



Evolution of NO_x in the Denver Urban Plume during the Front Range Air Pollution and Photochemistry Experiment

Carlena J. Ebben¹, Tamara L. Sparks¹, Paul J. Wooldridge¹, Teresa L. Campos², Christopher A. Cantrell³, Roy L. Mauldin³, Andrew J. Weinheimer², Ronald C. Cohen^{1,4}

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¹Department of Chemistry, University of California Berkeley, Berkeley, California 94720, United States
 ²National Center for Atmospheric Research, Boulder, Colorado 80301, United States
 ³Department of Atmospheric and Oceanic Sciences, University of Colorado, Boulder, Colorado 80309, United States
 ⁴Department of Earth and Planetary Sciences, University of California Berkeley, Berkeley, California 94720, United States

10 Correspondence to: Ronald C. Cohen (rccohen@berkeley.edu)

Abstract. As NO_x (NO_x=NO+NO₂) is transported away from cities, it undergoes photochemical oxidation to peroxynitrates (RO₂NO₂, Σ PNs), alkyl nitrates (RONO₂, Σ ANs), and nitric acid (HNO₃). These higher oxide species each have different lifetimes to permanent removal or conversion back to NO_x, resulting in nitrogen oxide chemistry that evolves as plumes are transported away from cities. Here, observations from the Front Range Air Pollution and Photochemistry Experiment

- 15 (FRAPPÉ) are used to describe the evolution of NO_x and NO_y (NO_y≡NO_x+ΣPNs+ΣANs+HNO₃+...) as the Denver urban plume flows outward from the city center. We evaluate the chemistry, dilution, and deposition rates in the plume to provide numerical constraints on the NO_x and NO_{y,i} lifetimes. We find that plume dilution with background air occurs with a lifetime of 3.5 hours. NO_x concentrations decrease more rapidly with a lifetime to chemical loss and dilution of 2 hours in the near field of the city center. NO_y has an effective lifetime of 3 hours and due to a combination of HNO₃ deposition and dilution.
- 20 The results provide a useful test of conceptual and numerical models of chemistry during the evolution of urban plumes.





1 Introduction

The chemistry of nitrogen oxides regulates tropospheric oxidants including hydroxyl radicals (OH), nitrate radicals (NO₃), and ozone (O₃). Nitrogen oxide chemistry also affects formation of secondary organic aerosols (SOA) both through regulation of oxidants and, as has been recently demonstrated, through formation and condensation of organic nitrates (Fry et

- 5 al., 2014; Ayres et al., 2015; Rollins et al., 2012; Lee et al., 2014). In urban areas, emissions of NO_x (≡NO+NO₂) result from combustion for transportation, power generation, home heating, and industrial processes (Dallmann and Harley, 2010). In more rural locations, microbial nitrification and denitrification in soils, biomass fires, and lightning are the dominant sources (Hudman et al., 2012; Mebust et al., 2011; Schumann and Huntrieser, 2007). During transport out of cities, urban plumes are subject to mixing with the free troposphere and horizontal expansion, effects that result in the physical dilution of the high
- 10 concentrations found in the urban core. At the same time, oxidation and deposition act on the individual chemical species in the plume, resulting in differential production and removal and setting the spatial pattern of nitrogen deposition. For the nitrogen oxides, chemical processes that occur during plume evolution lead to the formation of higher oxides, including peroxynitrates (RO₂NO₂, ΣPNs), alkyl and multifunctional nitrates (RONO₂, ΣANs), and nitric acid (HNO₃). During daytime the major pathways for NO_x oxidization are the reactions:

15	$NO_2 + OH + M \rightarrow HNO_3 + M$	(R1)
	$NO + RO_2 + M \rightarrow RONO_2 + M$	(R2a)
	$NO + RO_2 \rightarrow RO + NO_2$	(R2b)
	$NO_2 + R(O)O_2 + M \rightleftharpoons R(O)OONO_2 + M$	(R3)

Understanding the balance between the various oxidation pathways of NO_x and whether and how the higher oxides of NO_x,
NO_z (≡RO₂NO₂+RONO₂+HNO₃+...), are returned to NO_x by further chemistry as a plume moves from the center of cities to more rural locations is essential to understanding ozone and aerosol. Here we use observations from the Front Range Air Pollution and Photochemistry Experiment (FRAPPÉ) that took place in the region around Denver, Colorado during summer 2014 to investigate spatial patterns of NO_x oxidation and NO_{y,i} production and deposition with the goal of describing the processes affecting evolution of NO_x and NO_{y,i} concentrations downwind of urban sources.

25 2 Observations

FRAPPÉ used the NCAR C-130 aircraft during July and August 2014 to sample air in the Northern Front Range region around Denver, Colorado. Flights centered in large part on the area immediately surrounding Denver to understand the regional chemistry and meteorology as it affects air quality. Research objectives also included assessing upslope flow into the foothills of the Rockies west of Boulder, CO and investigating agricultural and oil and gas emissions in the area north

30 and east of Denver.

 NO_2 and higher oxides of nitrogen were measured using thermal dissociation laser induced fluorescence (TDLIF) (Day et al., 2002). Briefly, a pulsed frequency-doubled YAG laser is used to pump a dye laser at 585 nm that provides excitation for the





detection of ambient NO₂ by laser-induced fluorescence. The fluorescence signal at wavelengths >700 nm is collected and imaged onto a red sensitive photocathode using gated photon counting techniques to discriminate against prompt scattering. The thermal dissociation portion of the instrument is operated using four channels: ambient temperature for detection of NO₂, \sim 200° C for total RO₂NO₂, \sim 350° C for total RONO₂, and the fourth channel held at \sim 550° C and used for HNO₃ (Day

- 5 et al., 2002). By taking the difference between the NO₂ signals of two adjacent channels, the concentrations of each class of molecules are obtained. Calibration of the instrument was carried out by flowing mixtures of zero air and known concentrations of NO₂ standard gas. These measurements have previously been shown to compare well with other instruments when making similar measurements (Beaver et al., 2012; Thornton et al., 2000; Wooldridge et al., 2010). Other observations used in this analysis include NO measured by chemiluminescence (Weinheimer et al., 1994). VOCs were
- 10 measured using the trace organic gas analyzer (TOGA) a fast GC/MS instrument (Apel et al., 2003; Apel et al., 2010). The TOGA instrument runs on a 2 minute sampling cycle, and all measurements used in this analysis are 2 minute averages on that time base. Measurements of CO were made by vacuum UV resonance fluorescence (Gerbig et al., 1999). HO_x radicals, including OH, were measured by chemical ionization mass spectrometry (Mauldin et al., 2001; Hornbrook et al., 2011). We analyzed observations within the boundary layer (<1,000 m above ground level) and averaged over all wind speeds and</p>
- 15 directions. Transport time was approximated as the transport distance divided by the median observed wind speed of 13 km hr⁻¹.

3 The lifetimes of NO_{y,i}

Denver is an isolated urban area. As an approximation, we think of it as an extended point source emitting into air with concentrations of trace chemicals characteristic of the continental background. In other examples downwind of a city, the

20 transition from urban emissions to background conditions typically occurs over length scales of order 50 km (Dillon et al., 2002; Perring et al., 2013). Here we describe observations of the spatial evolution of NO_x and its higher oxides within and downwind of Denver and examine the role of physical and chemical factors that set the lifetime of nitrogen oxides in the Denver plume.

We begin with the simplest model of the NO_x lifetime, τ_{NOx} , where τ_{NOx} is set by only two factors – dilution and reaction

- 25 with OH. Dilution rates are typically reported in the range 0.1-0.25 hr⁻¹, corresponding to a lifetime of 4–10 hours (Dillon et al., 2002; Lin et al., 1996; Nunnermacker et al., 1998). At 10⁷ molec cm⁻³ OH, the NO_x lifetime to chemical removal by OH is comparable, ~4 hours. Combining this chemical removal with dilution, the NO_x lifetime is predicted to be 2 hours. The lifetime of NO_x with respect to midday oxidation by OH in other plumes has been reported to range from 2–8 hours (Alvarado et al., 2010; Valin et al., 2013; Ryerson et al., 1998; Ryerson et al., 2003). Additional terms in the atmosphere that
- 30 affect the apparent chemical lifetime of NO_x include reactions to form organic nitrates (ΣPNs and ΣANs), reactions to produce NO_x from its higher oxides, and emission and deposition of both NO_x and the higher oxides downwind of the source region. Different treatment of these terms in previous analyses of NO_x lifetimes reported in the literature make it difficult to





effectively summarize the apparent lifetime of NO_x in other plumes or to compare the results here to those plumes. For example, the effect of temperature on both source molecules for peroxyacyl radicals and on the lifetime of peroxynitrates can impact the apparent lifetime of NO_x . Additionally, peroxynitrates can serve to extend the NO_x lifetime (LaFranchi et al., 2009; Finlayson-Pitts and Pitts Jr., 1999). In the southeast U.S. during summer where it is warm and isoprene emissions are

5 strong, Romer et al. (2016) showed that the sum of NO_x and peroxynitrates function as a family where the family lifetime is set by chemical conversion to $RONO_2$ and HNO_3 , and the $\Sigma PNs:NO_x$ ratio is maintained in steady-state at a near constant value. As we show below, circumstances in the Denver plume are different, and ΣPNs are effectively a permanent sink of NO_x .

Figure 1a shows the concentrations of NO_x (gray), Σ PNs (blue), Σ ANs (green), and HNO₃ (red) during transport away from

- 10 Denver. NO_x is the most abundant NO_y component near the city, and its concentration quickly drops off, due to a combination of dilution and oxidation. Consistent with our simple model, the observed NO_x lifetime, defined as the point where the city center value decreases to e⁻¹, is ~2 hours. Figure 1b shows the fractional composition of NO_y, as a function of distance from Denver. In the area directly surrounding Denver, NO_x is unsurprisingly the largest fraction of NO_y, ~50%. HNO₃ initially is ~25% of NO_y, and ΣPNs and ΣANs account for ~10% and ~15%, respectively. As air is transported away
- 15 from Denver and undergoes chemical processing, the NO_x fraction decreases, falling to ~20% of NO_y. The fractions of ΣPNs and ΣANs each increase to approximately 20% of NO_y. HNO₃ becomes the dominant fraction, making up ~40% of NO_y after 100 km of transport. These fractions are typical of previous observations (Farmer et al., 2011; Browne and Cohen, 2012; Romer et al., 2016). The total concentration of NO_y decreases by a factor of 4 over the first 160 km of transport out of Denver, due to dilution and deposition.
- 20 In order to isolate the role of dilution in plume evolution, we compare the NO_{y,i} chemicals to CO, which is a chemically conserved tracer on the time scale of plume evolution with a lifetime to chemical removal of $\tau = 3$ days in full sunlight, corresponding to ~1% hr⁻¹ at 10⁷ molec cm⁻³ OH. We assume CO is diluted by mixing with background air and derive a dilution lifetime subject to that constraint. The loss of all other species to dilution is assumed to occur at the same mixing rate with different values for the background concentration. To facilitate a comparison to CO, it is useful to define a
- 25 fractional difference F:

$$F = (X - X_{background}) / (X_{initial} - X_{background})$$
⁽¹⁾

which normalizes the decay of molecules observed in the plume to the difference between their initial and final concentrations (Perring et al., 2010). By definition, F begins at 1 and ends at 0.

For a molecule lost only to dilution, the concentration would decay at the same rate as that of CO resulting in a fractional difference identical to that of CO at every time and location along the plume. Species with fractional difference lower than that of CO are, in the net, being removed by chemistry or deposition, while those with fractional difference greater than that of CO are being produced within the plume. Figure 2 shows the fractional difference, F, of each NO_y species and of CO over the first 160 km of transport out of Denver. Initial concentrations, *X*_{initial}, are defined as the median values observed within ~10 km of Denver. The background conditions, *X*_{background}, are defined as the median values observed at 160 km from





Denver. The campaign average initial and background concentrations are 4290 and 475 ppt for NO_x , 835 and 422 ppt for ΣPNs , 1270 and 439 ppt for ΣANs , 2240 and 1200 ppt for HNO_3 , 9.2 and 2.5 ppb for NO_y and 150 and 91 ppb for CO. Adjusting the initial and background concentrations within the standard variance of the mean or median does not change our interpretation of the data.

- 5 Using the mean wind speed of 13 km hr⁻¹, the transport time to reach the e⁻¹ point for CO is 3.5 hours, corresponding to a dilution rate of approximately 0.29 hr⁻¹. This dilution rate is similar to mixing timescales observed in previous studies in Denver and other locations. For example, McDuffie et al. (2016) derived a dilution rate of 0.38 hr⁻¹ from model fits of diel average observations at the Boulder Atmospheric Observatory, a location within the domain of our study, Dillon et al. (2002) derived a dilution rate of 0.2-0.22 hr⁻¹ was
- estimated by Nunnermacker et al. (1998) for the Nashville urban plume, and a dilution rate of 0.1 hr⁻¹ was estimated by Lin et al. (1996) for the Toronto urban plume.

Both NO_y and NO_x decrease to e⁻¹ more quickly than CO, in ~3 and ~2 hours, respectively. To highlight differences from effects of dilution on the NO_y species, we compare the fractional difference ratio of each NO_y species to that of CO, given by F_{X}/F_{CO} , in Fig. 3.

- 15 For the first two hours of plume evolution, dilution dominates, and all of the molecules exhibit rapid decay. NO_x decreases most rapidly, with a lifetime of ~2 hours. HNO₃ decreases most slowly, decaying by only 25% at 2 hours transport time. This HNO₃ decay is much slower than CO, which has decreased by 40% at 2 hours, an indication that HNO₃ is being produced faster than it is being deposited early in plume transport. Later in the plume, at 100 km distance, HNO₃ has a lower *F* than CO, indicating deposition has become more important than production. After the initial decay due to dilution, Σ PNs sustain
- 20 the highest fractional difference, reflecting the chemical production of ΣPNs later in the plume at a rate that exceeds the rate of dilution. For the first ~3 hours, the *F* for ΣANs decreases more rapidly than CO, indicating ΣANs are lost to reaction with OH or deposition more rapidly than they are produced. After ~3 hours, ΣANs appear to be lost at approximately the same rate as CO.

As total NOy is conserved in chemical reactions, the observed loss of NOy beyond that of CO is a measure of the role of

- 25 deposition. Using the difference between the e-folding lifetimes of CO and NO_y 3.5 and 2.8 hours, respectively we derive a lifetime to deposition of NO_y of ~14 hours. This corresponds to a deposition rate of 0.07 hr⁻¹, assuming a boundary layer height of 1 km. Vertical profiles of NO₂ and other gases are consistent with a 1 km PBL estimate. If we assume HNO₃ is the only species depositing, then we derive V_{dep} for HNO₃ of 2 cm s⁻¹. Neuman et al. (2009) reported the lifetime of HNO₃ to dry deposition was 14 hours in Houston. Nunnermacker et al. (2000) calculated an NO_z lifetime in the Nashville urban plume of
- 30 8.7 hours, although they acknowledge that this short lifetime would correspond to an unexpectedly fast deposition velocity of 6.7 cm s⁻¹ for HNO₃. In a pine forest environment, Farmer and Cohen (2008) calculated a deposition velocity of HNO₃ of 3.4 cm s⁻¹. Nguyen et al. (2015) measured a deposition velocity for HNO₃ of 3.8 ± 1.3 cm s⁻¹ based on eddy covariance observations at a rural site in Alabama. Our derived deposition velocity is lower than some of the recent measurements in forests, consistent with terrain that has less tree cover and therefore less surface roughness (Seinfeld and Pandis, 2006).



(2)



To a first approximation, the difference between F of CO and NO_x represents loss due to chemistry, specifically reaction with OH and/or production of organic nitrates. If the primary oxidation pathway of NO₂ is reaction with OH to form HNO₃ ($k_{OH+NO2} = 9.2 \times 10^{-12}$ cm³ molec⁻¹ s⁻¹ at 298 K), then the difference between the lifetimes of NO_x and CO can be used to calculate a lifetime with respect to reaction with OH of 5.3 hours. Assuming a ratio of NO₂ to NO_x of 0.72, the derived OH

5 concentration is 7.9x10⁶ molec cm⁻³. The OH concentration can also be estimated by assuming HNO₃ is in steady state and setting the production of HNO₃ via reaction of NO₂ with OH equal to its loss to dilution and deposition. Following Day et al. (2009) we incorporate the derived deposition and dilution rates, along with observed HNO₃ and NO₂ concentrations at several points along the transect of the plume, and solve for the OH concentration, according to Eq. (2):

 $k_{OH+NO_2}[NO_2]_t[OH] = K_{dep}[HNO_3]_t + K_{dil}([HNO_3]_t - [HNO_3]_{bg}),$

- 10 where K_{dep} is the deposition rate (0.07 hr⁻¹), equal to the deposition velocity divided by the boundary layer height (1 km), and K_{dil} is the dilution rate (0.29 hr⁻¹). We note that applying the steady-state approximation to species with lifetimes on the timescale of hours where steady-state is not achieved could lead to over- or under-estimation of OH concentration, especially in the near field of large emissions sources (Fried et al., 2011). This calculation yields an OH concentration in the range $4x10^6$ to $1x10^7$ molec cm⁻³. The average OH concentration used in the calculation is $\sim 7x10^6$ molec cm⁻³, similar to that
- 15 derived from the observed lifetime of NO_x and nearly identical to the observed median OH level during FRAPPÉ of 7.3×10^6 molec cm⁻³. Although we use production and loss of HNO₃ in the calculation of OH, this analysis also implicitly includes loss to organic nitrates, since we use the observed NO_x concentration as the source term for HNO₃, which decreases due to oxidation by all sink species. The NO_x lifetime with respect to photochemical oxidation can also be derived from the correlation between the NO_x concentration and the calculated production rates of its oxidation products, i.e. the sum of 20 production of Σ PNs, Σ ANs, and HNO₃. We find that this lifetime is ~3 hours.

Depending on conditions, Σ PNs may be appropriately considered as part of a short-lived reactive nitrogen pool (Romer et al., 2016) or a terminal sink of NO_x. Production of peroxynitrates is initiated by reaction of oxygenated VOCs. Their primary loss mechanism, aside from dilution, is via thermal decomposition, followed by reaction of the peroxy radical with NO. Assuming steady state conditions, we are able to use these known loss mechanisms to calculate the production rate

25 of peroxynitrates:

$$P(\Sigma PNs)_t = L(\Sigma PNs)_{TD,t} + K_{dil} ([\Sigma PNs]_t - [\Sigma PNs]_{bg})$$
(3)

Using this method to solve for the production rate of Σ PNs, we determine that P(Σ PNs) decreases from an average of ~400 ppt hr⁻¹ in Denver to ~100 ppt hr⁻¹ after 160 km of transport. P(Σ PNs) can also be calculated directly from observations of the oxygenated VOCs that react to produce peroxy acyl radicals and the associated reaction rate constants, following the

30 derivation described by LaFranchi et al. (2009). This calculation gives a similar range of production rates throughout transport of the plume. We determine that the average lifetime of Σ PNs is ~4 hours, sufficiently long that Σ PNs can be treated approximately as separate from NO_x, which has a lifetime of ~2 hours.





Production and loss of Σ ANs can be treated similarly. Σ ANs are produced by the reaction of NO with RO₂ radicals. This reaction pathway can also result in the production of NO₂ + RO radicals; the branching ratio associated with production of Σ ANs from these competing reactions is referred to as α . P(Σ ANs) is calculated using the summation of VOC reactivities and associated α values. P(Σ ANs) is highest in Denver, ~75 ppt hr⁻¹, and the rate decreases quickly during the first 30 km of

5 transport, averaging about 10 ppt hr⁻¹ beyond 30 km. Based on these production rates, we determine that $\tau(\Sigma ANs)$ is at least 9 hours, significantly longer than the lifetime of NO_x or HNO₃.

4 Conclusions

The observations and analysis of plume evolution described here contribute to our overall understanding of air quality in the region around Denver. We find that most of the NO_x emitted in the Denver urban plume is deposited as HNO_3 within 100 km

- 10 of the city. Export to further regions is much smaller, and at 140 km the export is a small perhaps imperceptible increment above the background. At this distance, the $NO_{y,i}$ distribution is 40% HNO₃ with equal amounts NO_x , ΣPNs , and ΣANs . In the intermediate distances between these endpoints, we note there is substantial net removal of NO_x and net production of PNs throughout the full extent of the plume. In contrast, in the near field of the city, we observe net production of HNO₃ that exceeds deposition, while beyond 100 km, the net sink to deposition exceeds the chemical product.
- 15 We observe a dilution rate of 0.29 hr⁻¹, and we find that over the first 2 hours of transport of the plume away from Denver, dilution is the primary loss process. The decay of NO_y to e⁻¹ occurs in ~3 hours, as a result of dilution and the additional removal by deposition at a rate of 0.07 hr⁻¹. This corresponds to a deposition velocity for HNO₃ of 2 cm s⁻¹, a number on the low side of recent observations, presumably because of flatter terrain. NO_x is lost most quickly from the plume, with $\tau_{NOx} \approx 2$ hours, which can be derived using either observations of the decay of NO_x concentration or fractional difference. The total
- 20 NO_y concentration decreases by a factor of 3–4 during transport, due to dilution and deposition, and we observe that the fractional composition of NO_y evolves throughout transport. HNO₃ has the largest increase as a fraction of NO_y during transport.

Data Availability. All data is available for download at the FRAPPÉ data archive (http://catalog.eol.ucar.edu/frappe)

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Competing Interests. The authors declare that they have no conflict of interest.

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Figure 1: (a) NO_x (gray), ΣPNs (blue dashed), ΣANs (green dotted), and HNO₃ (red) concentrations as a function of distance (km)
and transport time (hr) from Denver. (b) NO_x (gray), ΣPNs (blue), ΣANs (green), and HNO₃ (red) as fractions of NO_y as a function of distance and transport time from Denver. The traces for each NO_{y,i} species are stacked on top of one another to show the NO_y closure, and the fractions of each species are represented by the filled areas.







Figure 2: Fractional differences of CO (gold), NO_y (black), and its constituents: NO_x (gray), Σ PNs (blue dashed), Σ ANs (green dotted), and HNO₃ (red) as a function of distance from Denver.

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Figure 3: Fractional enhancement ratios, relative to CO, of NO_y species: NO_x (gray), ΣPNs (blue dashed), ΣANs (green dotted), and HNO₃ (red) as a function of distance from Denver. The gold line at 1 indicates the fractional enhancement of CO; fractional enhancement ratios above this line indicate production of a species within the plume, and ratios below this line indicate loss to deposition and/or chemistry.