Manuscript prepared for Atmos. Chem. Phys.
with version 2014/09/16 7.15 Copernicus papers of the LaTeX class copernicus.cls.
Date: 27 July 2015

Proposed additions to Organic Nitrate Aerosol Formation via NO_3 + BVOC in the Southeastern United States

Benjamin R. Ayres[1], Hannah M. Allen[1,2], Danielle C. Draper[1,3], Steven S. Brown[4], Robert J. Wild[4], Jose L. Jimenez[5,6], Douglas A. Day[5,6], Pedro Campuzano-Jost[5,6], Weiwei Hu[5,6], Joost de Gouw[5,6], Abigail Koss[5,6], Ronald C. Cohen[7], Kaitlin C. Duffey[7], Paul Romer[7], Karsten Baumann[8], Eric Edgerton[8], Satoshi Takahama[9], Joel A. Thornton[10], Ben H. Lee[10], Felipe D. Lopez-Hilfiker[10], Claudia Mohr[10,11], Paul O. Wennberg[12], Tran B. Nguyen[12], Alex Teng[12], Allen H. Goldstein[13], Kevin Olson[13], and Juliane L. Fry[1]

[1]Department of Chemistry, Reed College, Portland, OR, USA
[2]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA
[3]Department of Chemistry, University of California, Irvine, CA, USA
[4]Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO, USA
[5]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, USA
[6]Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA
[7]Department of Chemistry, University of California at Berkeley, CA, USA
[8]Applied Research Associates, Inc., Research Triangle Park, N.C., USA
[9]Department of Environmental Engineering, École polytechnique fédérale de Lausanne (EPFL), Switzerland
[10]Department of Atmospheric Sciences, University of Washington, Seattle, WA, USA
[11]Karlsruhe Institute of Technology, Karlsruhe, Germany
[12]Division of Geological and Planetary Sciences and Environmental Science and Engineering Program, California Institute of Technology, Pasadena, CA, USA
[13]Department of Environmental Science, Policy, and Management, University of California, Berkeley, CA, USA

Correspondence to: J. L. Fry (fry@reed.edu)

Abstract. Since submitting the paper, we have become aware of another dataset that can provide valuable additional correlations to assess NO_3 + BVOC chemistry. This document shows updated figures (which would replace existing figures 7 and 8, adding new panels) and edited sections of the paper discussing these new correlations of CIMS-measured organonitrate concentrations with calculated NO_3 loss to monoterpenes and isoprene. We have also added a brief discussion to section 3.1.1. about the effect of normalization by CO to account for changing nocturnal boundary layer height, as suggested. There is no improvement in scatter, suggesting that this is not a substantial source of error in this analysis. Only those sections that would be changed are included below.

We post this text now as a comment on our own manuscript so that our reviewers might have a chance to offer any additional comments on this, if desired. Since both reviews have now been posted, we apologize that it was not in time to be included in those original reviews, but we would be grateful of any additional comments. We note that we have also revised how we analyze the relative correlations, a change which will be reflected throughout our reviewer responses, which we will post separately addressing all reviewer comments after the discussion has closed. Thank you very much!

1 Introduction

2 Experimental

Two chemical ionization mass spectrometers (Caltech's cTOF-CIMS and University of Washington's HR-ToF-CIMS, hereafter both referred to as CIMS, Bertram et al., 2011; Yatavelli et al., 2012; Lee et al., 2014) were used to identify specific organic nitrate product ions, specifically monoterpene (Eddingsaas et al., 2012) and isoprene products (Crounse et al., 2013, 2006; Beaver et al., 2012). One CIMS measured only gas phase products (California Institute of Technology, CIT, Beaver et al., 2012) while the other CIMS employed a Filter Inlet for Gas and Aerosol (FIGAERO) to separate aerosol and gas species (University of Washington, UW, Lopez-Hilfiker et al., 2014; Lee et al., 2014). Both used time-of-flight mass spectrometers capable of resolving ions with different elemental formulae at common nominal m/z.

3 Results

3.1 Organic $\mathrm{NO_x}$ sink: $\mathrm{NO_3}$ + BVOC production of organic nitrate SOA

3.1.1 Calculation of $\mathrm{NO_3}$ loss to BVOC

Using literature $\mathrm{NO_3}$ + BVOC rate coefficients and calculated $\mathrm{NO_{3,SS}}$, we can calculate instantaneous $\mathrm{NO_3}$ loss rates ($(\mathrm{NO_{3,loss}})_{\mathrm{inst}}$) for the campaign (1). BVOC mixing ratios from GC-MS and rate constants shown in Table 1 were used to calculate the time-integrated nitrate loss to reactions with BVOC (2). Specifically, time loss of $\mathrm{NO_3}$ radical to reaction with BVOC ($(\mathrm{NO_{3,loss}})_{\mathrm{integ}}$, defined below in Eq. 2) were calculated during periods of increasing $\mathrm{RONO_2}$ concentrations as monitored by CIMS or aerosol-phase $\mathrm{RONO_2}$ monitored by AMS or TD-LIF during SOAS. This buildup of aerosol $\mathrm{RONO_2}$ was only observed after sunset. The boundary layer during night hours is relatively stable, such that $\mathrm{NO_x}$ and BVOC measurements can be considered an area-wide average and this simple box model can be used to calculate $(\mathrm{NO_{3,loss}})_{\mathrm{integ}}$ (1, 2). Under the assumption of a constant nighttime boundary layer height and an approximately uniform, area wide source that limits the time rate of change due to horizontal advection (i.e., a nighttime box), the time integrals of $\mathrm{RONO_2}$ produced provide estimates of the evolution of $\mathrm{RONO_2}$ concentrations at night. This assumption was tested using CO to minimize first order effects of dilution (Blanchard et al., 2011). By dividing organic nitrate concentrations from AMS by CO concentrations in the correlation analysis reported below, we saw little change, suggesting that variability in nighttime boundary layer is not a substantial source of error in this analysis. Time periods of CIMS $\mathrm{RONO_2}$ or aerosol buildup were used to determine time intervals for calculation of $(\mathrm{NO_{3,loss}})_{\mathrm{integ}}$.

$$(\mathrm{NO_{3,loss}})_{\mathrm{inst}} = \sum_{\mathrm{i}} k_{\mathrm{NO_3+VOC_i}}[\mathrm{VOC}]_{\mathrm{i}}[\mathrm{NO_3}]_{\mathrm{SS}} \qquad (1)$$

$$(\mathrm{NO}_{3,\mathrm{loss}})_{\mathrm{integ}} = \sum_{i,t} (\mathrm{NO}_{3,\mathrm{loss}})_{\mathrm{inst,i}} \times \Delta t \qquad (2)$$

3.1.2 Organic Nitrate Product Analysis

Specific first generation monoterpene organic nitrate compounds have been identified and measured in the gas and aerosol phases by CIMS (Lopez-Hilfiker et al., 2014; Lee et al., 2015; Beaver et al., 2012). Using the $(\mathrm{NO}_{3,\mathrm{loss}})_{\mathrm{integ}}$ calculations, a similar correlation analysis is conducted to identify key gas- and aerosol-phase products of NO_3 oxidation. Observed buildups in gas- and aerosol-phase organic nitrate concentrations from each CIMS are scattered against predicted $(\mathrm{NO}_{3,\mathrm{loss}})_{\mathrm{integ}}$ to monoterpenes (Figure 1). The generally good correlations suggest that all of the molecular formulae shown here have contributions from NO_3 chemistry. Comparisons of observed R^2 values and slopes for each of these correlation plots may then provide some mechanistic insight. For example, the species with larger R^2s ($\mathrm{C}_{10}\mathrm{H}_{17}\mathrm{NO}_5$) may indicate a greater contribution to these species from nitrate radical chemistry. In the cases where the same species is observed in gas and particle phase (Figure 1a/b and d/e), if we assume the same sensitivity across phases, we can estimate the relative amount in each phase by the ratio of the slopes. This would suggest that $\mathrm{C}_{10}\mathrm{H}_{15}\mathrm{NO}_5$ partitions more preferentially to the particle phase, while $\mathrm{C}_{10}\mathrm{H}_{17}\mathrm{NO}_5$ partitions preferentially to the gas phase.

Although the gas-phase monoterpene nitrate product correlations display substantial scatter, likely due to their multiple possible sources and rapid partitioning to the aerosol phase, we can use the calibrated mixing ratios measured by the CIT CIMS to calculate approximate lower limit molar yields for $\mathrm{C}_{10}\mathrm{H}_{15}\mathrm{NO}_5$ (0.4%), $\mathrm{C}_{10}\mathrm{H}_{17}\mathrm{NO}_5$ (3%), and $\mathrm{C}_{10}\mathrm{H}_{17}\mathrm{NO}_5$ (3%) from NO_3, based on the slope of correlations shown in panels c, f and h. We estimate these to be lower limits, because no losses of these species during the period of buildup is taken into account in this correlation analysis.

About 12% of total particle-phase organic nitrates observed with the UW CIMS (Lee et al., 2015) were C_5 molecules, likely isoprene oxidation products, suggesting that most isoprene nitrate products remain in the gas phase. The correlation of gas-phase isoprene nitrate concentrations with NO_3 loss again gives hints to the oxidative sources of these molecules (Figure 2). $\mathrm{C}_5\mathrm{H}_9\mathrm{NO}_5$ (panels a and b) shows the strongest correlation with $(\mathrm{NO}_{3,\mathrm{loss}})_{\mathrm{integ}}$ to isoprene among all the individual molecules (R^2 = 0.54 for UW and 0.70 for CIT), suggesting that this compound is a NO_3 oxidized product. The better correlation than observed in Figure 1 may be due to the fact that this organonitrate has slower gas-phase losses relative to the semi-volatile C_{10} species. Using the calibrated mixing ratios from CIT for $\mathrm{C}_5\mathrm{H}_9\mathrm{NO}_5$, we calculate an approximate lower limit molar yield of 7%. The $\mathrm{C}_5\mathrm{H}_9\mathrm{NO}_4$ and $\mathrm{C}_4\mathrm{H}_7\mathrm{NO}_5$ isoprene products (panels c and d) show poorer correlation with $(\mathrm{NO}_{3,\mathrm{loss}})_{\mathrm{integ}}$ to isoprene (R^2=0.11 and 0.35, respectively), suggesting that $\mathrm{C}_5\mathrm{H}_9\mathrm{NO}_4$ is not (exclusively) a NO_3 + isoprene product, and may instead be a photochemically or ozonolysis produced organonitrate, via $RO_2 + NO$.

We note that the two CIMS for which data is shown in Figures 1 and 2 were located at different heights: the CIT CIMS was atop the 20 meter tower, collocated with the measurements used to determine $[NO_3]_{ss}$, while the UW CIMS measured at ground level. Particularly at nighttime, it is possible that this lower 20 meters of the nocturnal surface layer can become stratified, so some scatter and differences in correlations between instruments arising from this occasional stratification are not unexpected. For this reason, we employ all available data from both instruments to minimize any error this might introduce.

3.2 Comparison to Inorganic NO_x sink: NO_3^- aerosol production from heterogeneous uptake of HNO_3

3.3 Implications of NO_3 oxidation on SOA formation in the Southeastern United States

4 Conclusions

The contribution of NO_3 + BVOC to SOA formation is found to be substantial in the terpene-rich southeastern United States. An estimated 23-44% of nitrate radical lost to reaction with monoterpenes becomes aerosol-phase organic nitrate. A predicted nitrate loss to terpenes is calculated from the steady-state nitrate and terpene mixing ratios and then time integrated during evenings and nights as $RONO_2$ aerosol builds up. Nitrate losses are correlated to CIMS, TD-LIF and AMS measurements of gas- and aerosol-phase organic nitrate and show good agreement between $(NO_{3,\mathrm{loss}})_{\mathrm{integ}}$ to monoterpene and total aerosol organic nitrate maxima. Two specific C_{10} structures measured by CIMS are shown to be NO_3 radical products by their good correlation with cumulative $(NO_{3,\mathrm{loss}})_{\mathrm{integ}}$; their semi-volatile nature leads to their variable partitioning between gas and aerosol phase. Calibrated gas phase mixing ratios of selected organonitrates allow estimation of lower limit molar yields of $C_5H_9NO_5$, $C_{10}H_{17}NO_4$, $C_{10}H_{17}NO_5$ from NO_3 reactions (7%, 3%, and 3% respectively). The fact that these molar yields of monoterpene nitrates are substantially lower that the aggregated aerosol-phase organic nitrate yield may suggest that further chemical evolution is responsible for the large SOA yields from these reactions, consistent with Lee et al., 2015. The NO_3 + BVOC source of nitrate aerosol is comparable in magnitude to inorganic nitrate aerosol formation, and is observed to be a substantial contribution to regional $PM_{2.5}$.

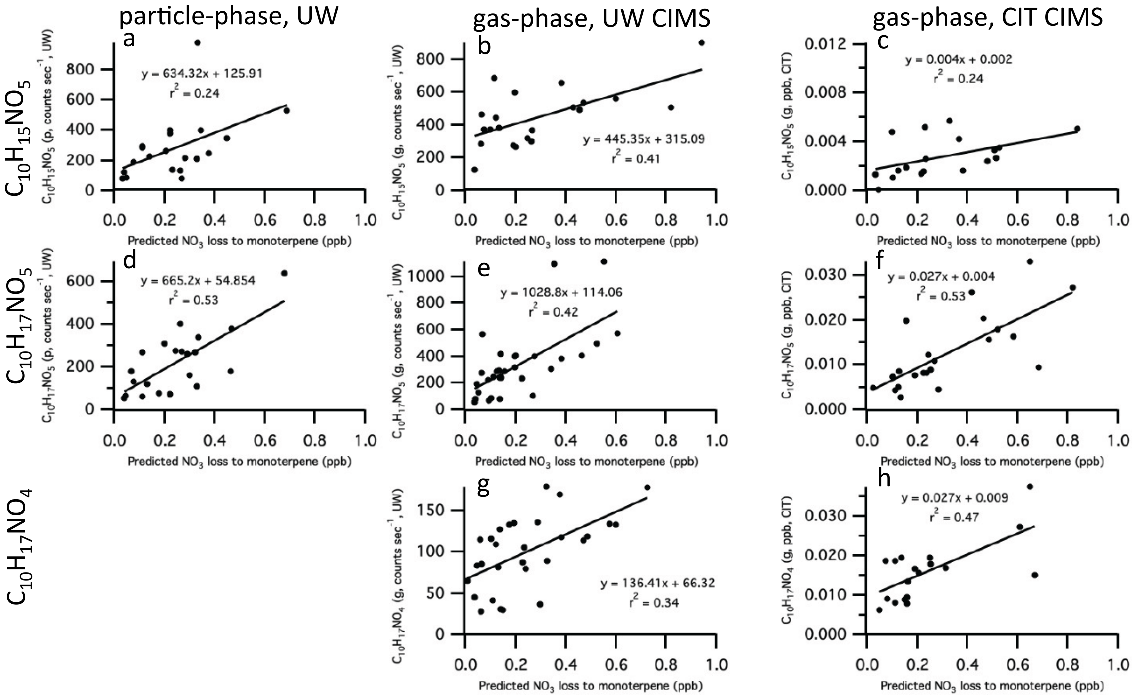

Figure 1. Scatter plots of selected molecules' concentration buildups against time-integrated monoterpene losses to NO_3 radical, during periods of observed organic nitrate buildup measured by CIMS. Panels a & d show particle phase $C_{10}H_{15}NO_5$ and $C_{10}H_{17}NO_5$ measured by the UW FIGAERO; b & e show gas phase $C_{10}H_{15}NO_5$ and $C_{10}H_{17}NO_5$ also measured by UW; c & f show the same gas phase species measured by the CIT CIMS, with calibrated concentrations. Panels g & h show gas phase $C_{10}H_{17}NO_4$ measured by both CIMS. The gas phase correlations with calibrated mixing ratios measured by the CIT CIMS (panels c, f, & h) allow for a rough estimation of the lower limit molar yields via the slopes: $C_{10}H_{15}NO_5$, 0.4%; $C_{10}H_{17}NO_5$, 3%; and $C_{10}H_{17}NO_4$, 3%.

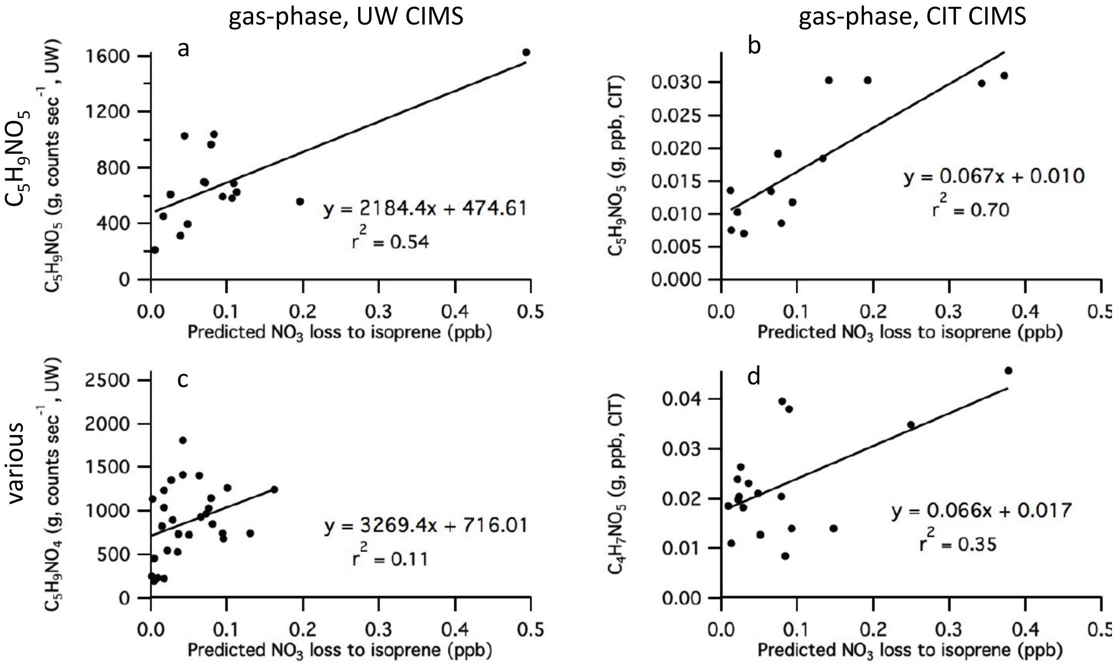

Figure 2. Gas phase CIMS data correlated to predicted isoprene + NO_3, during periods of buildup of these C_5 and C_4 nitrates as measured by each CIMS. Panels a & b show $C_5H_9NO_5$, which is well correlated to predicted isoprene + NO_3 suggesting this is a NO_3 gas-phase product, with the calibrated mixing ratios measured by CIT enabling estimation of an approximate lower limit molar yield of 7%. Panel c shows that $C_5H_9NO_4$ is poorly correlated to isoprene + NO_3 suggesting that this product comes (at least in part) from another oxidative source (ex. RO_2+NO). b Panel d $C_4H_7NO_5$ also shows a poorer correlation than panels a & b, suggesting it is not exclusively a product of NO_3 oxidation, or has rapid losses.

References

Beaver, M. R., Clair, J. M. S., Paulot, F., Spencer, K. M., Crounse, J. D., LaFranchi, B. W., Min, K. E., Pusede, S. E., Wooldridge, P. J., Schade, G. W., Park, C., Cohen, R. C., and Wennberg, P. O.: Importance of biogenic precursors to the budget of organic nitrates: observations of multifunctional organic nitrates by CIMS and TD-LIF during BEARPEX 2009, Atmospheric Chemistry and Physics, 12, 5773–5785, doi:10.5194/acp–12–5773–2012, 2012.

Bertram, T. H., Kimmel, J. R., Crisp, T. A., Ryder, O. S., Yatavelli, R. L. N., Thornton, J. A., Cubison, M. J., Gonin, M., and Worsnop, D. R.: A field-deployable, chemical ionization time-of-flight mass spectrometer, Atmospheric Measurement Techniques, 4, 1471–1479, doi:10.5194/amt–4–1471–2011, 2011.

Blanchard, C., Hidy, G., Tanenbaum, S., and Edgerton, E.: NMOC, ozone, and organic aerosol in the southeastern United States, 1999–2007: 3. Origins of organic aerosol in Atlanta, Georgia, and surrounding areas, Atmospheric Environment, 45, 1291–1302, 2011.

Crounse, J. D., McKinney, K. A., Kwan, A. J., and Wennberg, P. O.: Measurement of Gas-Phase Hydroperoxides by Chemical Ionization Mass Spectrometry, Analytical Chemistry, 78, 6726–6732, 2006.

Crounse, J. D., Nielsen, L. B., and Jørgensen, S.: Autoxidation of Organic Compounds in the Atmosphere, The Journal of Physical Chemistry Letters, 4, 3513–3520, 2013.

Eddingsaas, N., Loza, C., Yee, L., Seinfeld, J., and Wennberg, P.: α-pinene photooxidation under controlled chemical conditions–Part 1: Gas-phase composition in low- and high-$\mathrm{NO_x}$ environments, Atmospheric Chemistry and Physics, 12, 6489–6504, doi:10.5194/acp–10 12–6489–2012, 2012.

Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurtén, T., Worsnop, D. R., and Thornton, J. A.: An Iodide-Adduct High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer: Application to Atmospheric Inorganic and Organic Compounds, Environmental Science & Technology, 48, 6309–6317, doi:10.1021/es500362a, http://dx.doi.org/10.1021/es500362a, pMID: 24800638, 2014.

Lee, B. H., Mohr, C., Lopez-Hilfiker, F. D., Lutz, A., Hallquist, M., Hu, W. W., Jimenez, J., Xu, L., Ng, N. L., Romer, P., Cohen, R. C., Wild, R. J., Kim, S., de Gouw, J., Goldstein, A. H., Shepson, P. B., Wennberg, P. O., and Thornton, J. A.: Highly functionalized particle-phase organic nitrates observed in the Southeastern U.S.: contribution to secondary organic aerosol and reactive nitrogen budgets, in preparation, 2015.

Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Lutz, A., Hallquist, M., Worsnop, D., and Thornton, J. A.: A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROsols (FIGAERO), Atmospheric Measurement Techniques, 7, 983–1001, doi:10.5194/amt–7–983–2014, 2014.

Yatavelli, R., Lopez-Hilfiker, F., Wargo, J., Kimmel, J., Cubison, M., Bertram, T., Jimenez, J., Gonin, M., Worsnop, D., and Thornton, J.: A Chemical Ionization High-Resolution Time-of-Flight Mass Spectrometer Coupled to a Micro Orifice Volatilization Impactor (MOVI-HRToF-CIMS) for Analysis of Gas and Particle-Phase Organic Species, Aerosol Science and Technology, 46, 1313–1327, 2012.