

We thank both reviewers for thoughtful and detailed comments. We have outlined each comment in bold, and our responses in plain text underneath. We respond to Reviewer 2 first, as many of those questions provide useful context for our responses to Reviewer 1.

Responses to Reviewer #2:

1) The authors speculate that surface reactions of ozone might be responsible for the observed acid enhancements, but do not attempt to test this in any way, though ozone was also measured. Are there temporal or vertical correlations that provide any evidence for this? What kind of yield / precursor abundance would be required for this to work (esp for formic acid, with its 2-3 ppb enhancement)?

The source of formic acid is an interesting question, and one that we do not have a clear answer for – merely suggestions of options. To clarify, we speculate that that surface reactions of ozone may contribute to the acid enhancements, but cannot fully attribute this potential source. We have clarified the text (*italics represent addition*) to make it clear that we are not attributing the organic acid gradients entirely to surface+O₃ reactions:

“Multiple processes could be responsible for the observed surface-level source of alkanolic acids. We hypothesize that reactions between O₃ and organic surfaces (i.e. soil, organic films) could be one non-photochemical surface-level source of alkanolic acids near the site, *though unlikely to account for the entire source.*”

We later clarify: “*However, we emphasize that while O₃ reactions with surfaces could act as one source of organic acids, there is no evidence that they account for the entire surface-level organic acid source.*”

However, we did indeed make ozone measurements. Noon, night, and morning vertical profile measurements of ozone (along with NO_x, CO, ambient temperature, and relative humidity) have been added to the Supplemental Info (Figure S3), and has been reproduced below (Figure R1). The positive concentration gradient of ozone with respect to height during nighttime is consistent with dry deposition – that is, a nocturnal surface-level sink of ozone (and with the hypothesis that ozone reacts with organic surfaces to produce alkanolic acids). Photochemical production is the dominant ozone source during the daytime, and, consistent with that idea, we do not observe vertical gradients in ozone in the morning or noon vertical profiles.

Numerous assumptions are required to directly estimate the yields/precursor abundances required for this source – mostly due to limited micrometeorology measurements on or near the tower during the campaign dates. Due to our discomfort with these assumptions (and the subsequent order of magnitude differences in our estimates), we have not provided a source yield estimate. However, we have added the following text to the manuscript into the relevant part of the Discussion:

“*We report noon, night, and morning vertical profile measurements of O₃ in Figure S3. The positive concentration gradient of O₃ with respect to height during nighttime is consistent with a nocturnal surface-level sink of O₃, and the hypothesis that O₃ reacts with organic surfaces to produce alkanolic acids. Known photochemical production mechanisms are the dominant O₃ source throughout the daytime, and no net surface-level exchanges are observed in the morning or noon vertical profiles.*”

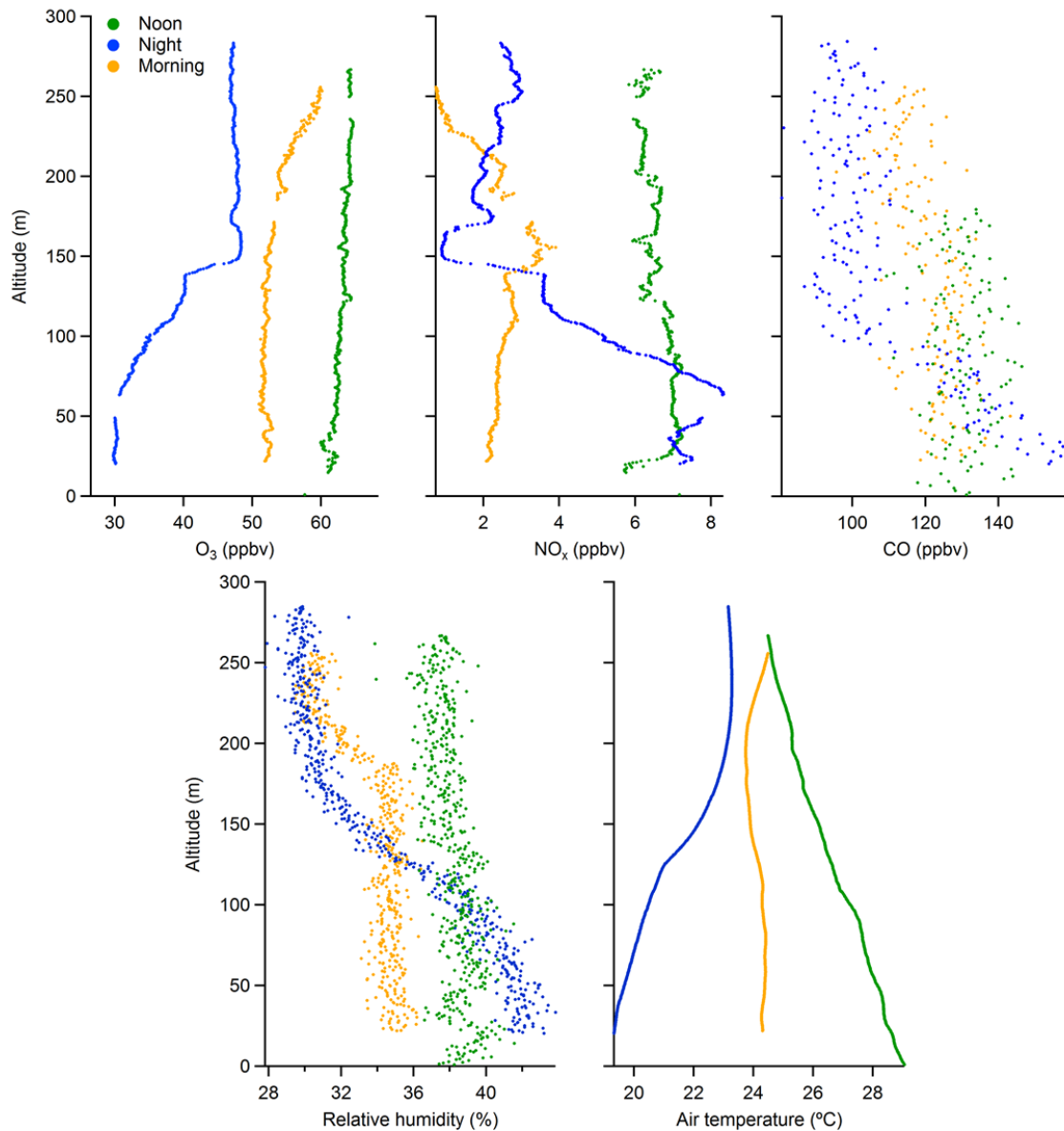


Figure R1 (and S3). Vertical profiles of O₃, NO_x, CO, relative humidity, and air temperature at representative noon, night, and morning periods.

2) 4, 29 and Fig 3. “vertical profiles show a strong, near-surface gradient below 75m”. Indeed, the profiles tend to show this gradient at the same altitude regardless of time of day (morning, noon, night). Wouldn’t we expect the positive or negative vertical gradients to manifest through a deeper layer of the atmosphere for the daytime profiles (due to mixing depth changes)?

The strong gradients observed in these vertical profiles are likely within the surface layer (i.e. lowest layer) of the tropospheric boundary layer, which occurs within both the stable boundary layer (during night) and mixed layer (during day). The height of this layer remains relatively consistent during both day and night. The dynamics of the surface layer at BAO are such that micrometeorology and fluxes display little variability throughout the day, leading to a nearly constant exchange of atmospheric scalars and

pollutants within this layer (Oke, 1987). This can be seen by the fairly constant concentration gradients observed in most of the acid vertical profiles near the surface.

3) 1, 26-27 “influence the acidity of precipitation, fog, and cloud droplets (. . .) and can thus impact ecosystem health”. The papers cited appear to refer to impacts associated with industrial release of organic acids in the first case, and with agricultural treatments in the second case. Are these relevant to the quantities found in wet deposition?

Regarding the first citation: Keene and Galloway (1984) report that the quantities of formic and acetic acid measured in precipitation in Central Virginia contribute to 16% volume weighed free acidity, and estimate that organic acids in total contribute to 18-35% of free acidity of precipitation in the continental U.S. These findings indicate that organic acids influence precipitation acidity in more urbanized areas—albeit less than inorganic species.

Regarding the second citation: we agree with the reviewer that it may not be the clearest citation to this statement. We removed the Gasche et al. (2002) citation, and replaced it with a study by Andreae et al. (1988), as it more clearly supports the claims made in this sentence. Andreae et al. report that organic acids contribute to the majority of acidity measured in precipitation samples collected in the Central Amazon Region.

4) 5, 35 “despite the demonstrable traffic source of propionic, butyric, and valeric acid, there is little evidence that traffic was the near-surface source observed in the vertical profiles”. The basis for this argument is not clear to me.

We agree that the wording of this sentence was unclear. We rephrased the sentence to the following:
“Despite the demonstrable importance of traffic emissions as a source of alkanolic acids in the troposphere during morning rush-hour periods, the reduction of these emissions during other times of day make it unlikely that traffic was the dominant surface-level alkanolic acid source persisting throughout the noon, night, and morning vertical profiles (Fig. 3).”

5) Supplement, estimating aqueous-phase partitioning of gas-phase acids. “this estimation is limited in that it does not account for the effects of pH or other dissolved ions of [note, should be “on”] a given acid’s acidity, but we would not expect a change of several orders of magnitude by accounting for these effects.” Given the environmental conditions at hand I think you are probably correct about this conclusion. However H can indeed vary a lot with pH and it would be straightforward to repeat the calculation using effective Henry’s law constants for a feasible range of pH to demonstrate that your conclusion is robust.

The reviewer makes an interesting point, and we have modified the text in the ‘*Estimating aqueous-phase partitioning of gas-phase acids*’ section of the Supplemental to the following:

“Aqueous-phase partitioning was evaluated as a potential sink for gas-phase acids by using Henry’s Law:

$$H_x = \frac{[X]_{aq}}{P_x}$$

where H_x is the Henry's Law constant for a given gas-phase acid, and $[X]_{aq}$ and P_x are the aqueous concentration and partial pressure of said acid species, respectively. P_x was calculated by gas-phase acid mixing ratio data, as well as meteorological data collected during the campaign. Moles of a given acid in the aqueous-phase was determined by $[X]_{aq}$ and ambient liquid water concentration (LWC). LWC in the Front Range during the summer is estimated to be around $1 \mu\text{g m}^{-3}$, based on continental estimates of LWC reported by Carlton and Turpin (2013). To account for the effects of pH on solubility, $[X]_{aq}$ was calculated as the following:

$$[X]_{aq} = H_x P_x \left(1 + \frac{K_a}{[H^+]} \right)$$

where K_a is the acid dissociation equilibrium constant for a given acid (Levanov et al., 2017; Fischer and Warneck, 1991; Borduas et al., 2016; Smith and Martell, 2004), and $[H^+]$ is the aqueous concentration of hydronium ion. Combining aqueous-phase moles of a given acid with the ideal gas law, and meteorological data from the site yields a total loss of said acid from the gas-phase through partitioning. Total loss of each acid calculated at various atmospherically-relevant pH values are reported below. This estimation is limited in that it neglects the effects of other dissolved ions on solubility, though we would not expect a change of several orders of magnitude by accounting for these effects.”

Estimations reported in supplemental have been updated to account for variability of Henry's Law at pH values of 2 to 6, which Borduas et al. (2016) have demonstrated to be relevant pH values to atmospheric liquid water content. We have reproduced the table of these data below:

Loss via aqueous partitioning (ppbv)							
pH	Formic	Propionic	Butyric	Valeric	Pyruvic	Nitric	Isocyanic
2	1.4E-10	1.4E-10	1.1E-10	5.4E-11	1.5E-08	1.8E-05	1.4E-10
3	1.6E-10	1.4E-10	1.2E-10	5.4E-11	8.3E-08	1.8E-04	1.6E-10
4	3.8E-10	1.6E-10	1.3E-10	6.1E-11	7.6E-07	1.8E-03	4.2E-10
5	2.5E-09	3.2E-10	2.9E-10	1.3E-10	7.6E-06	1.8E-02	2.9E-09
6	2.4E-08	1.9E-09	1.8E-09	8.0E-10	7.6E-05	1.8E-01	2.8E-08

6) 3, 36 “2.35E4 ncps/ppb”. Ncps is not defined until the subsequent paragraph; consider re-ordering or inserting ‘as defined below’. I suggest also reporting here the raw sensitivity in cps/ppb as this gives a more directly interpretable measure of the instrumental response / LOD.

Definition issue has been fixed. Regarding your suggestion: The CIMS data reported here are normalized to reagent ion (acetate) signal, to ensure that any observed changes in signal are not due to changes in reagent ion signal.

7) 4, 5: misplaced comma at beginning of line

Fixed.

8) 5, 13 “biogenic emissions typically cease during the night”. Should specify here that this is the case for light-dependent emissions but not for solely temperature-dependent emissions.

This sentence has been rewritten as the following: *“Further, the near-surface source persists through both day and night, while biogenic light-dependent emissions typically cease during the night when stomata are closed and photosynthesis has stopped.”*

9) 3, 14 “PISA” not defined

Fixed.

References

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Gasche, R., Papen, H., and Rennenberg, H.: Trace gas exchange in forest ecosystems, Springer, 2002.

Keene, W. C., and Galloway, J. N.: Organic Acidity in Precipitation of North-America, *Atmos. Environ.*, 18, 2491-2497, doi:10.1016/0004-6981(84)90020-9, 1984.

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Responses to Reviewer #1:

1) The authors suggest that the strong gradient in formic acid could be sustained by O₃ deposition to the surface. Is this possible? Using an upper limit for O₃ deposition velocity and unit yield for formic acid production, is the surface flux large enough to sustain the concentrations seen here?

As mentioned in our response to the first comment posted by Reviewer #2, we do not intend to suggest that O₃+surface reactions could account for the entire gradient. We have revised the paper to make this more clear as described in our response to Reviewer 2 (comment 1). Numerous assumptions are required to directly estimate the yields/precursor abundances required for this source, and due to our discomfort with these assumptions, we have not provided a source yield estimate.

2) The vertical profiles show a strong inflection point at 75m. It is not clear what is driving this. The authors should include some discussion of vertical mixing in this region that could lead to this. Further, I was very surprised that the vertical profiles look almost identical (if normalized to concentration at 250m) over the course of the day. It would be helpful for the authors to provide some discussion of why the profiles are so similar in morning, at noon, and at night.

Regarding the ‘inflection point’ mentioned in the first part of this comment—as mentioned in our response to the second comment posted by Reviewer #2, these gradients likely fall within the surface layer of the tropospheric boundary layer. The dynamics of the surface layer at BAO are such that micrometeorology and fluxes display little variability throughout the day, leading to a nearly constant exchange of atmospheric scalars and pollutants within this layer (Oke, 1987).

We agree with the reviewer that the similarities in alkanolic acid profiles are intriguing, and suspect that they are due to persistent surface-level sources occurring throughout day and night, and that the similarity in the nitric and pyruvic acid profiles are due to net surface-level deposition. That is, similar trends in profiles indicate that sources and sinks are controlled on similar timescales.

3) It would be extremely helpful to also include paired vertical profiles for T, CO, NO_x, O₃, and H₂O to assess the extent of vertical mixing during these profiles. I recognize that these measurements are discussed in McDuffie (2016), but it would be very nice to include the vertical profiles here as a reference panel in Fig. 3 for the profiles used in this study.

Vertical profiles of O₃, NO_x, CO, air temperature, and relative humidity have been added to the Supplemental Info (Figure S3), and have been reproduced above (see response to first comment posted by Reviewer #2; Figure R1). A short passage mentioning this addition has been added to the end of the third paragraph in the Results section: “Noon, night, and morning vertical profiles of O₃, NO_x, CO, air temperature, and relative humidity are reported in Figure S3.”

4) There is no discussion of the inlet used or inlet characterization in the manuscript. This should be included. What is the inlet transmission efficiency for these molecules and how was this corrected for? I also do not see a discussion in the supplement. In addition, how substantial is the water dependence in sensitivity and how was this accounted for? Is there enough of a gradient in H₂O to make this important for the interpretation of the vertical profiles? There is mention of hysteresis that could be related to inlet transmission in section 3. This should be elaborated on.

This is an excellent point, and we thank the reviewer for highlighting the missing information. We have added a short description of the sampling inlet to the Methods (section 2.2): “Ambient air was sampled through a 1 m inlet of 0.635 cm OD PEEK tubing at a sampling rate of approximately 2000 sccm.”

We assume that the transmission efficiency of sampled analytes will reach 100% after a sufficient delay time has passed allowing for analytes to establish gas-wall equilibrium with the surface of the inlet tubing. We acknowledge that this is not an entirely satisfactory assumption, but note that this gas-wall partitioning has been well characterized by Pagonis et al. (2017), who modeled sampling delay times (defined as the time required for the measured signal to reach 90% of the total signal change caused by a step-change in concentration) in Teflon tubing as a function of tubing diameter, sample flow rate, and analyte saturation vapor concentration (c^*). They reported sample delay times of a few minutes or less for compounds with c^* of between $\sim 10^4$ and $\sim 10^7$ $\mu\text{g}/\text{m}^3$ when sampling at a flow rate of 2.7 L/min through a

3 m length of 3/16 in. ID tubing. Most compounds reported here have a c^* greater than $10^6 \mu\text{g}/\text{m}^3$ (calculated using SIMPOL.1; Pankow and Asher, 2008), and therefore likely have similar delay times to those reported by Pagonis et al. (2017). These delay times are also likely negligible relative to the 1 hour ambient sampling periods reported herein. Furthermore, the first five minutes of ambient sampling data were filtered from analysis, to help ensure that gas-wall equilibrium was established in the data reported herein.

Brophy and Farmer (2015) reported that relative humidity is a negligible matrix effect for acetate ionization.

We agree that the mention of “inlet interferences” leading to hysteresis in the vertical profiles measurements is vague and somewhat misleading—it has thus been removed, as we believe that shaking of the elevator carriage (thus creating instability in the acetic anhydride reservoir used for the acetate ionization) during periods of downward carriage movement is more likely responsible for the observed hysteresis. The passage mentioning hysteresis in the vertical profiles measurements now reads as the following: *“We observe hysteresis in analyte measurements during periods of downward carriage movement, potentially due to shaking of the elevator carriage affecting acetate ion generation, so focus our analysis solely on profiles collected during upward carriage movement.”*

References

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- Pagonis, D., Krechmer, J. E., de Gouw, J., Jimenez, J. L., and Ziemann, P. J.: Effects of gas-wall partitioning in Teflon tubing and instrumentation on time-resolved measurements of gas phase organic compounds, *Atmos. Meas. Tech.*, 10, 4687–4696, <https://doi.org/10.5194/amt-10-4687-2017>, 2017.

Tropospheric sources and sinks of gas-phase acids in the Colorado Front Range

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Abstract. We measured organic and inorganic gas-phase acids in the Front Range of Colorado to better understand their tropospheric sources and sinks using a high-resolution time-of-flight chemical ionization mass spectrometer. Measurements were conducted from 4 to 13 August 2014 at the Boulder Atmospheric Observatory during the Front Range Air Pollution and Photochemistry Experiment. Diurnal increases in mixing ratios are consistent with photochemical sources of HNO₃, HNCO, formic, propionic, butyric, valeric, and pyruvic acid. Vertical profiles taken on the 300 m tower demonstrate net surface-level emissions of alkanolic acids, but net surface deposition of HNO₃ and pyruvic acid. The surface-level alkanolic acid source persists through both day and night, and is thus not solely photochemical. Reactions between O₃ and organic surfaces may contribute to the surface-level alkanolic acid source. Nearby traffic emissions and agricultural activity are a primary source of propionic, butyric, and valeric acid, and likely contribute photochemical precursors to HNO₃ and HNCO. The combined diel and vertical profiles of the alkanolic acids and HNCO are inconsistent with dry deposition and photochemical losses being the only sinks, suggesting additional loss mechanisms.

1 Introduction

Organic acids comprise a major fraction of gas-phase acids in the troposphere. They influence the acidity of precipitation, fog, and cloud droplets, particularly in rural areas (Keene and Galloway, 1984; [Andreae et al., 1988](#); [Gasehe et al., 2002](#)), and can thus impact ecosystem health (Sverdrup et al., 2001; Himanen et al., 2012). Organic acids are also involved in the formation of secondary organic aerosol (SOA) (Vogel et al., 2013; Yatavelli et al., 2014; Yatavelli et al., 2015), which affects human health, visibility, and climate. Yatavelli et al. (2015) estimated that molecules containing carboxylic acid moieties account for 10 – 50% of continental Northern Hemispheric organic aerosol mass. Sources and sinks determine tropospheric concentrations of gas-phase organic acids, and thus their impacts on biological health and air quality. However, several model-measurement comparisons for tropospheric formic and acetic acid indicate missing sources, potentially coupled to missing sinks (Paulot et al., 2011; Yuan et al., 2015; Millet et al., 2015; Schobesberger et al., 2016). Model-measurement comparisons for other tropospheric organic acids are lacking. Field and laboratory measurements investigating the sources and sinks of these compounds are therefore necessary to reduce model uncertainties and improve our understanding of organic acids in the troposphere.

A variety of primary biogenic and anthropogenic sources can introduce organic acids into the troposphere. Several organic acids have been identified in vegetative emissions (Kesselmeier et al., 1998; Kesselmeier, 2001), soil emissions (Sanhueza and Andreae, 1991; Enders et al., 1992), and biomass burning (Goode et al., 2000). Automobile exhaust is also a primary source of

alkanoic acids, with formic (CH_2O_2) and acetic ($\text{C}_2\text{H}_4\text{O}_2$) acid typically being the most abundant in these emissions (Kawamura et al., 1985; Kawamura et al., 2000; Friedman et al., 2017). Secondary production from the photochemical oxidation of volatile organic compounds (VOCs) serves as another major source. Photochemical oxidation of isoprene (C_5H_8) produces several organic acids, including formic and pyruvic acid ($\text{C}_3\text{H}_4\text{O}_3$) (Orzechowska and Paulson, 2005; Jacob and Wofsy, 1988; Paulot et al., 2009; Paulot et al., 2011). Friedman et al. (2017) measured formic, propionic ($\text{C}_3\text{H}_6\text{O}_2$), and butyric acid ($\text{C}_4\text{H}_7\text{O}_2$) in photochemically-aged diesel exhaust. Wet and dry deposition, and photochemical loss processes are the major known tropospheric sinks of organic acids (Grosjean, 1989; Talbot et al., 1995; Atkinson et al., 2006; Grosjean, 1983). Despite their ubiquity, our understanding of tropospheric organic acid sources and sinks is incomplete. This is especially apparent for formic acid—measured tropospheric concentrations are often several times higher than modeled values (Paulot et al., 2011; Yuan et al., 2015; Millet et al., 2015; Schobesberger et al., 2016). Model simulations have also failed to capture the temporal variation and vertical gradients of formic acid (Millet et al., 2015). These model-measurement discrepancies are likely due to underestimated sources and/or overestimated sinks, as well as missing sources and sinks that are not considered altogether.

Gas-phase inorganic acids, including nitric (HNO_3) and isocyanic acid (HNCO), also impact air quality. HNO_3 is produced in the troposphere from nitrogen dioxide (NO_2) reactions with hydroxyl radical (OH), and through the reaction of NO_2 with ozone (O_3). Anthropogenic emissions of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) from fossil fuel combustion and agricultural activity constitute a major secondary source of HNO_3 (Shepherd et al., 1991; Dignon, 1992; Kurvits and Marta, 1998; Almaraz et al., 2018). HNO_3 readily partitions into the aqueous-phase, contributes to acid deposition, and reduces the vapor pressure of water during cloud droplet growth—affecting the growth rate and resulting size of these droplets (Kulmala et al., 1993). HNO_3 also reacts with ammonia (NH_3) in the gas- or aqueous-phase to form ammonium nitrate (NH_4NO_3) aerosols (Adams et al., 1999). HNCO is of growing interest because exposure levels > 1 ppbv are linked to various human health issues, including atherosclerosis, cataracts, and rheumatoid arthritis (Jaisson et al., 2011; Roberts et al., 2011). Primary emission and secondary photochemical production sources of gas-phase HNCO have been identified and reported (Borduas et al., 2013; Roberts et al., 2014), but the magnitudes of these sources remain highly uncertain (Young et al., 2012). Combustion processes, including biomass burning, gasoline/diesel fuel combustion, and tobacco smoke are a primary source of HNCO (Roberts et al., 2011; Roberts et al., 2014; Link et al., 2016). Secondary sources of HNCO include OH oxidation of amine and amide precursors, which are particularly important in urban environments (Link et al., 2016; Roberts et al., 2014; Borduas et al., 2013). HNCO readily partitions into the aqueous-phase given its high solubility at atmospherically relevant pH values, and can hydrolyze to NH_3 (Roberts et al., 2011). Wet and dry deposition are other known HNCO sinks (Young et al., 2012; Roberts et al., 2014).

Here, we present ambient measurements of various gas-phase organic and inorganic acids taken during the Front Range Air Pollution and Photochemistry Experiment (FRAPPÉ) in Weld County, CO (McDuffie et al., 2016; Tevlin et al., 2017; Pfister et al., 2017b; Wild et al., 2017). We use diel trends and vertical profiles of these compounds, as well as correlations in timeseries data to investigate their tropospheric sources and sinks. The peri-urban Boulder Atmospheric Observatory (BAO) site lies at the intersection of agricultural sources, traffic, oil and gas development, and other industrial processes, providing a contrast to the strictly urban or forest sites that are often the focus of atmospheric chemistry measurements.

2 Methods

2.1 Site description

Measurements took place at the BAO tower in Weld County, CO during the FRAPPÉ field campaign in summer 2014. This work focuses on measurements taken between 4 and 13 August 2014. The land surrounding the tower is a sparsely vegetated region of the Colorado Front Range located on the outskirts of several urbanized Colorado municipalities (Boulder, Denver, Fort

Collins, and Greeley). The site lies about 2 km west of highway traffic from Interstate 25, is surrounded by oil and natural gas (ONG) wells, and is near (> 7 km) concentrated animal feeding operations (CAFOs) (Fig. 1) (Kaimal and Gaynor, 1983; Brown et al., 2013; Swarthout et al., 2013; Abeleira et al., 2017; Tevlin et al., 2017).

The 300 m BAO tower was equipped with an elevator carriage capable of continuous vertical movement between altitudes of 0 – 285 m, allowing for the generation of vertical profiles of measured compounds. A timeseries of carriage altitude throughout the reported measurement period is provided in Fig. S1. The carriage height was typically parked at 100 m (accounting for 62% of data described herein). This carriage housed a high-resolution time-of-flight chemical ionization mass spectrometer (TOF-CIMS) allowing for fast (1 Hz) detection of gas-phase compounds (discussed further in Sect. 2.2), as well as an IRGASON Integrated CO₂ and H₂O Open-Path Gas Analyzer, and 3-D Sonic Anemometer (Campbell Scientific) for air temperature, water vapor, and wind speed/direction measurements. Additional meteorological measurements at 10, 100, and 300 m were provided by the BAO Tower Meteorological Station. A filter radiometer (Metcon, GmbH, Shetter et al. (2003)) measured downwelling NO₂ photolysis rates (j_{NO_2}) near the base of the tower, from which total photolysis rates were calculated. Instruments to measure various trace gases of interest, including NO_x/O₃ (custom built Cavity Ring-Down Spectroscopy), CO/CO₂/CH₄/H₂O (Picarro 6401 Cavity Ring-Down Spectrometer), and NH₃ (QC-TILDAS; Aerodyne Research, Inc.) were also housed on the carriage PISA during the campaign. The CO/CO₂/CH₄/H₂O measurement details can be found in McDuffie et al. (2016) and Zaragoza et al. (2017). Instrument details on the NH₃ measurements are provided by Tevlin et al. (2017). All measurements presented here are reported in local time (Mountain Daylight Time; MDT; UTC – 6). Rainfall did not exceed 0.3 cm day⁻¹ near the site throughout the reported measurement period. We plot j_{NO_2} by hour of day as a proxy for solar exposure (Fig. 2). Solar exposure at the site peaks around 12:00.

2.2 TOF-CIMS measurements

The TOF-CIMS (Tofwerk AG and Aerodyne Research, Inc.) has been described extensively elsewhere (Bertram et al., 2011; Lee et al., 2014; Brophy and Farmer, 2015; Brophy and Farmer, 2016; Lopez-Hilfiker et al., 2016). When coupled to acetate (CH₃COO⁻) reagent ions, this instrument detects an array of molecules including HNO₃, HNCO, formic, propionic, butyric, valeric (C₅H₁₀O₂), and pyruvic acid in the atmosphere at high acquisition rates (i.e. < 1 s time resolution). Acetate reagent ions provide high sensitivity and selectivity for gas-phase acids (Veres et al., 2008; Bertram et al., 2011; Brophy and Farmer, 2015; Brophy and Farmer, 2016). Acetate reagent ions are generated by passing N₂ saturated with acetic anhydride through a ²¹⁰Po ionizer (NRD). These reagent ions enter the ion-molecule reactor along with sampled ambient air and selectively ionize gas-phase acids (HA) via either a proton-exchange reaction (Veres et al., 2008) or a clustering reaction with HA followed by declustering prior to detection (Brophy and Farmer, 2016). Under both mechanisms, the analyte of interest is detected by the mass spectrometer as a deprotonated, gas-phase anion (A⁻). Detection of acetic acid is not possible using this ion chemistry.

Ambient air was sampled through a 1 m inlet of 0.635 cm OD PEEK tubing at a sampling rate of approximately 2000 sccm. Instrument background is monitored hourly at the beginning of each data acquisition period using an overflow of ultra zero grade air (UZA, Airgas). Hourly online two-point external standard calibrations of formic acid are also taken in UZA prior to each ambient air measurement period, enabling direct calculation of instrument sensitivity to formic acid, and thus formic acid mixing ratios. Formic acid standard is generated from a permeation tube (Dynacal, VICI) in a heated oven held at 40 °C. Ultra-high purity (UHP) nitrogen (Airgas) flows through this permeation system, introducing the standard into the TOF-CIMS. Mass spectral data acquisition is controlled with TofDaq Recorder (Tofwerk AG), and automated using home-built programs (LabVIEW, National Instruments). Instrument sensitivity to formic acid during the campaign was 2.35×10^4 ncps ppb_v⁻¹ (defined in section 2.3), determined from a Gaussian fit to the histogram of sensitivity values. The low dispersion in these sensitivity values (% RSD = 1.4)

indicates high instrument stability throughout the campaign. We used offline external calibrations of other detected compounds to estimate mixing ratios for other gas-phase acids detected during the campaign (see Supplemental).

2.3 Mass spectral data processing and analysis

We process mass spectral data in Igor Pro (WaveMetrics Inc., Version 6) with Tofware (Tofwerk AG, Aerodyne Research Inc, Version 2.5.10), which determines mass spectral baseline, fitted peak shape, and peak resolution, and applies a TOF duty cycle correction ($m/z = 59$). We mass calibrate post-acquisition using a three-parameter fit and the O_2^- , Cl^- , CHO_2^- , NO_2^- , $\text{C}_2\text{H}_3\text{O}_2^-$, NO_3^- , and I^- peaks; these peaks were fully resolved during the measurements with consistently high signal throughout the measurement and calibration periods. Additional conjugate bases of various other organic acids (such as $\text{C}_3\text{H}_3\text{O}_2^-$ and $\text{C}_3\text{H}_5\text{O}_3^-$), as well as the [acetic acid + acetate] cluster ($\text{C}_4\text{H}_7\text{O}_4^-$) are included in the mass calibration when signal is sufficiently high and the peaks do not contain interferences. During FRAPPÉ, the mass accuracy of the TOF-CIMS was 2 ppm (campaign average of mass calibrant ions), and the resolution ($m/\Delta m$) was > 3000 . Tofware's high-resolution peak fitting procedures extract timeseries of detected compounds. Further data analysis, including background subtraction, normalization, mixing ratio calculation, and the generation of diel and vertical profiles are performed in Igor Pro. Mass spectral data are normalized to convert raw instrumental ion counts per second (cps) to normalized cps (ncps) by multiplying the measured analyte signal by the ratio of acetate reagent ion signal taken during an instrumental background to reagent ion signal taken during periods of analyte measurements (Bertram et al., 2011).

3 Results

Campaign statistics for each measured acid are reported in Table 1. Formic acid was the most abundant compound quantified by TOF-CIMS, with an average mixing ratio of 1.9 ppb_v. Compounds with negative minimum mixing ratio values are reported as below the instrumental limit of detection (LOD). We determined correlation coefficients between each measured gas-phase acid, and for each gas-phase acid compared to CO (subsamped from 8:30 to 10:30), NH_3 , air temperature, and j_{NO_2} (Table 2). Timeseries for measured acid mixing ratios are provided in Fig. S2.

We bin mixing ratio data from periods of constant carriage height (100 m) by hour of the day to generate diel profiles for all gas-phase acids (Fig. 2). A diel maximum occurs between 09:00 – 10:00 for HNO_3 , and 12:00 – 15:00 for all other acids. Secondary maxima occur around 09:00 – 10:00 for propionic, butyric, and valeric acid.

We select three typical vertical profiles to investigate noon, night, and morning trends (Fig. 3); these profiles started at 12:00 on 12 August 2014, 03:30 on 13 August 2014, and 10:00 on 13 August 2014. We observe hysteresis in analyte measurements during periods of downward carriage movement, potentially due to shaking ~~or inlet interferences in~~ the elevator carriage affecting acetate ion generation, so focus our analysis solely on profiles collected during upward carriage movement. Unfortunately, these three profiles are the sole profiles in which upward carriage movement occurred simultaneously with ambient air sampling during morning or noon periods, preventing us from replicating those time periods. Vertical profiles for nearly all gas-phase acids show a strong, near-surface gradient below 75 m. Negative gradients (i.e. mixing ratio decreases with height above ground) imply upward fluxes and net surface-level emission, while positive gradients imply downward fluxes, or net deposition. HNO_3 and pyruvic acid exhibit surface-level deposition in their noon, night, and morning vertical profiles. HNCO had a strong negative near-surface gradient during noon, and a weaker negative gradient during morning. All alkanolic acids exhibit surface-level emission in their noon, night, and morning vertical profiles (except for butyric acid during nighttime). Noon, night, and morning vertical profiles of O_3 , NO_x , CO, air temperature, and relative humidity are reported in Figure S3.

4 Discussion

4.1 Alkanoic acids

Formic acid at BAO (1.9 ppb_v average) is comparable to previous measurements in urban and rural areas (Glasius et al., 2000; Kawamura et al., 1985; Veres et al., 2011). All alkanoic acid mixing ratios increase throughout the day (Fig. 2), consistent with previously reported diurnal trends (Veres et al., 2011; Brophy and Farmer, 2015). Additionally, formic acid mixing ratios correlate strongly with j_{NO₂} ($r^2 = 0.738$). These data point to a photochemical source of alkanoic acids, consistent with known reaction mechanisms. For example, ozonolysis of alkenes and photooxidation of isoprene are photochemical sources of formic acid in the troposphere (Orzechowska and Paulson, 2005; Jacob and Wofsy, 1988; Paulot et al., 2009; Paulot et al., 2011; Millet et al., 2015). Alkanoic acids are also produced during photooxidation of diesel exhaust (Friedman et al., 2017).

Vertical profiles indicate an additional, non-photochemical surface source of alkanoic acids. Alkanoic acid vertical profiles exhibit negative gradients, demonstrating upward fluxes from near the surface (< 75 m) to the atmosphere throughout the day and night (with the exception of butyric acid at night) (Fig. 3). Possible drivers of this near-surface source are explored below. While photochemistry is an important atmospheric source of all observed alkanoic acids, the persistent near-surface gradient through both night and day requires an additional non-photochemical source at or near the surface.

Light- and temperature-dependent primary emissions of alkanoic acids from the stomata of plants have been reported previously (Kesselmeier et al., 1998), and could contribute to their observed diurnal increases (Fig. 2). However, vegetation in the region is sparse, particularly during the hot, dry Front Range summer. ~~Further, the near-surface source persists through both day and night, while biogenic light-dependent emissions typically cease during the night when stomata are closed and photosynthesis has stopped. Further, the near-surface source persists through both day and night, while biogenic emissions typically cease during the night when stomata are closed and photosynthesis has stopped.~~ Soil emissions are another plausible source of alkanoic acids, but typically thought to be minor (Sanhueza and Andreae, 1991; Enders et al., 1992). We thus expect that biogenic sources of the alkanoic acids were minor during the campaign.

Traffic emissions are a primary, and potentially secondary, source of propionic, butyric, and valeric acid. These compounds have been observed as primary and secondary emissions from automobile exhaust (Kawamura et al., 1985; Kawamura et al., 2000; Friedman et al., 2017). Peaks in the diel profiles of these compounds between 09:00 – 10:00 are consistent with morning rush-hour traffic and NO_x (Fig. S54). NO_x is commonly used as a tracer for near-field automobile emissions (Abeleira et al., 2017). CO is also an effective tracer for primary automobile emissions in the Front Range (Abeleira et al., 2017). Propionic, butyric, and valeric acid correlate particularly well with CO during morning rush-hour periods ($r^2 = 0.635$ for propionic, $r^2 = 0.615$ for butyric, and $r^2 = 0.721$ for valeric), suggesting that traffic dominated the source of these acids during that time. Correlations between the three acids and CO throughout the entire timeseries were lower ($r^2 = 0.237$ for propionic, $r^2 = 0.062$ for butyric, and $r^2 = 0.128$ for valeric), indicating that other sources influenced their gas-phase mixing ratios throughout the rest of the day. Much like CO, propionic, butyric, and valeric acid showed noticeable increases in measured mixing ratios from winds between 90° – 180° during morning rush-hour periods, consistent with the hypothesis that nearby traffic dominated the propionic, butyric, and valeric acid sources during morning rush hour (Fig. 4). McDuffie et al. (2016) and Zaragoza et al. (2017) have shown that wind direction analysis alone is not effective for determining the direction/magnitude of upwind sources near BAO, due to significant mixing and recirculation of air near the site. However, we use these profiles merely to show that these acids share the same incoming air parcels measured at the site as CO—i.e. these compounds are transported to the site from the same traffic source, irrespective of the exact direction of this source relative to the site. Formic acid behaves quite differently from the other alkanoic acids with respect to a potential traffic source. While automobile emissions are a known production source of formic acid (Kawamura et al., 1985; Kawamura et al., 2000; Friedman et al., 2017), formic acid did not exhibit a morning rush hour maximum,

was only weakly correlated to CO during rush hour ($r^2 = 0.026$), and did not share the rush hour directionality with the other acids (Fig. 4). ~~Despite the demonstrable importance of traffic emissions as a source of alkanolic acids in the troposphere during morning rush-hour periods, the reduction of these emissions during other times of day make it unlikely that traffic was the dominant surface-level alkanolic acid source persisting throughout the noon, night, and morning vertical profiles (Fig. 3). Despite the demonstrable traffic source of propionic, butyric and valeric acid, there is little evidence that traffic was the near-surface source observed in the vertical profiles (Fig. 3).~~

Agricultural activity is another primary emission source of alkanolic acids (McGinn et al., 2003; Paulot et al., 2011), and may have contributed to the observed alkanolic acid mixing ratios. NH_3 in the Colorado Front Range comes primarily from agricultural sources (Tevlin et al., 2017). NH_3 correlates more strongly with butyric ($r^2 = 0.453$) and valeric ($r^2 = 0.355$) acids than propionic acid ($r^2 = 0.221$) throughout the entire day. Like NH_3 (Fig. S65), all three acids increase with winds from $0^\circ - 90^\circ$, which is likely attributable to transport from nearby CAFOs (Fig. S76). Correlations between these acids and NH_3 were stronger during daytime (12:00 – 5:00) periods ($r^2 = 0.517$ for propionic, $r^2 = 0.649$ for butyric, and $r^2 = 0.426$ for valeric), suggesting that agricultural activity was predominantly a daytime source. Agricultural sources of formic acid have been suggested previously (Paulot et al., 2011). The weak correlation with NH_3 ($r^2 = 0.044$ for entire day, $r^2 = 0.228$ during daytime) suggests that agricultural activity was likely a minor daytime source of formic acid.

Photochemical oxidation of VOCs is an established atmospheric source of formic acid, and is consistent with the observed formic acid diel cycle and correlation with j_{NO_2} ($r^2 = 0.738$). Formic acid is produced during ozonolysis of ethene and propene (Atkinson et al., 2006; Millet et al., 2015), both of which have known combustion sources (Gilman et al., 2013), and during OH oxidation of diesel emissions (Friedman et al., 2017). ONG wells were dominantly to the east of the site (Fig. 1). These wells were a potential source of formic acid precursors due to the combustion processes associated with their operation (such as gas flaring). Isoprene is a known photochemical precursor of formic acid (Jacob and Wofsy, 1988; Orzechowska and Paulson, 2005; Paulot et al., 2009), though it has been observed in relatively low mixing ratios at BAO during the summer (0.2 ± 0.3 ppbv average) (Abeleira et al., 2017). Further, anthropogenic sources dominate summertime OH reactivity at the site (Abeleira et al., 2017), and reports of isoprene oxidation as a major source of formic acid typically occur in heavily vegetated areas (Jacob and Wofsy, 1988; Stavrou et al., 2012; Millet et al., 2015). The diurnal increases in propionic, butyric, and valeric acid reported here are consistent with previous field observations (Satsumabayashi et al., 1995; Veres et al., 2011) and reported photochemical production mechanisms of these compounds (Satsumabayashi et al., 1995; Orzechowska et al., 2005).

Photochemical sources are unlikely responsible for the near-surface source that persists throughout the day. We note that while photochemical processing of anthropogenic precursors is a known source of HNO_3 and pyruvic acid (see Sect. 4.2), the vertical profiles of these two acids are dominated by dry deposition and not surface sources. However, HNCN also has known photochemical and traffic sources, and displays a negative (upward flux) daytime, but not nighttime, near-surface vertical gradient (see Sect. 4.3). While it is possible that photochemical or traffic sources could cause the surface source implied by the alkanolic acid vertical profiles, it is less likely that they are responsible for the nighttime source.

The identity of the surface-level non-photochemical source thus remains unclear. Several other recent studies invoke missing alkanolic acid sources—i.e. sources not typically considered when modeling tropospheric VOC budgets. Paulot et al. (2011) suggested that photochemical aging of aerosols could serve as a major missing source of formic and acetic acid. Model-measurement discrepancies led Schobesberger et al. (2016) to suggest significant, unresolved surface-level sources of formic acid, although that study noted temperature and light dependences similar to emission parameterizations of other well-characterized biogenic VOCs. Millet et al. (2015) and Nguyen et al. (2015) also observed similar model-measurement discrepancies of formic acid, which were attributed to missing/underestimated chemical production and/or biogenic emissions sources.

Multiple processes could be responsible for the observed surface-level source of alkanolic acids. We hypothesize that reactions between O₃ and organic surfaces (i.e. soil, organic films) could be one non-photochemical surface-level source of alkanolic acids near the site, though unlikely to account for the entire source. Reactions of O₃ on organic surfaces such as organic films (Donaldson et al., 2005), plant surfaces (Cape et al., 2009; Jud et al., 2016), and human skin (Liu et al., 2016; Liu et al., 2017) have been reported previously. Soil organic matter and organic films are often rich in alkenes (Vancampenhout et al., 2009; Donaldson et al., 2005; Simpson et al., 2006), which undergo ozonolysis reactions in the presence of O₃ (Criegee, 1975; Wolff et al., 1997). Hydroxyalkyl hydroperoxides formed via the ozonolysis of alkenes can further decompose to alkanolic acids (Moortgat et al., 1997; Anglada et al., 2002; Hasson et al., 2003; Millet et al., 2015). O₃ mixing ratios measured at the site were relatively high at nighttime (~ 40 ppb_v) (Fig. S87), further suggesting that this process may contribute to the persistent upward flux of alkanolic acids through both day and night. We report noon, night, and morning vertical profile measurements of O₃ in Figure S3. The positive concentration gradient of O₃ with respect to height during nighttime is consistent with a nocturnal surface-level sink of O₃, and the hypothesis that O₃ reacts with organic surfaces to produce alkanolic acids. Known photochemical production mechanisms are the dominant O₃ source throughout the daytime, and no net surface-level exchanges are observed in the morning or noon vertical profiles. However, we emphasize that while O₃ reactions with surfaces could act as one source of organic acids, there is no evidence that they account for the entire surface-level organic acid source.

Wet and dry deposition are major sinks of alkanolic acids (Grosjean, 1989; Talbot et al., 1995). Removal via reactions with OH are slow, corresponding to atmospheric lifetimes of several days (Dagaut et al., 1988). C₁ – C₅ alkanolic acids have negligible absorption cross sections at wavelengths greater than ~250 nm (Singleton et al., 1987; Vicente et al., 2009); photolysis is thus not considered to be a major tropospheric alkanolic acid sink. Wet deposition was minimal in the Front Range during the study period due to the lack of rainfall events during the reported measurement period. Dry deposition should thus have been the only major alkanolic acid sink during the night. However, the vertical profiles showed upward fluxes of these compounds at night (Fig. 3). The nocturnal decrease in mixing ratio necessitates an additional non-photochemical sink for these compounds, consistent with previous suggestions by Brophy and Farmer (2015). Cloud processing, gas-particle phase partitioning, and aqueous-phase reactions are possible alkanolic acid sinks. The high Henry's Law constants (H) of these acids suggest that aqueous-phase partitioning (aqueous aerosols, fog and cloud droplets, etc.) would be favorable ($H = 5.5 \times 10^3$, 5.7×10^3 , 4.7×10^3 , and 2.2×10^3 mol L⁻¹ atm⁻¹ for formic, propionic, butyric, and valeric acid, respectively at T = 298 K) (Khan et al., 1995). However, this was likely not a significant sink given the arid climate of the Front Range. Carlton and Turpin (2013) suggest that liquid water concentration in the Front Range during summer is ~1 μg m⁻³. Combining this with known constants, campaign mean mixing ratios, and meteorological conditions, aqueous-phase partitioning accounts for an estimated loss of $< 2 \times 10^{-10}$ ppb_v of each alkanolic acid (see Supplemental). While this ignores effects of pH and other dissolved ions on solubility, aqueous partitioning is unlikely a substantial loss process for the alkanolic acids during the measurement campaign. Gas-phase reactions between the alkanolic acids and atmospheric bases, such as NH₃, amines, or amides have not been reported extensively. Grosjean (1989) suggested that carboxylic acids can react with NH₃ in the atmosphere to produce carboxylate ammonium salts, though the importance of this process as a tropospheric sink of alkanolic acids remains uncertain.

4.2 Nitric and pyruvic acid

HNO₃ and pyruvic acid follow similar diel and vertical trends ($r^2 = 0.603$), and their diel profiles are consistent with photochemical sources (Fig. 2). Additionally, pyruvic acid correlates particularly well with j_{NO2} ($r^2 = 0.783$). Unlike the alkanolic

acids, HNO₃ and pyruvic acid exhibit persistent net deposition to the surface near the site during the noon, night, and morning periods (Fig. 3).

Traffic was likely an important secondary source of HNO₃ and pyruvic acid. HNO₃ is produced from NO₂ + OH, and pyruvic acid is produced from photooxidation of diesel exhaust (Friedman et al., 2017), including from 1,3,5-trimethylbenzene in the presence of NO_x (Praplan et al., 2014). Both NO_x and 1,3,5-trimethylbenzene are abundant components of automobile exhaust (Nelson and Quigley, 1984; Khoder, 2007). However, correlations between these acids and CO during morning rush-hour traffic were weak ($r^2 = 0.274$ for HNO₃, and $r^2 = 0.264$ for pyruvic acid), perhaps unsurprising as CO is directly emitted from traffic exhaust, whereas HNO₃ and pyruvic acid require photochemistry. This observation suggests that regional, rather than nearby traffic is the source of these two acids. Neither HNO₃ nor pyruvic acid correlate with NH₃. However, agricultural activity is a known source of NO_x, which is primarily emitted from fertilizer and heavy-duty diesel farm vehicles (Shepherd et al., 1991; Kurvits and Marta, 1998). We therefore speculate that agricultural sources also served as a secondary source of HNO₃ near the site. Reports of pyruvic acid from agricultural sources are sparse, and we cannot evaluate the potential of this source with the data presented here. ONG and industrial activities are also sources of NO_x in the Front Range (Pfister et al., 2017a), and thus likely secondary sources of HNO₃. There is no evidence for strong surface-level emission sources of HNO₃ or pyruvic acid in the vertical profile data.

Vertical profiles of both HNO₃ and pyruvic acid are consistent with dry deposition (Fig. 3). While both HNO₃ and pyruvic acid readily partition into the aqueous-phase ($H = 2.1 \times 10^5 \text{ mol L}^{-1} \text{ atm}^{-1}$ and $3.1 \times 10^5 \text{ mol L}^{-1} \text{ atm}^{-1}$ for HNO₃ and pyruvic acid, respectively) (Khan et al., 1995; Schwartz and White, 1981), we estimate that aqueous-phase partitioning is a negligible sink for both compounds. Photochemistry is not a major sink of HNO₃, but pyruvic acid readily undergoes photolysis—corresponding to a typical atmospheric lifetime of a few hours (Grosjean, 1983). However, the reaction of pyruvic acid with OH is negligible, corresponding to a lifetime on the order of months (Grosjean, 1983). Reactions between ambient NH₃ and HNO₃ produce NH₄NO₃ aerosol (Li et al., 2014), though we estimate that this process would not be a significant sink of gas-phase HNO₃ (see Supplemental).

4.3 Isocyanic acid

The afternoon diurnal peak of HNCO is consistent with photochemical production sources (Fig. 2). The diel profile of HNCO at BAO is similar to that observed previously in rural NE Colorado during BioCORN 2011, which was attributed to secondary photochemical production from amine and formamide (Roberts et al., 2014). The daytime vertical profiles show clear, upward fluxes of HNCO from the surface (Fig. 3). This vertical gradient is strongest at noon, smaller in the morning and unclear at night, implying a surface source that is driven by photochemistry.

Roberts et al. (2014) suggested that farmland and cattle feedlots located along Interstate 25 serve as a source of photochemical precursors (various amine and amide compounds) of HNCO in the Colorado Front Range. This is supported by the correlation between HNCO and temperature ($r^2 = 0.773$) as these agricultural precursors are likely temperature-dependent. Sintermann et al. (2014) reported that alkaline compounds such as amines undergo enhanced volatilization from agricultural sites when air temperatures are higher due to a decrease in temperature-dependent solubility and an increase in soil/waste pH due to accelerated hydrolysis of urea. HNCO mixing ratios were possibly influenced by additional sources, including traffic, ONG wells, and industrial activity. Traffic exhaust is a primary emission source of HNCO (Brady et al., 2014; Link et al., 2016), but the lack of a morning rush-hour peak or correlation with CO suggests that it was not a strong primary source of HNCO at the site (Fig. 2). Link et al. (2016) found that diesel exhaust was a precursor for photochemical HNCO production, but Jathar et al. (2017) suggested that the kinetics do not substantially outcompete dilution, and that urban HNCO is not strongly enhanced by diesel exhaust photochemistry.

Dry deposition is a major sink of HNCO (Roberts et al., 2014; Young et al., 2012), although HNCO readily partitions into the aqueous-phase ($H = 10^5 \text{ mol L}^{-1} \text{ atm}^{-1}$), where it can hydrolyze to NH_3 (Roberts et al., 2011). We estimate that aqueous partitioning of HNCO was negligible. No major sinks of HNCO aside from wet deposition, dry deposition, and aqueous-phase chemistry have been reported, and photochemical loss reactions are negligible, with a photolysis lifetime of several months (Roberts et al., 2011), and an OH oxidation lifetime of several years (Tsang, 1992; Roberts et al., 2011; Borduas et al., 2016). HNCO has a relatively high gas-phase acidity (Wight and Beauchamp, 1980; Veres et al., 2010), and we hypothesize that non-photochemical gas-phase acid-base reactions could be a nighttime sink for HNCO.

5 Conclusions

Diurnal increases in all gas-phase acids are consistent with photochemical sources. We observe net surface-level emissions of alkanolic acids through both day and night, suggesting additional non-photochemical surface sources. We speculate that reactions between O_3 and organic surfaces (i.e. soil, organic films) near the site could be driving this persistent upward alkanolic acid flux. Correlations with chemical tracers suggest that traffic emissions and agricultural activity near the site are a primary source of propionic, butyric, and valeric acid, and potentially a secondary source of HNO_3 , and HNCO.

Dry deposition is the dominant sink of HNO_3 and pyruvic acid, but was not large enough to out-compete the surface source of the alkanolic acids. Which sinks control the lifetime of the alkanolic acids remain unclear. A non-photochemical sink of HNCO on top of dry deposition is also suggested by the vertical profile data and warrants further investigation.

Data availability. Meteorological data taken at the BAO tower are available at: <https://www.esrl.noaa.gov/psd/technology/bao/browser/>. All other data supporting the analysis are available at: <https://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html>.

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

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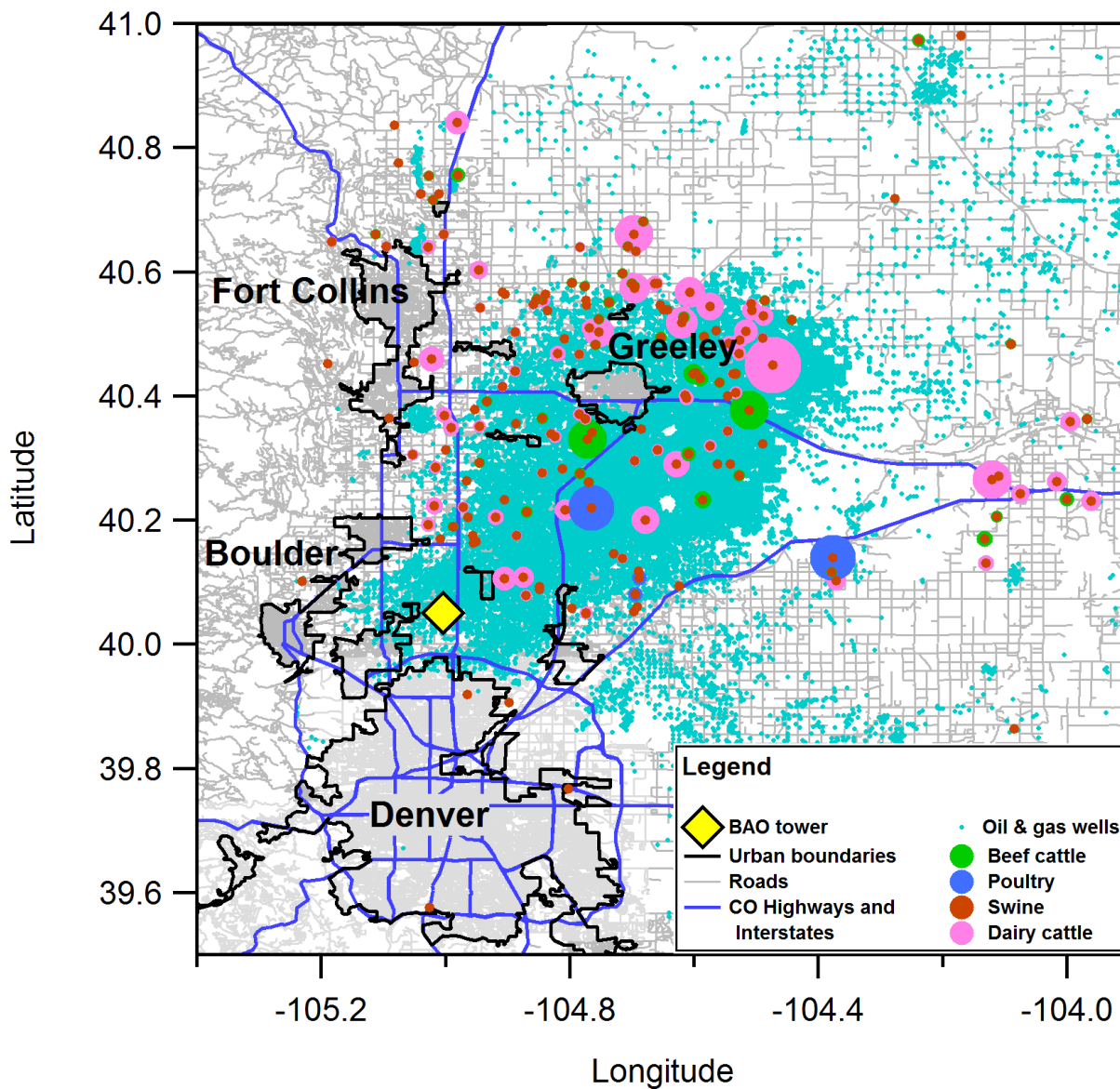
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Figures



5 Figure 1. Area surrounding BAO site, including major nearby urban municipalities, roads and highways, ONG wells, and CAFOs. CAFOs are colored by operation type and sized by number of animal units per operation.

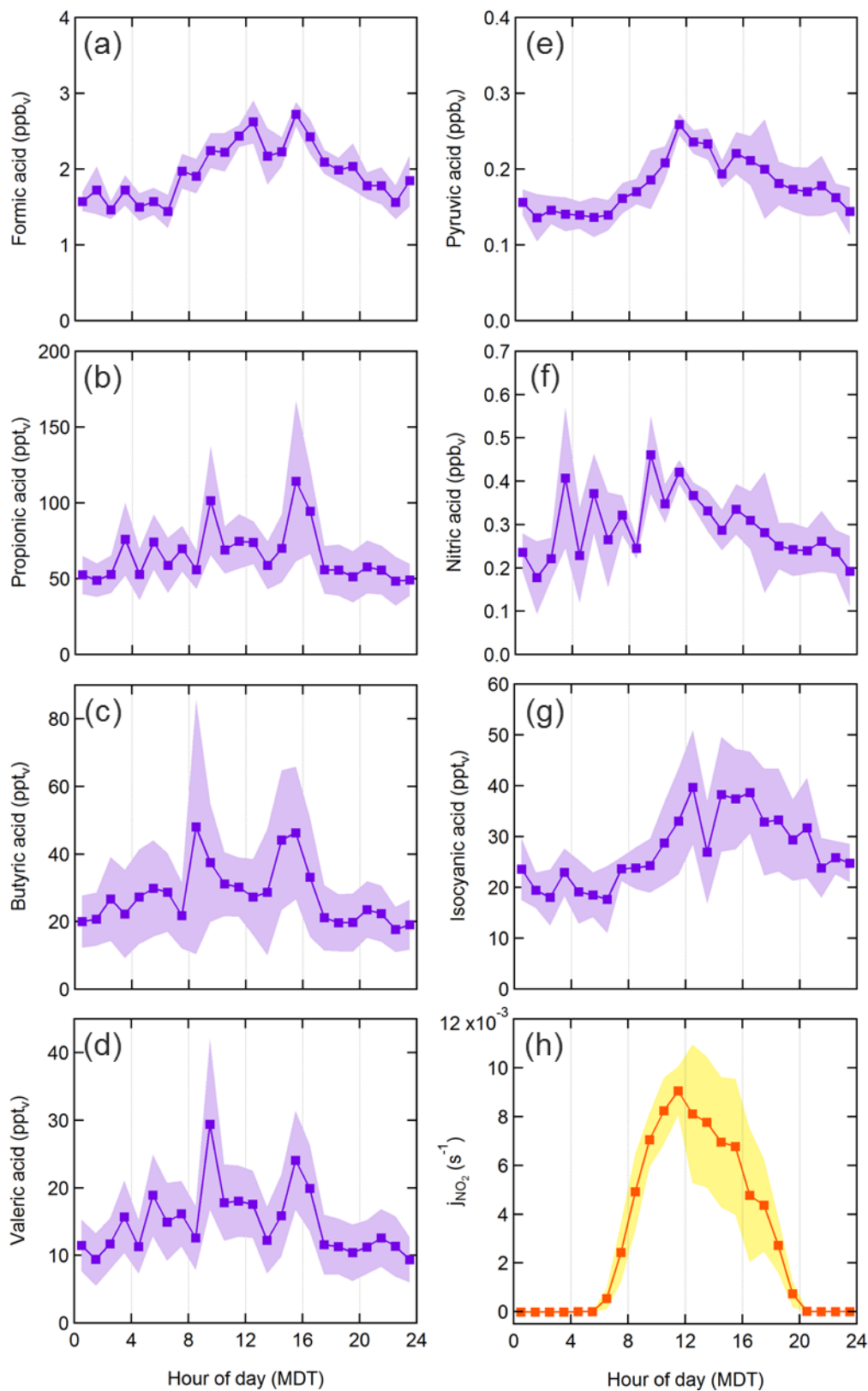


Figure 2. (a–g) Diel profiles for all detected gas-phase acids at 100 m. (h) Diel profile for j_{NO_2} measured at the site. Data are binned by hour. Data points are means of hourly bins. Shaded area represents \pm one standard deviation of binned data.

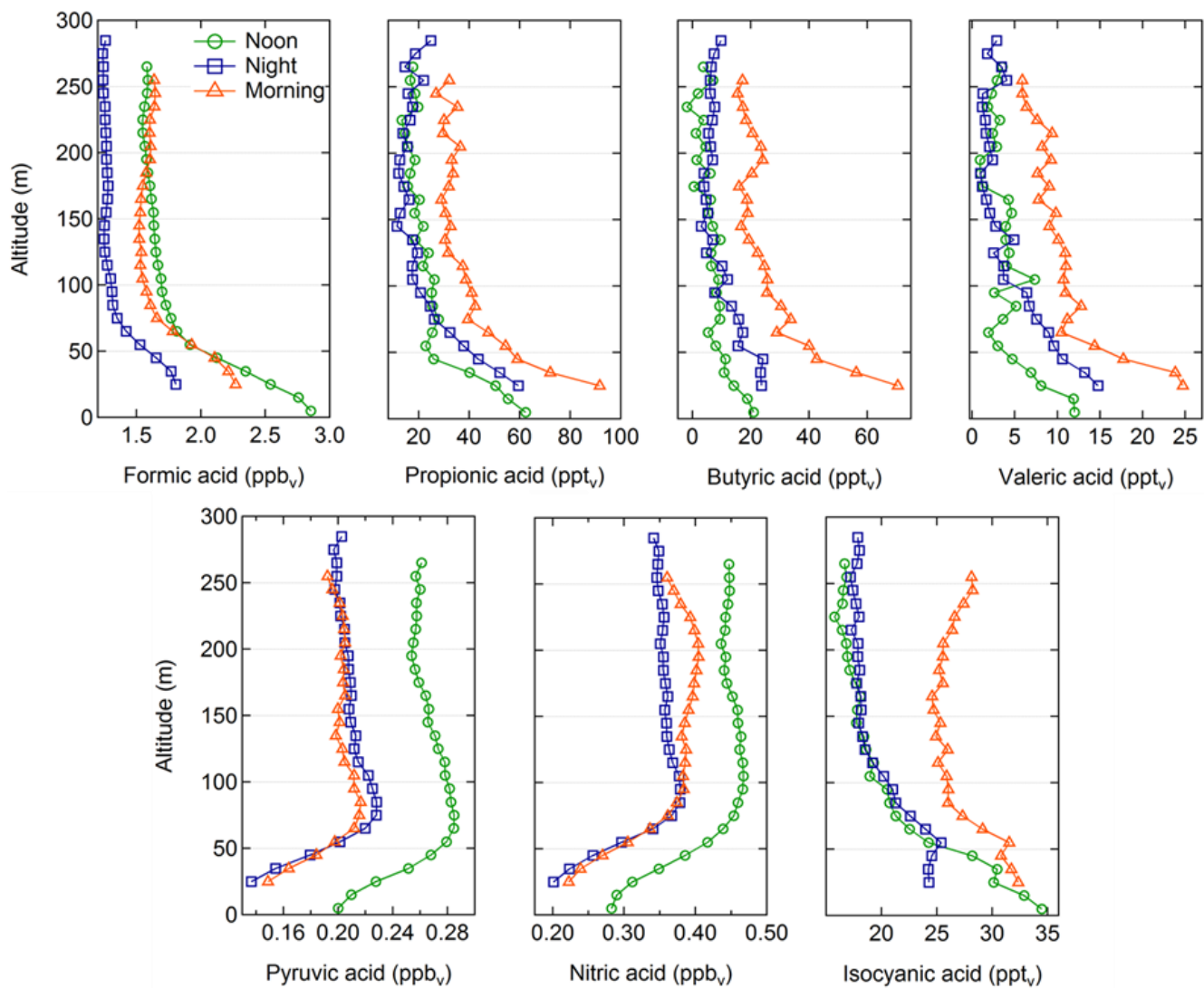


Figure 3. Vertical profiles for all detected gas-phase acids at representative noon, night, and morning periods, showing mixing ratio as a function of altitude. Data are binned by altitude (10 m per bin). Data points are means of each bin. Error bars have been removed for clarity, and are included in Fig. S43.

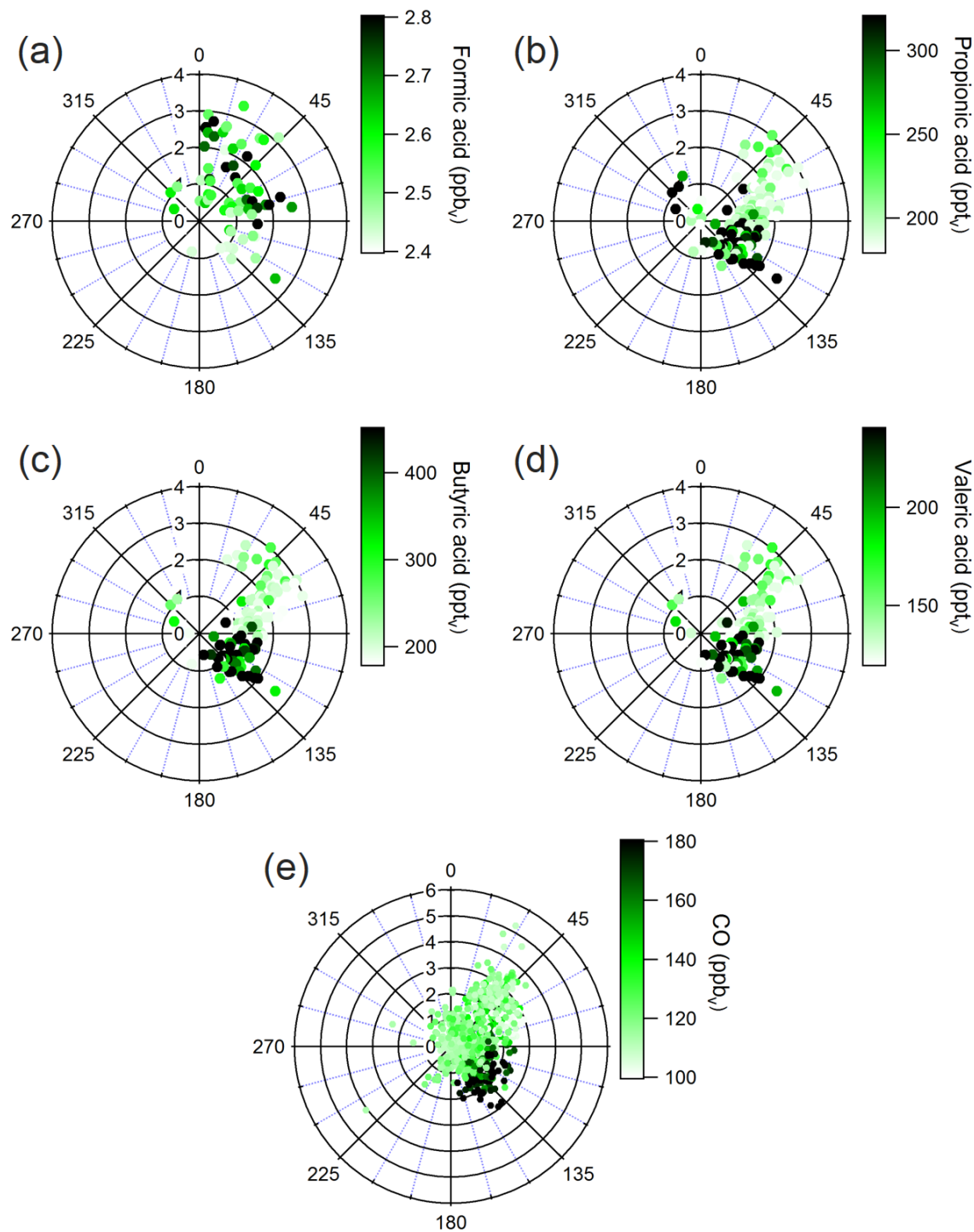


Figure 4. Wind plots of (a) formic acid, (b) propionic acid, (c) butyric acid, (d) valeric acid, and (e) CO measured at the site. Data are selected during periods of morning rush-hour traffic (08:30–10:30). Data points are colored by mixing ratio. Radial and angular axes represent wind speed (m s^{-1}) and direction (degrees), respectively. Degrees correspond to cardinal directions (i.e. 0° is N, 90° is E, etc.).

Tables

Table 1 – Campaign statistics for measured gas-phase acids.

Gas-phase acid	Mean (ppb _v)	Max (ppb _v)	Min. (ppb _v)	Standard deviation (ppb _v)
Formic	1.9	3.6	1.0	0.4
Propionic	0.06	0.70	Below LOD	0.03
Butyric	0.03	0.16	Below LOD	0.02
Valeric	0.01	0.06	Below LOD	0.01
Pyruvic	0.18	0.51	Below LOD	0.06
Nitric	0.30	1.11	0.00	0.07
Isocyanic	0.03	0.07	0.00	0.01

5 Table 2 – Correlation coefficients (r^2) for each gas-phase acid in the leftmost column compared to other gas-phase acids, chemical tracers, and other meteorological parameters in the table header (Propion. = propionic acid, Isocyan. = isocyanic acid, Temp. = air temperature).

	Formic	Isocyan.	Pyruvic	Propion.	Valeric	Nitric	Butyric	CO	NH ₃	Temp.	jNO ₂
Formic	—	0.375	0.194	0.257	0.120	0.091	0.089	0.026	0.044	0.504	0.738
Isocyan.	0.375	—	0.030	0.102	0.007	0.005	0.001	0.093	0.002	0.773	0.411
Pyruvic	0.194	0.030	—	0.077	0.074	0.603	0.068	0.264	0.002	0.560	0.783
Propion.	0.257	0.102	0.077	—	0.776	0.231	0.714	0.635	0.221	0.058	0.310
Valeric	0.120	0.007	0.074	0.776	—	0.312	0.856	0.721	0.355	0.005	0.331
Nitric	0.091	0.005	0.603	0.231	0.312	—	0.332	0.274	0.113	0.005	0.382
Butyric	0.089	0.001	0.068	0.714	0.856	0.332	—	0.615	0.453	0.017	0.365

Supplemental Figures

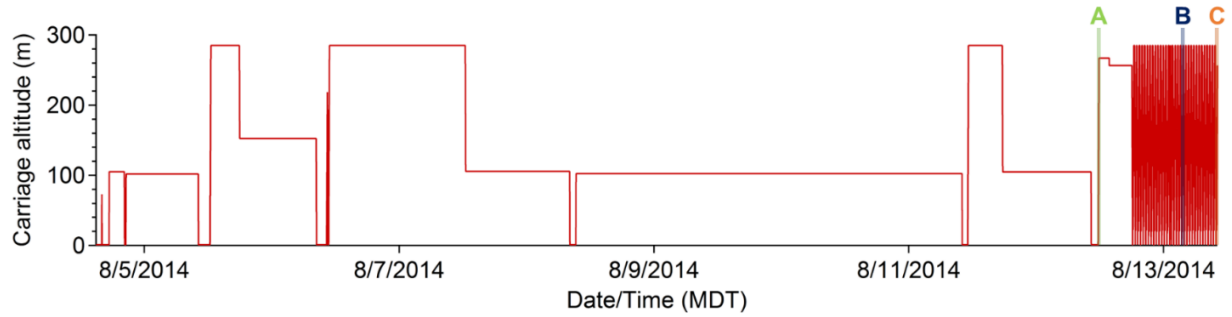


Figure S1. Timeseries of tower elevator carriage altitude throughout the reported measurement period. Representative noon, night, and morning vertical profiles were measured at the periods denoted 'A', 'B', and 'C', respectively.

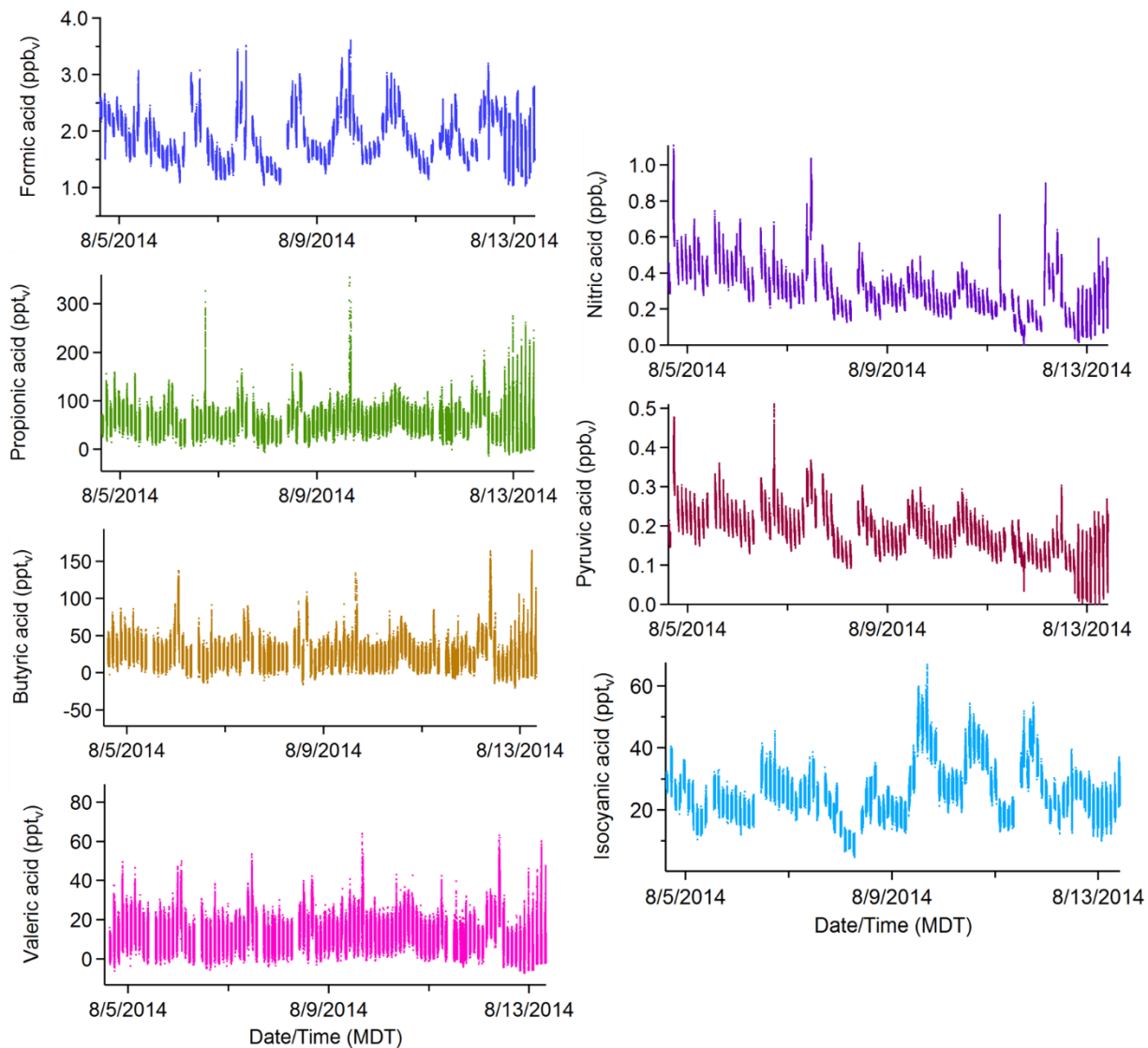


Figure S2. Mixing ratio data timeseries for all detected gas-phase acids spanning the reported data acquisition period. All data were collected at 1 Hz acquisition rates.

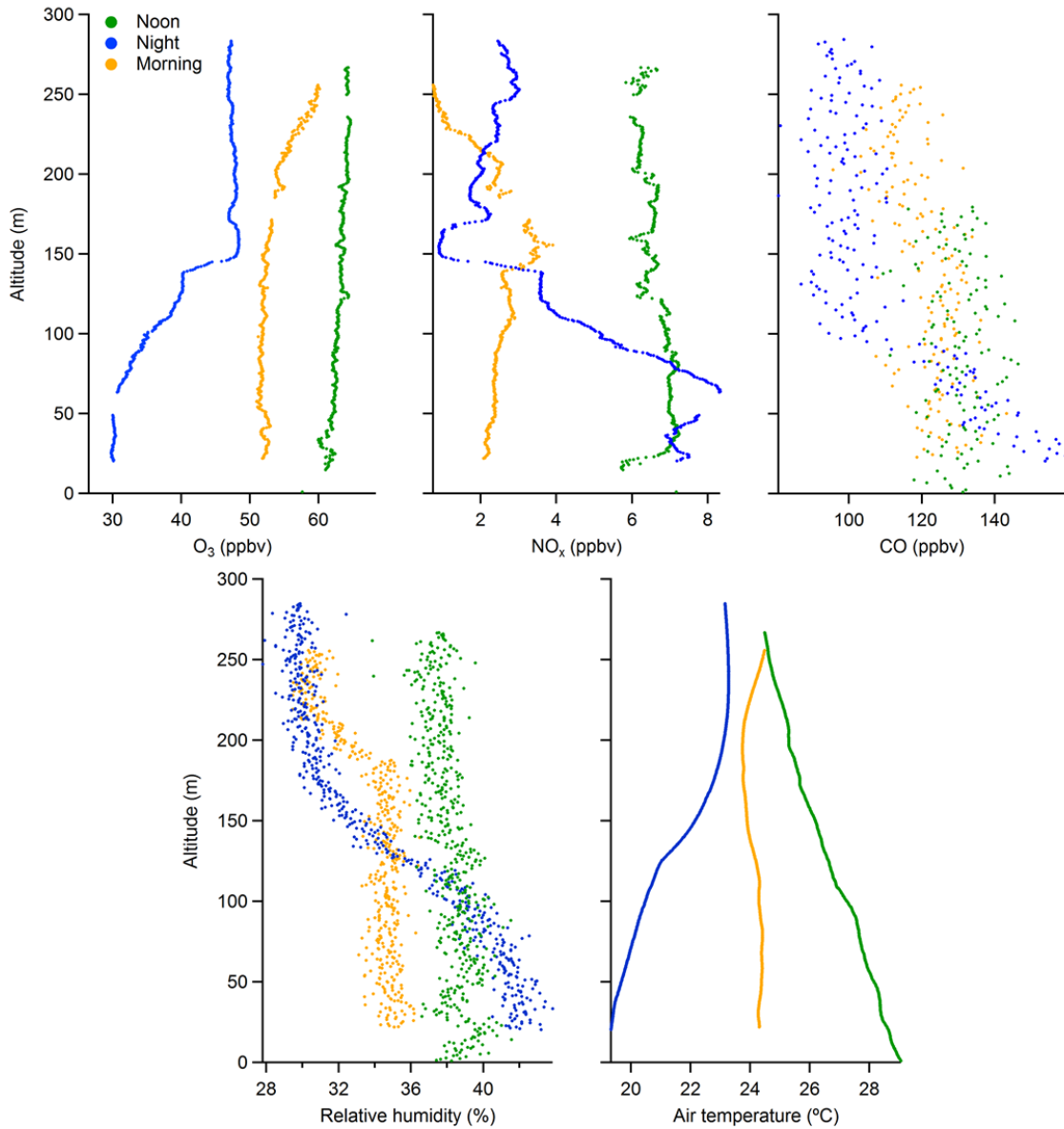


Figure S3. Vertical profiles of O₃, NO_x, CO, relative humidity, and air temperature at representative noon, night, and morning periods.

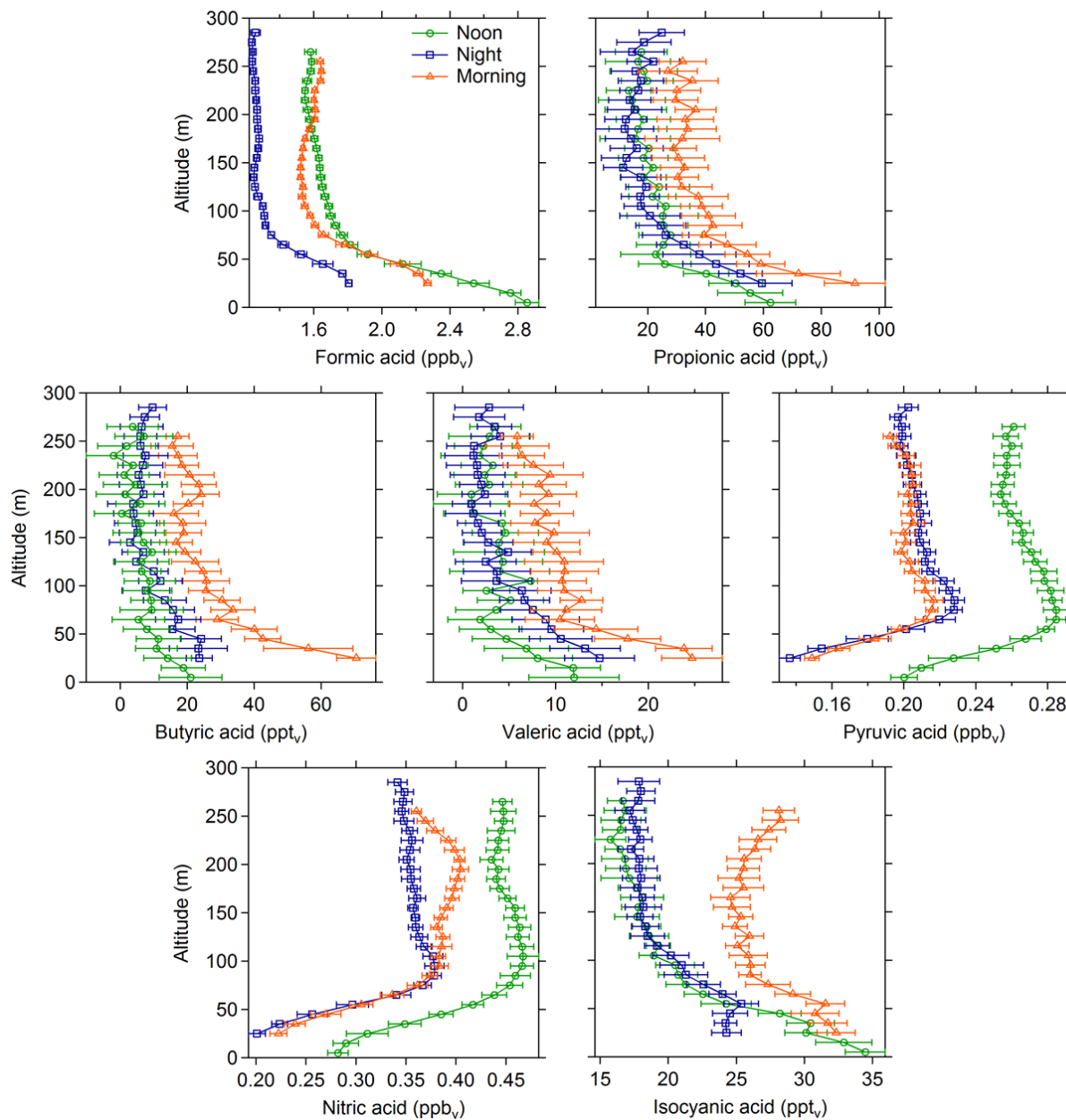


Figure S43. Vertical profiles for all detected gas-phase acids at representative noon, night, and morning periods, showing mixing ratios as a function of altitude. Data are binned by altitude (10 m per bin). Data points are means of each bin. Error bars represent \pm one standard deviation of binned values.

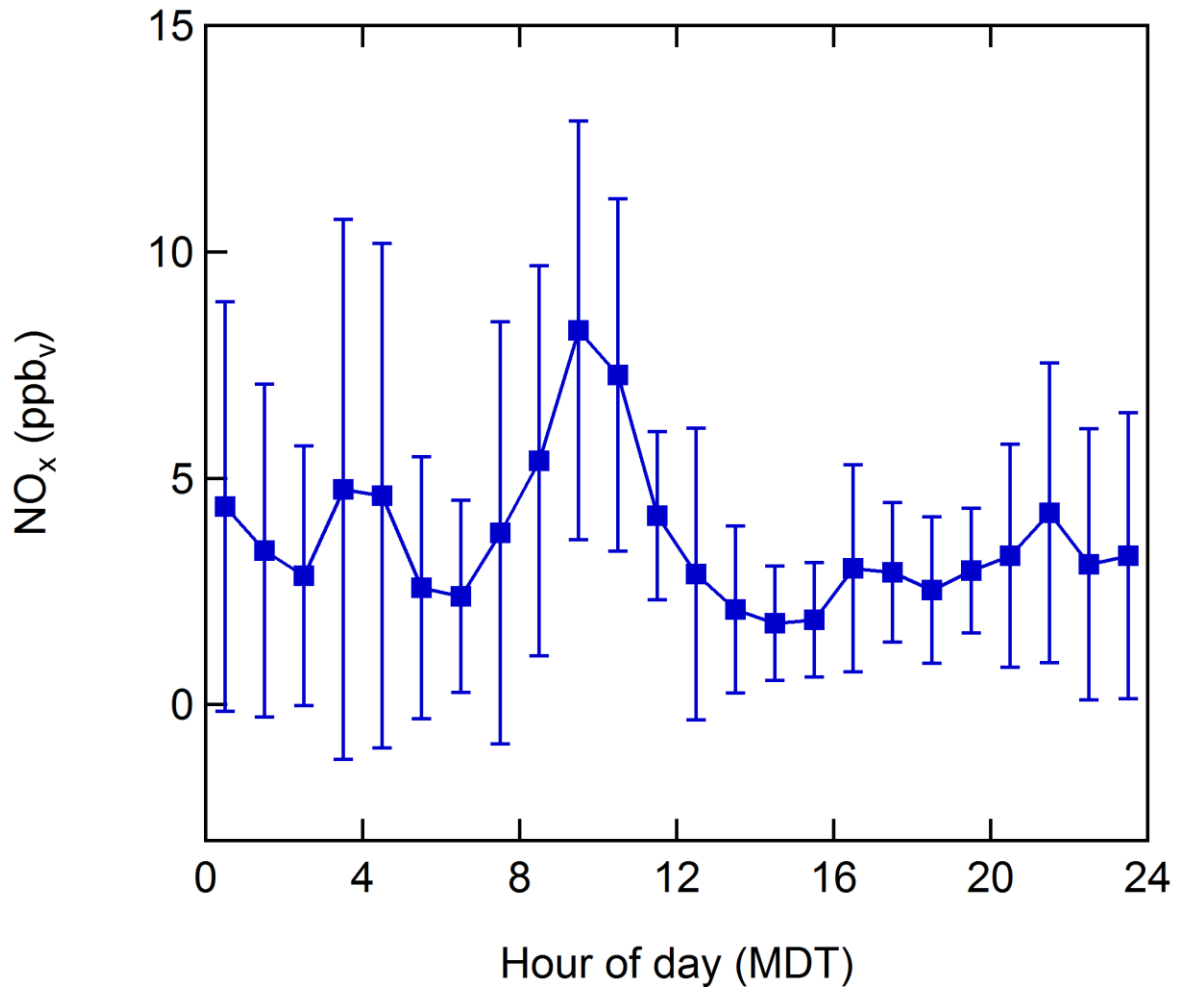


Figure S54. Diel profile of NO_x measured at the site throughout the reported measurement period. Data are binned by hour of day. Data points are binned means, and error bars are ± one standard deviation of binned data.

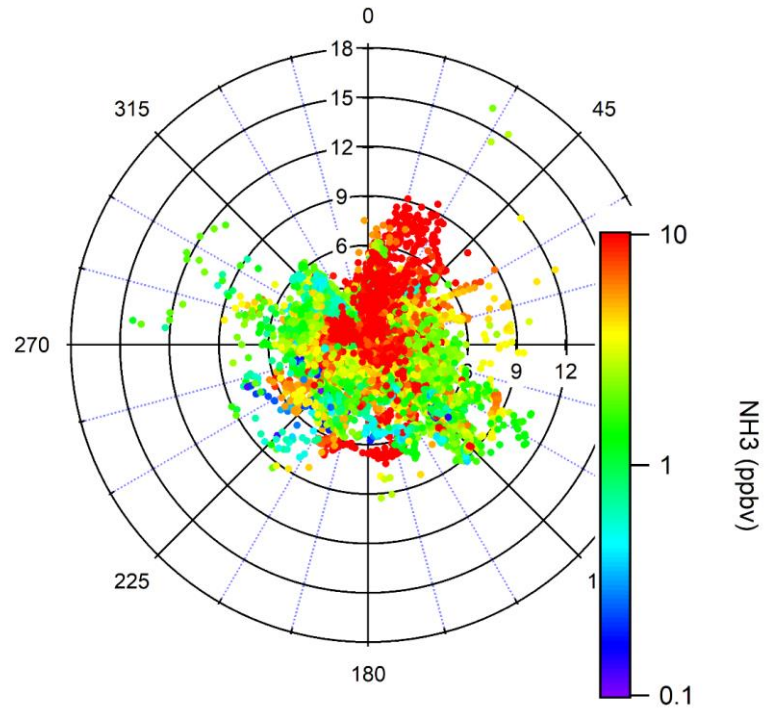


Figure S65. Wind plot of ammonia measured at the BAO tower during the reported measurement period. Data points are colored by mixing ratio. Angular axis corresponds to wind direction (degrees), with 0, 90, 180, and 270 degrees corresponding to N, E, S, and W cardinal directions, respectively. Radial axes correspond to wind speed (m s^{-1}).

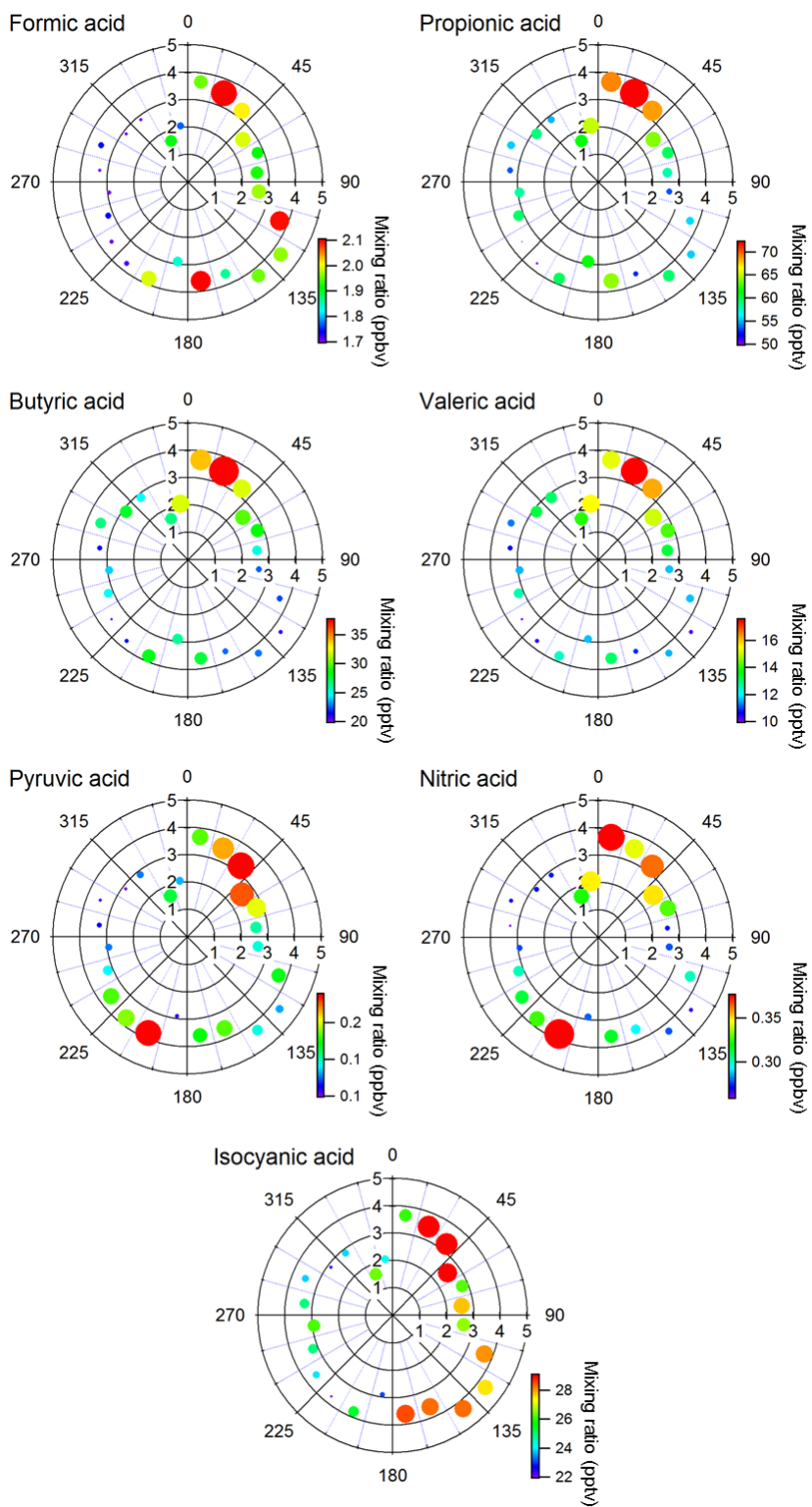


Figure S76. Radial plots with wind speed (m s^{-1}), direction (degrees), and acid mixing ratio data binned into 15° angular bins. Degrees correspond to cardinal directions (i.e. 0° is N, 90° is E, etc.). Radial positions of markers represent the diel average wind speed within each angular bin. Markers are colored and sized by the diel average mixing ratio of each acid within each angular bin.

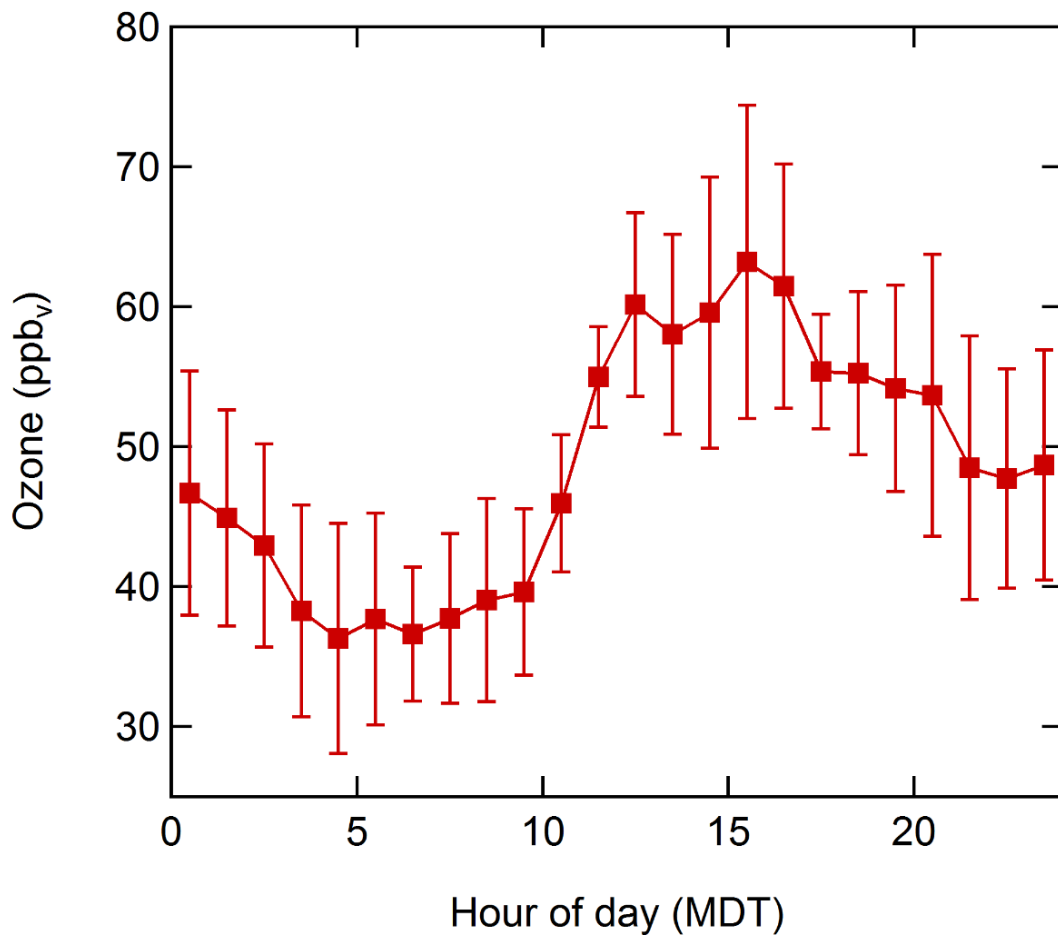


Figure S87. Diel profile of ozone measured at the site throughout the reported measurement period. Data are binned by hour of day. Data points are binned means, and error bars are \pm one standard deviation of binned data.

Supplemental Discussion

In-laboratory gas-phase acid calibrations and FRAPPE sensitivity estimations

The calibration setup shown in Figure S7 was recreated in a laboratory setting, with the heated calibration oven containing permeation standards of all gas-phase acid compounds presented here. External standard calibrations of these compounds were performed to determine ToF-CIMS sensitivities of these compounds. A sensitivity-ratio estimation was employed to estimate instrumental sensitivity of these compounds during the FRAPPE campaign:

$$S_{x,FRAPPE} = \frac{S_{x,lab}}{S_{FA,lab}} S_{FA,FRAPPE}$$

where $S_{x,FRAPPE}$ is the estimated sensitivity of a given gas-phase compound during FRAPPE, $S_{x,lab}$ is the measured sensitivity of a given gas-phase compound from in-lab calibrations, $S_{FA,lab}$ is the measured sensitivity of formic acid from in-lab calibrations, and $S_{FA,FRAPPE}$ is the mean sensitivity of formic acid during FRAPPE. A table of estimated sensitivity values for all gas-phase species measured during FRAPPE is provided below.

Gas-phase acid	Propionic	Butyric	Valeric	Pyruvic	Nitric	Isocyanic
Est. Sensitivity (ncps/ppbv)	2590	4700	6300	20400	24000	85900

Estimating NH_4NO_3 aerosol formation as sink for HNO_3

Reactions between gas-phase HNO_3 and NH_3 produce NH_4NO_3 aerosol, and therefore act as a potential tropospheric sink for gas-phase HNO_3 . Gas-particle phase partitioning is an equilibrium process that depends on ambient temperature and relative humidity (RH) (Seinfeld and Pandis, 1998; Li et al., 2014). Methods for estimating NH_4NO_3 formation from HNO_3 and NH_3 are outlined by Seinfeld and Pandis (1998). Deliquescence relative humidity (DRH) can be calculated by the following:

$$\ln(DRH) = \frac{723.7}{T} + 1.6954$$

Ambient RH at the site was below the DRH for > 90% data reported here, indicating that most NH_4NO_3 produced was in the solid phase. Neglecting aqueous phase aerosol production allows for a simplified estimation of NH_4NO_3 partitioning (as previously performed by Li et al. (2014)), which can be expressed by the following equilibrium expression:



and the accompanying equilibrium constant is therefore given by:

$$K = [NH_3][HNO_3]$$

where $[\text{NH}_3]$ and $[\text{HNO}_3]$ are the gas-phase mixing ratios of NH_3 and HNO_3 , respectively. The expected equilibrium constant, K_p , is calculated by:

$$\ln(K_p) = 84.6 - \frac{24200}{T} - 6.1 \ln\left(\frac{T}{298}\right)$$

where T is ambient temperature. Solid NH_4NO_3 formation is favorable when $K > K_p$ —i.e. when the system is supersaturated with NH_3 and HNO_3 . $K > K_p$ for < 10% of the data reported here, indicating that NH_4NO_3 formation was predominantly unfavorable, and therefore suggesting that this process does not serve as a major sink of gas-phase HNO_3 . NH_4NO_3 formation is typically less favorable when RH is low and temperature is high (Li et al., 2014), as is the case for a typical summer day in the Front Range.

Estimating aqueous-phase partitioning of gas-phase acids

Aqueous-phase partitioning was evaluated as a potential sink for gas-phase acids by using Henry's Law:

$$H_x = \frac{[X]_{aq}}{P_x}$$

where H_x is the Henry's Law constant for a given gas-phase acid, and $[X]_{aq}$ and P_x are the aqueous concentration and partial pressure of said acid species, respectively. P_x was calculated by gas-phase acid mixing ratio data, as well as meteorological data collected during the campaign. Moles of a given acid in the aqueous-phase was determined by $[X]_{aq}$ and ambient liquid water concentration (LWC). LWC in the Front Range during the summer is estimated to be around $1 \mu\text{g m}^{-3}$, based on continental estimates of LWC reported by Carlton and Turpin (2013). To account for the effects of pH on solubility, $[X]_{aq}$ was calculated as the following:

$$[X]_{aq} = H_x P_x \left(1 + \frac{K_a}{[H^+]}\right)$$

where K_a is the acid dissociation equilibrium constant for a given acid (Levanov et al., 2017; Fischer and Warneck, 1991; Borduas et al., 2016; Smith and Martell, 2004), and $[H^+]$ is the aqueous concentration of hydronium ion. Combining aqueous-phase moles of a given acid with the ideal gas law, and meteorological data from the site yields a total loss of said acid from the gas-phase through partitioning. Total loss of each acid calculated at various atmospherically-relevant pH values are reported below. This estimation is limited in that it neglects the effects of other dissolved ions on solubility, though we would not expect a change of several orders of magnitude by accounting for these effects.

	Loss via aqueous partitioning (ppbv)						
pH	Formic	Propionic	Butyric	Valeric	Pyruvic	Nitric	Isocyanic
<u>2</u>	<u>1.4E-10</u>	<u>1.4E-10</u>	<u>1.1E-10</u>	<u>5.4E-11</u>	<u>1.5E-08</u>	<u>1.8E-05</u>	<u>1.4E-10</u>
<u>3</u>	<u>1.6E-10</u>	<u>1.4E-10</u>	<u>1.2E-10</u>	<u>5.4E-11</u>	<u>8.3E-08</u>	<u>1.8E-04</u>	<u>1.6E-10</u>
<u>4</u>	<u>3.8E-10</u>	<u>1.6E-10</u>	<u>1.3E-10</u>	<u>6.1E-11</u>	<u>7.6E-07</u>	<u>1.8E-03</u>	<u>4.2E-10</u>
<u>5</u>	<u>2.5E-09</u>	<u>3.2E-10</u>	<u>2.9E-10</u>	<u>1.3E-10</u>	<u>7.6E-06</u>	<u>1.8E-02</u>	<u>2.9E-09</u>
<u>6</u>	<u>2.4E-08</u>	<u>1.9E-09</u>	<u>1.8E-09</u>	<u>8.0E-10</u>	<u>7.6E-05</u>	<u>1.8E-01</u>	<u>2.8E-08</u>

Aqueous phase partitioning was evaluated as a potential sink for gas phase acids by using Henry's Law:

$$H_x = \frac{[X]_{aq}}{P_x}$$

where H_x is the Henry's Law constant for a given gas phase acid, and $[X]_{aq}$ and P_x are the aqueous concentration and partial pressure of said acid species, respectively. P_x was calculated by gas phase acid mixing ratio data, as well as meteorological data collected during the campaign. Moles of a given acid in the aqueous phase was determined by $[X]_{aq}$ and ambient liquid water concentration (LWC). LWC in the Front Range during the summer is estimated to be around $1 \mu\text{g m}^{-3}$, based on continental estimates of LWC reported by Carlton and Turpin (2013). Combining aqueous phase moles of a given acid with the ideal gas law, and meteorological data from the site yields a total loss of said acid from the gas phase through partitioning. This estimation is limited in that it does not account for the effects of pH or other dissolved ions of a given acid's solubility, but we would not expect a change of several orders of magnitude by accounting for these effects.

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