise, T., and Rudich, Y.: Reactive uptake of ozone by proxies for organic aerosols: Surface versus bulk processes, *Journal of Geophysical Research-Atmospheres*, 105, 14667-14676, 2000.

Molina, M. J., Ivanov, A. V., Trakhtenberg, S., and Molina, L. T.: Atmospheric evolution of organic aerosol, *Geophysical Research Letters*, 31, L22104, 10.1029/2004gl020910, 2004.

Muller, J. F., and Brasseur, G.: Sources of upper tropospheric HOx: A three-dimensional study, *Journal of Geophysical Research-Atmospheres*, 104, 1705-1715, 1999.

Murphy, D. M., Thomson, D. S., and Mahoney, T. M. J.: In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers, *Science*, 282, 1664-1669, 1998.

Poschl, U., Letzel, T., Schauer, C., and Niessner, R.: Interaction of ozone and water vapor with spark discharge soot aerosol particles coated with benzo a pyrene: O₃ and H₂O adsorption, benzo a pyrene degradation, and atmospheric implications, *Journal of Physical Chemistry A*, 105, 4029-4041, 2001.

Quinn, P. K., Bates, T. S., Baynard, T., Clarke, A. D., Onasch, T. B., Wang, W., Rood, M. J., Andrews, E., Allan, J., Carrico, C. M., Coffman, D., and Worsnop, D.: Impact of particulate organic matter on the relative humidity dependence of light scattering: A simplified parameterization, *Geophysical Research Letters*, 32, L22809, 10.1029/2005gl024322, 2005.

Rudich, Y.: Laboratory perspectives on the chemical transformations of organic matter in atmospheric particles, *Chemical Reviews*, 103, 5097-5124, 10.1021/cr020508f, 2003.

Singh, H., Chen, Y., Staudt, A., Jacob, D., Blake, D., Heikes, B., and Snow, J.: Evidence from the Pacific troposphere for large global sources of oxygenated organic compounds, *Nature*, 410, 1078-1081, 2001.

Singh, H. B., Kanakidou, M., Crutzen, P. J., and Jacob, D. J.: High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere, *Nature*, 378, 50-54, 1995.

Singh, H. B., Salas, L. J., Chatfield, R. B., Czech, E., Fried, A., Walega, J., Evans, M. J., Field, B. D., Jacob, D. J., Blake, D., Heikes, B., Talbot, R., Sachse, G., Crawford, J. H., Avery, M. A., Sandholm, S., and Fuelberg, H.: Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P, *Journal of Geophysical Research-Atmospheres*, 109, D15s07, 10.1029/2003jd003883, 2004.

Staudt, A. C., Jacob, D. J., Ravetta, F., Logan, J. A., Bachiochi, D., Krishnamurti, T. N., Sandholm, S., Ridley, B., Singh, H. B., and Talbot, B.: Sources and chemistry of nitrogen oxides over the tropical Pacific, *Journal of Geophysical Research-Atmospheres*, 108, 8239, 10.1029/2002jd002139, 2003.

Tervahattu, H., Hartonen, K., Kerminen, V. M., Kupiainen, K., Aarnio, P., Koskentalo, T., Tuck, A. F., and Vaida, V.: New evidence of an organic layer on marine aerosols, *Journal of Geophysical Research-Atmospheres*, 107, 4053, 10.1029/2000jd000282, 2002a.

Tervahattu, H., Juhanaja, J., and Kupiainen, K.: Identification of an organic coating on marine aerosol particles by TOF-SIMS, *Journal of Geophysical Research-Atmospheres*, 107, 4319, 10.1029/2001jd001403, 2002b.

Tervahattu, H., Juhanaja, J., Vaida, V., Tuck, A. F., Niemi, J. V., Kupiainen, K., Kulmala, M., and Vehkamäki, H.: Fatty acids on continental sulfate aerosol particles, *Journal of Geophysical Research-Atmospheres*, 110, D06207, 10.1029/2004jd005400, 2005.

Thornberry, T., and Abbatt, J. P. D.: Heterogeneous reaction of ozone with liquid unsaturated fatty acids: detailed kinetics and gas-phase product studies, *Physical Chemistry Chemical Physics*, 6, 84-93, 10.1039/b310149e, 2004.

Wennberg, P. O., Hanisco, T. F., Jaegle, L., Jacob, D. J., Hintsala, E. J., Lanzendorf, E. J., Anderson, J. G., Gao, R. S., Keim, E. R., Donnelly, S. G., Del Negro, L. A., Fahey, D. W., McKeen, S. A., Salawitch, R. J., Webster, C. R., May, R. D., Herman, R. L., Proffitt, M. H., Margitan, J. J., Atlas, E. L., Schauffler, S. M., Flocke, F., McElroy, C. T., and Bui, T. P.: Hydrogen radicals, nitrogen radicals, and the production of O₃ in the upper troposphere, *Science*, 279, 49-53, 1998.

Wisthaler, A., Hansel, A., Dickerson, R. R., and Crutzen, P. J.: Organic trace gas measurements by PTR-MS during INDOEX 1999, *Journal of Geophysical Research-Atmospheres*, 107, 8024, 10.1029/2001jd000576, 2002.

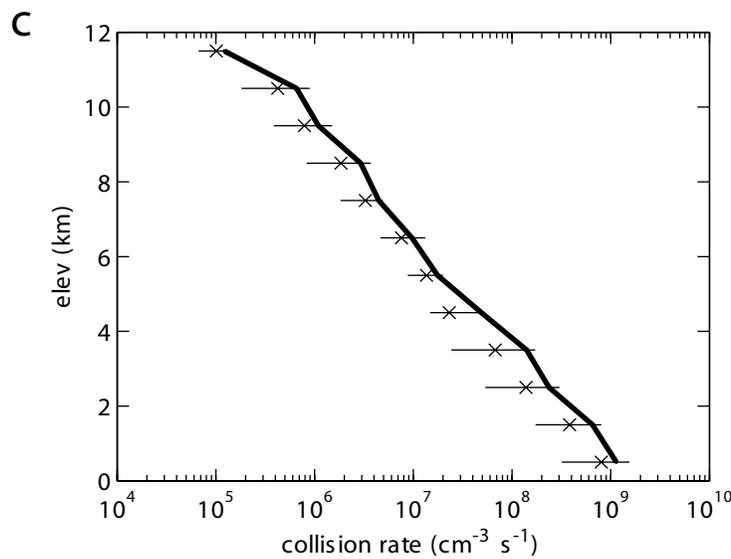
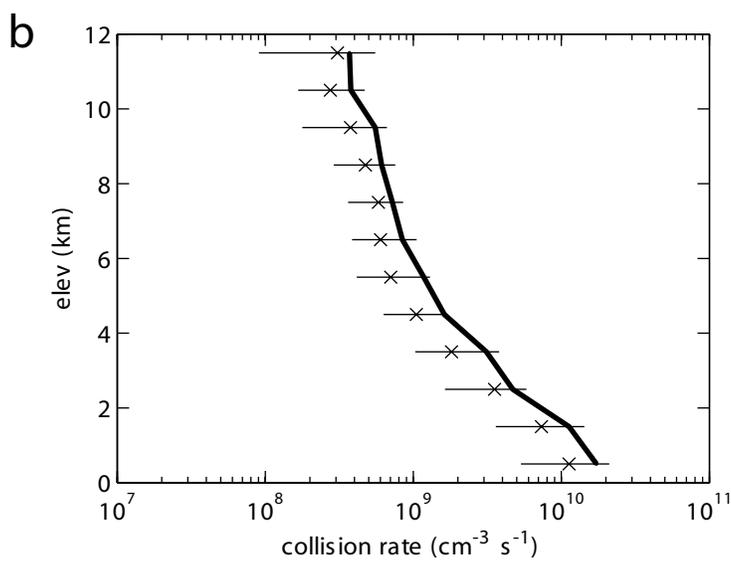
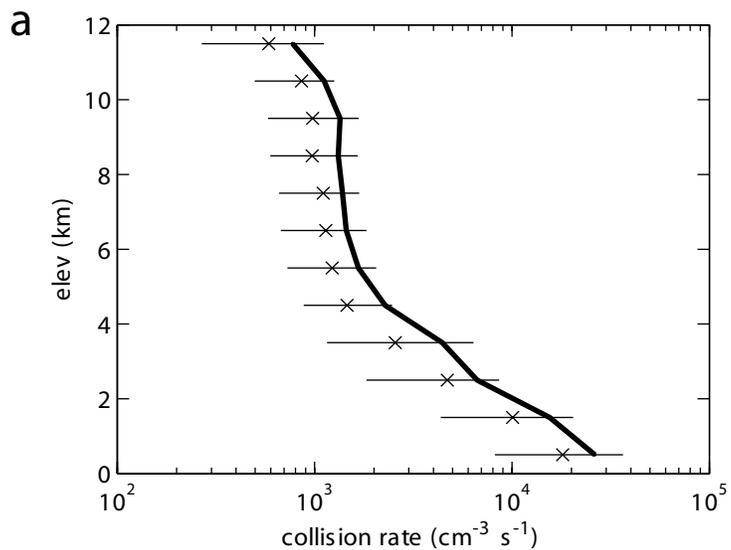


Figure 4.1. Mean elevation profiles of aerosol collision rates with a) OH, b) O₃, and c) H₂O₂. Horizontal lines show the interquartile range and x's are the elevation bin median.

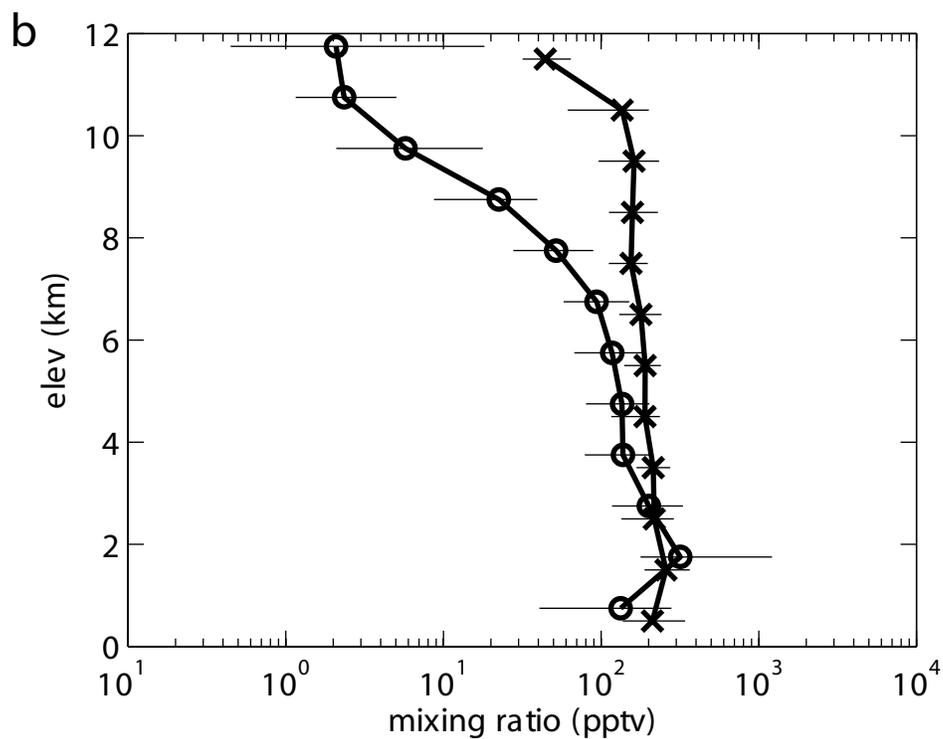
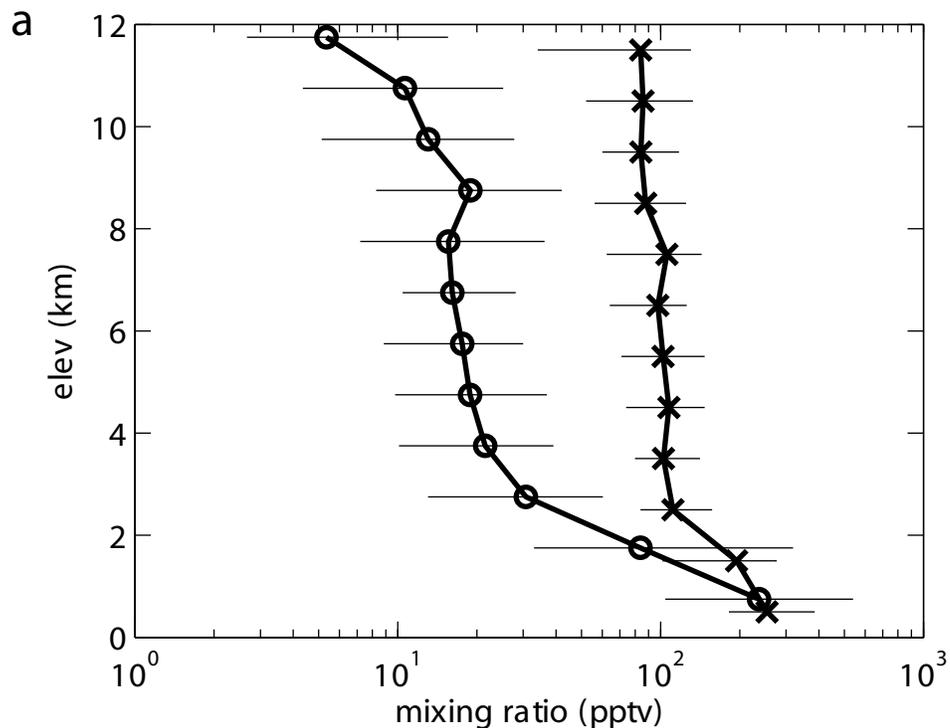


Figure 2. Modeled (circle) vs. measured (x) elevation profiles for acetaldehyde (a) and peroxyacetic acid (b). Marks are bin medians, lines are interquartile range. Model predictions offset by .25 km for clarity. Model assumes a PAA lifetime of ~ 20 days (upper limit).