

Ammonia sources in the California South Coast Air Basin and their impact on ammonium nitrate formation

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[1] Observations from the NOAA WP-3D aircraft during CalNex in May and June 2010 are used to quantify ammonia (NH_3) emissions from automobiles and dairy facilities in the California South Coast Air Basin (SoCAB) and assess their impact on particulate ammonium nitrate (NH_4NO_3) formation. These airborne measurements in the SoCAB are used to estimate automobile NH_3 emissions, 62 ± 24 metric tons day^{-1} , and dairy facility NH_3 emissions, 33 ± 16 to 176 ± 88 metric tons day^{-1} . Emission inventories agree with the observed automobile NH_3 :CO emission ratio, but substantially underpredict dairy facility NH_3 emissions. Conditions observed downwind of the dairy facilities were always thermodynamically favorable for NH_4NO_3 formation due to high NH_3 mixing ratios from the concentrated sources. Although automobile emissions generated lower NH_3 mixing ratios, they also can thermodynamically favor NH_4NO_3 formation. As an aerosol control strategy, addressing the dairy NH_3 source would have the larger impact on reducing SoCAB NH_4NO_3 formation. **Citation:** Nowak, J. B., J. A. Neuman, R. Bahreini, A. M. Middlebrook, J. S. Holloway, S. A. McKeen, D. D. Parrish, T. B. Ryerson, and M. Trainer (2012), Ammonia sources in the California South Coast Air Basin and their impact on ammonium nitrate formation, *Geophys. Res. Lett.*, **39**, L07804, doi:10.1029/2012GL051197.

1. Introduction

[2] Anthropogenic emissions of ammonia (NH_3) can react with nitric acid (HNO_3), resulting from NO_x emission and subsequent oxidation, to form ammonium nitrate (NH_4NO_3) aerosol in the troposphere. Tropospheric aerosols, such as NH_4NO_3 , lower visibility and can cause adverse health effects [U.S. Environmental Protection Agency (EPA), 2009a], and may also have a net cooling effect on climate by scattering solar radiation [Intergovernmental Panel on Climate Change, 2007]. The South Coast Air Basin (SoCAB) of California (www.aqmd.gov) is designated by the US Environmental Protection Agency (EPA) as being in non-attainment of the National Ambient Air Quality Standards (NAAQS) for $\text{PM}_{2.5}$ [EPA, 2009b]. In the SoCAB, secondary formation of fine aerosol nitrates, including NH_4NO_3 , accounts for a large fraction of the $\text{PM}_{2.5}$ mass [Kim *et al.*, 2010]. The conditions and sources in the SoCAB that lead to high levels of particulate NH_4NO_3 have been studied extensively [e.g., Russell and

Cass, 1986; Kleeman *et al.*, 1999]. These studies show that NH_3 mixed into areas of active urban photochemistry can form NH_4NO_3 . Thus, it is important for development of effective aerosol precursor emissions control strategies to quantify NH_3 sources and evaluate their representation in emission inventories.

[3] Confined animal dairy facilities located in the eastern SoCAB are a known NH_3 source [Russell and Cass, 1986]. The United States Department of Agriculture (USDA) California livestock inventory (www.nass.usda.gov/ca) estimated 298,000 cattle in the SoCAB in 2010. Automobiles equipped with three-way catalytic converters are an additional NH_3 source [Livingston *et al.*, 2009]. Previous studies have shown that automobile NH_3 emissions come primarily from light-duty gasoline vehicles and depend both on the driving mode and age of the vehicle [Bishop *et al.*, 2010]. In 2010 the California Department of Motor Vehicle (www.dmv.ca.gov) estimated approximately 9.9 million automobiles registered in the SoCAB. In this work, airborne measurements of NH_3 are used to quantify total NH_3 emissions from both automobile and dairy facility sources in the SoCAB, compare the two emission sources with each other and emission inventories, and assess the impact of these NH_3 sources on NH_4NO_3 formation.

2. Data

[4] A National Oceanic and Atmospheric Administration (NOAA) WP-3D aircraft flew 18 research flights from Ontario, CA between 4 May and 20 June 2010 during the CalNex 2010 experiment. Details of the instrument payload and program objectives are given at the CalNex 2010 website (esrl.noaa.gov/csd/calnex/). This analysis uses daytime measurements within the mixed layer from five flights that focused on sampling SoCAB emissions and the resulting photochemical products.

[5] Airborne observations of NH_3 , HNO_3 , particulate ammonium (NH_4^+), particulate nitrate (NO_3^-), and carbon monoxide (CO), along with meteorological parameters measured from the aircraft are used to quantify and analyze NH_3 emissions from automobiles and dairy facilities. NH_3 was measured at 1 Hz (equivalent to 100 m spatial resolution) by chemical ionization mass spectrometry (CIMS) with typical inaccuracies of $\pm(30\% + 0.2 \text{ ppbv})$ and a 1σ imprecision of 0.08 ppbv [Nowak *et al.*, 2010]. HNO_3 was measured at 1 Hz by a separate CIMS instrument with an uncertainty of $\pm(15\% + 0.040 \text{ ppbv})$ and a 1σ imprecision of 0.012 ppbv [Neuman *et al.*, 2002]. NH_4^+ and NO_3^- were measured in a pressure-controlled region downstream of a low-turbulence inlet using a compact time-of-flight aerosol mass spectrometer (Aerodyne, Billerica, Massachusetts) [Bahreini *et al.*,

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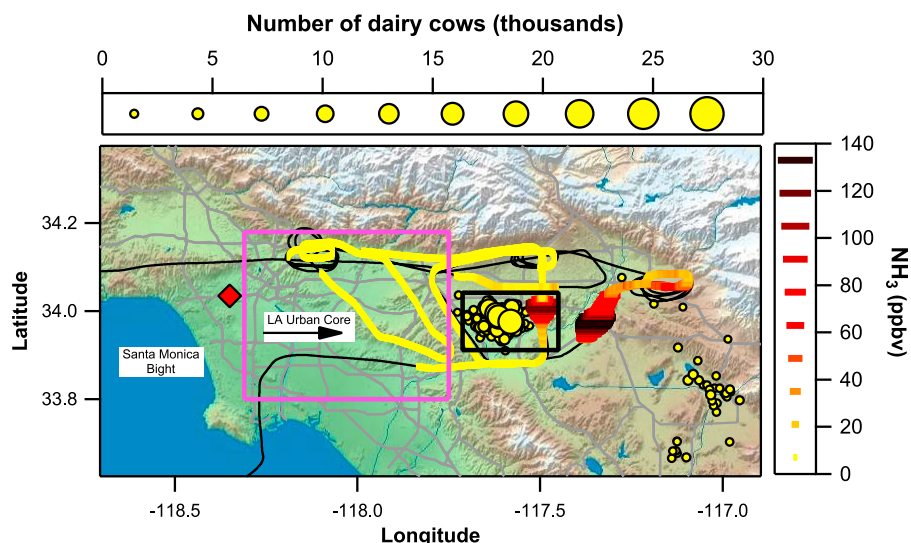


Figure 1. The WP-3D 14 May flight track (black line) through the SoCAB. Segments of the flight track in the mixed layer (<600 m above ground level) are colored and sized by NH_3 observations (scale on right). The prevailing wind direction is indicated by the black arrow. The pink box (33.80°N , 34.18°N , -118.31°W , -117.75°W) indicates the area of west Los Angeles used to compare inventory NH_3 :CO molar ratios to the WP-3D observations. The black box (33.91°N , 34.05°N , -117.70°W , -117.45°W) indicates the area used to compare inventory NH_3 emissions from the eastern SoCAB dairy farms to the NH_3 flux calculated from WP-3D observations. The dairy facility locations (yellow circles) are sized by number of dairy cows reported by *Salas et al.* [2008] (scale on top). The red diamond indicates the sampling location used by *Bishop et al.* [2010].

2009]. The NH_4^+ and NO_3^- data are reported as 10-s averages with estimated 2σ uncertainties of $\pm(34\% + 0.06 \mu\text{g Sm}^{-3})$ and $\pm(34\% + 0.01 \mu\text{g Sm}^{-3})$, respectively. The sum of gas and particle phase ammonia, NH_x , is calculated by summing the measured NH_4^+ , converted to volume mixing ratio, and measured NH_3 averaged over the 10 s NH_4^+ time base. The estimated uncertainty of calculated NH_x , determined by the sum in quadrature of NH_3 and NH_4^+ uncertainties, is approximately $\pm(45\% + 0.21 \text{ ppbv})$. Total nitrate is similarly calculated using the measured HNO_3 and NO_3^- , with an estimated uncertainty of approximately $\pm(37\% + 0.04 \text{ ppbv})$. 1 s averaged CO measurements were made by a vacuum ultraviolet fluorescence instrument with $\pm 5\%$ uncertainty and 1 ppbv imprecision [*Holloway et al.*, 2000].

3. Results

3.1. NH_3 Emissions From Automobiles in the SoCAB

[6] Observed NH_x ($\text{NH}_3 + \text{NH}_4^+$):CO enhancement ratios are interpreted as NH_3 :CO emissions ratios and used in conjunction with SoCAB CO emission inventories to quantify the NH_3 mass emissions from automobiles in the SoCAB. Gas phase NH_3 has a long photochemical lifetime, but is physically removed from the atmosphere by deposition to surfaces or uptake on particles [*Dentener and Crutzen*, 1994]. NH_x takes into account conversion of gas phase NH_3 to particulate matter. Thus, it is a more conserved quantity than NH_3 and is used here when comparing the WP-3D observations to primary emission measurements and inventory data. NH_x depositional losses are assumed to be small in these measurements immediately downwind from sources. Mobile sources, including automobiles, account for 90% of SoCAB CO emissions [*California Air Resources Board (CARB)*, 2008]. Previous work has shown good agreement

between CARB CO emissions estimates and independent measurements [*Wunch et al.*, 2009].

[7] Figure 1 shows the aircraft flight track from the 14 May flight on a map of the SoCAB and the location and size of dairy facilities [*Salas et al.*, 2008]. The prevailing winds were from the west across the basin with speeds that ranged from 2 to 7 m s^{-1} . NH_3 emissions from automobiles were measured from the WP-3D on crosswind transects downwind of the urban core and upwind of the dairy facilities on five flights: 8, 14, 16, 19 May and 20 June.

[8] NH_x :CO emissions ratios for eight transects on the five flights downwind of the urban core are determined by two methods since NH_x and CO were strongly correlated in some transects but only weakly in others due to limited atmospheric variability on some days. For transects where NH_x and CO were highly correlated ($r^2 > 0.75$), the fitted slope determined by a bivariate, linear least squares (ODR) regression analysis, weighted by $1/\sigma^2$ (where σ is the measurement imprecision: see Section 2) is taken as the emissions ratio. In addition, $\Delta\text{NH}_x/\Delta\text{CO}$, is estimated for all transects from the difference between the average upwind CO and NH_x mixing ratios near the coast or over the Santa Monica bight and the larger values in the transects downwind of the urban core. For days where both methods are applicable the NH_x :CO emissions ratios derived using the two methods agree within $\pm 30\%$.

[9] Downwind from the urban core, the NH_3 enhancements over background ranged from 1.0 to 3.3 ppbv and the NH_4^+ enhancements ranged from 0.6 to 3.2 ppbv. Less than half the urban NH_3 was partitioned to the particle phase except in the transects sampled on 16 May when $\sim 75\%$ was partitioned to the particle phase. In the three transects on 14 May, NH_x mixing ratios were enhanced 2.5 to 3.8 ppbv and positively correlated with CO (Figure A1 in Text S1 in the auxiliary

Table 1. Comparison of WP-3D Observations to Emissions Inventories

NH ₃ Source	NEI-05 ^a	CARB – ARCTAS 08 ^b	CalNex 2010 (This Work)
Automobiles (metric tons day ⁻¹) ^c	38	56	62 ± 24
Dairy facilities (metric tons day ⁻¹)	0.7 to 1.3	11	33 to 176 ^d

^aNEI-05 – 2005 EPA National Emissions Inventory [Kim *et al.*, 2011].^bCARB-ARCTAS 08 – 2008 inventory by the California Air Resources Board for the NASA Arctic Research of the Composition of the Troposphere from Aircraft and Satellites study [Huang *et al.*, 2010].^cCalculated by multiplying the inventory NH₃:CO emissions ratio by the 2008 CARB inventory CO emissions [CARB, 2008].^dRange determined from upper and lower estimates on 14 and 16 May respectively. The uncertainty for each value is estimated as ±50%.

material).¹ Emissions ratios determined from the fitted slopes ranged from 0.031 to 0.038 mol mol⁻¹ with r^2 values of 0.75 to 0.89. Emissions ratios determined using $\Delta\text{NH}_x/\Delta\text{CO}$ ranged from 0.034 to 0.054 mol mol⁻¹, higher than those from the fitted slopes but within the variability estimated for the derived NH_x mixing ratios. These methods also agree well on 16 May, the only other flight where both methods can be used. The good agreement between the two methods on these days demonstrates that an emissions ratio estimate derived from $\Delta\text{NH}_x/\Delta\text{CO}$ can be used for transects where the correlation between NH_x and CO is poor. Poor correlations on 8, 19 May and 20 June are likely due to lack of dynamic range in the CO observations for those transects. The derived SoCAB automobile NH_x:CO emissions ratios using each method are within 7% (Table A1 in Text S1) with more variability in the $\Delta\text{NH}_x/\Delta\text{CO}$ calculation. The average enhancement ratio (±1 standard deviation) of $\Delta\text{NH}_x/\Delta\text{CO} = 0.033 \pm 0.013$ mol mol⁻¹ is the SoCAB automobile NH₃:CO emissions ratio determined from the CalNex measurements. Total 2008 CO emissions for the SoCAB are reported as 3097 metric tons day⁻¹ in the CARB inventory [CARB, 2008]. Multiplying the NH₃:CO ratio from the WP-3D observations by the 2008 CARB inventory CO emissions value, the automobile NH₃ emissions to the SoCAB are estimated as 62 ± 24 metric tons day⁻¹.

[10] Bishop *et al.* [2010] report 2008 fuel-based light duty vehicle NH₃ and CO emissions in west Los Angeles (Figure 1, red diamond). From their reported mean NH₃ and CO emissions, the mean west Los Angeles automobile NH₃:CO emissions ratio is calculated as 0.061 mol mol⁻¹. Bishop *et al.* [2010] measured CO directly emitted from light duty vehicles, while the CalNex 2010 observations include all SoCAB CO sources. The 2008 SoCAB light duty vehicle CO emissions are reported as 1554 metric tons day⁻¹, approximately 50% of the total CO emissions [CARB, 2008]. Using the average NH₃:CO measured by Bishop *et al.* [2010] with the 2008 CARB SoCAB CO light duty vehicle emissions inventory, the calculated automobile NH₃ emissions to the SoCAB are 58 metric tons day⁻¹ in excellent agreement with the value estimated from the CalNex 2010 observations.

3.2. NH₃ Emissions From Dairy Facilities in the SoCAB

[11] NH₃ emissions from SoCAB dairy facilities are determined from flux calculations using airborne NH₃ data

taken in concentrated downwind plumes. The atmospheric mass flux of NH₃ from dairy facilities located in the eastern part of the SoCAB (Figure 1) is calculated by integrating crosswind transect data after subtracting the background NH₃ mixing ratio downwind of the urban core and upwind of the dairy facilities (details in the auxiliary material) [White *et al.*, 1976].

[12] The WP-3D flew three crosswind transects (Figures A3–A5 in Text S1) in the mixed layer downwind of the SoCAB dairy facilities, two on 14 May and one on 16 May. NH₃ mixing ratio enhancements (>100 ppbv) in the dairy plumes during both 14 May transects (Figure 1) were approximately two orders of magnitude larger than the 14 May automobile enhancements (Figure A1 in Text S1). The meteorological conditions during the dairy NH₃ plume observations were similar for all transects (Table A2 in Text S1). The estimated dairy facilities NH₃ flux on 14 May was 136 ± 68 metric tons day⁻¹ (western transect) and 176 ± 88 metric tons day⁻¹ (eastern transect), and 33 ± 17 metric tons day⁻¹ on 16 May. NH₃ peaked at 126 and 140 ppbv in the 14 May dairy plumes and 40 ppbv in the 16 May dairy plume. NH₄⁺ levels reached 2.7 ppbv and 2.8 ppbv in the 14 May plumes and 3.4 ppbv in 16 May dairy plume, respectively, demonstrating that most of the NH_x was in the gas phase immediately downwind of the dairy facilities.

[13] The dairy NH₃ plumes were sampled downwind 11 and 24 km (14 May) and 12.5 km (16 May) from the dairy facility cluster (Figure 1). Dry deposition is assumed to be small over these distances and has been neglected in the flux calculation. Modeling work with the Community Multiscale Air Quality (CMAQ) by Dennis *et al.* [2010] suggests that only 5 to 20% of NH₃ emissions from agricultural animal operations are deposited locally, within the 12 km by 12 km grid cell from which they were emitted. This suggests that neglecting NH₃ deposition may cause a slight underestimation of emissions, but the bias is much smaller than the uncertainties in the flux determinations and unlikely to account for the differences between 14 and 16 May.

[14] NH₃ emissions from dairy facilities can be variable, ranging from 0.82 to 250 g day⁻¹ cow⁻¹, and depend on a variety of factors as discussed by Hristov *et al.* [2011] and references therein. The large difference between the 14 and 16 May estimated NH₃ fluxes may be due to the variability in dairy facility NH₃ emissions. Based on these dairy plume measurements of NH₃ and NH₄⁺, NH₃ emissions from the SoCAB dairy facilities are estimated to range from 33 ± 16 to 176 ± 88 metric tons day⁻¹.

3.3. Comparison to Emission Inventories

[15] Automobile and dairy facility NH₃ emissions derived from the WP-3D airborne in situ measurements are compared to two emission inventories (Table 1). Inventory emissions are calculated for the western SoCAB area (Figure 1, pink box), which is upwind of the dairy facilities and used as the basis for determining automobile NH₃:CO emissions ratios in the inventories. The NH₃:CO emissions ratio for this area from the NEI-05 [Kim *et al.*, 2011] NH₃ and CO emissions is 0.020 mol mol⁻¹ (38 metric tons day⁻¹ multiplying by 2008 CARB inventory CO emissions [CARB, 2008]). The CARB-ARCTAS 08 inventory [Huang *et al.*, 2010] NH₃:CO emissions ratio is 0.030 mol mol⁻¹ (56 metric tons day⁻¹ multiplying by 2008 CARB inventory CO emissions [CARB,

¹Auxiliary materials are available in the HTML. doi:10.1029/2012GL051197.

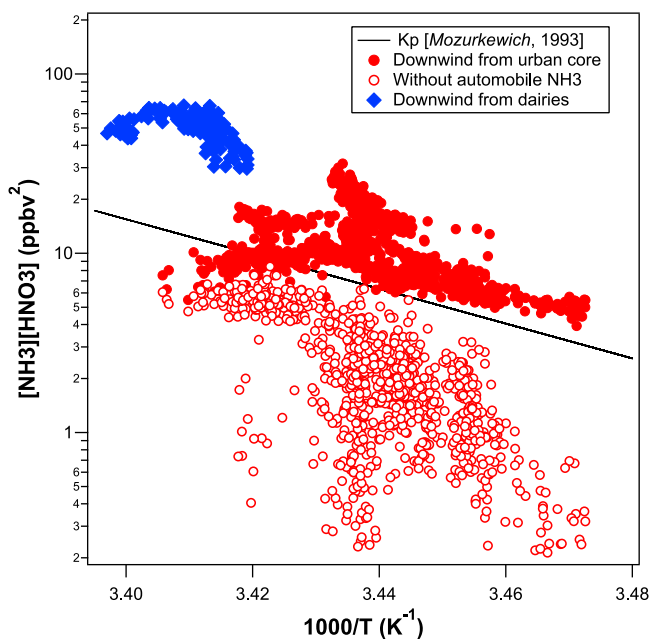


Figure 2. The theoretical solid NH_4NO_3 dissociation constant (K_p) [Mozurkewich, 1993] (black line), the observed urban core NH_3 and HNO_3 partial pressure product (solid circles), the estimated urban core NH_3 and HNO_3 partial pressure product without automobile NH_3 emissions (open circles), and the observed NH_3 and HNO_3 partial pressure product in the dairy plumes (blue diamonds) for the 14 May flight plotted as a function of ambient temperature.

2008]). Although the $\text{NH}_3\text{:CO}$ emissions ratios in both inventories are lower than the 0.033 ± 0.013 emissions ratio derived from the WP-3D measurements in the western SoCAB during CalNex 2010, the difference between the observations and inventories is within the estimated uncertainty of the observations.

[16] Dairy facility NH_3 emissions from the inventories are determined for an area encompassing the SoCAB dairy facilities (Figure 1, black box). The NEI-05 NH_3 area emissions from the SoCAB dairy facilities are 0.74 metric tons day^{-1} and the total NH_3 emissions from this region are 1.27 metric tons day^{-1} . Both are significantly lower than derived from the WP-3D observations (Table 1). Total CARB-ARCTAS 08 NH_3 emissions from this region are 10.97 metric tons day^{-1} . The NEI-05 underpredicts NH_3 emissions from the SoCAB dairies by factors of 10 to 100 in both the area and total categories, indicating that the inventory emissions are low and not just incorrectly apportioned. The CARB-ARCTAS 08 inventory also underpredicts NH_3 emissions from the SoCAB dairies by factors of 3 to 20. The underestimation of the dairy NH_3 emissions in the inventories, both in absolute magnitude and relative to automobile emissions, may be sufficiently large that current air quality models may not correctly predict particle concentrations, as discussed below.

4. Implications for Aerosol Control Strategies

[17] Atmospheric observations during CalNex in May 2010 show the total mass of NH_3 emitted to the atmosphere is similar for automobiles (62 metric tons day^{-1}) and dairy facilities (33 to 176 metric tons day^{-1}). However, the dairy

facility NH_3 sources are more spatially concentrated, resulting in much higher NH_3 mixing ratios. Automobile NH_3 emissions led to maximum NH_x enhancements ranging from 2 to 7 ppbv. In contrast, under similar meteorological conditions, dairy facility emissions led to NH_3 mixing ratios exceeding 100 ppbv downwind of the dairies. The average total nitrate ($\text{HNO}_3 + \text{NO}_3^-$) observed during the 14 and 16 May transects was similar both downwind of the urban core (2.3 ppbv to 5.1 ppbv) and downwind of the dairies (2.2 ppbv to 3.4 ppbv). However, more nitrate was in the particle phase downwind of dairies (51% to 68%) than downwind of the urban core (16%). The highly concentrated NH_3 plumes from dairy facilities had a more significant impact on aerosol formation and its subsequent air quality effects.

[18] The impact of these two NH_3 source types on SoCAB NH_4NO_3 aerosol formation is determined from their effect on gas-to-particle partitioning, which is explored here by using measurements of NH_3 , HNO_3 and the thermodynamics of NH_4NO_3 . The theoretical equilibrium dissociation constant (K_p) for solid NH_4NO_3 is calculated as a function of ambient temperature [Mozurkewich, 1993]. This provides an upper limit for the NH_4NO_3 dissociation constant, since this value is typically reduced when a particle deliquesces and/or the NH_4NO_3 ionic strength decreases [Stelson and Seinfeld, 1982]. Thus, if the observed NH_3 and HNO_3 partial pressure product is greater than K_p , conditions are thermodynamically favorable for NH_4NO_3 formation regardless of particle phase or composition.

[19] Non-equilibrium conditions (i.e., the NH_3 and HNO_3 partial pressure product $> K_p$) can exist if the volatile gas phase species (e.g., NH_3 or HNO_3) and/or particle concentrations are changing faster than the transport of mass between the gas and particle phase. Modeling studies show that the equilibration time between gas phase species and submicron particles ranges from a few minutes to less than a few hours [Meng and Seinfeld, 1996].

[20] Observations from 14 May are used as a case study (Figure 2) to assess the effect of NH_3 emissions on NH_4NO_3 equilibrium. The urban core NH_3 and HNO_3 partial pressure product in the absence of automobile NH_3 emissions is estimated by subtracting the automobile contribution from the observed NH_3 mixing ratios and multiplying by the observed HNO_3 . The NH_3 mixing ratio from automobiles is determined as $\Delta\text{NH}_x/\Delta\text{CO} \times (\text{CO} - \text{CO}_{\text{background}})$, where $\text{CO}_{\text{background}}$ is the upwind background mixing ratio near the coast or over the Santa Monica bight (as in Section 3.1) and $\Delta\text{NH}_x/\Delta\text{CO}$ is the emissions ratio for each individual transect.

[21] The observed urban core NH_3 and HNO_3 partial pressure product (Figure 2, solid circles) is greater than K_p for most of the SoCAB observations on this day. However, the NH_3 and HNO_3 partial pressure product calculated in the absence of automobiles (Figure 2, open circles) is significantly lower than K_p . This shows that automobile NH_3 emissions may create conditions favorable for NH_4NO_3 formation, but in the absence of these automobile NH_3 emissions, particle formation is not thermodynamically favored. The average total nitrate observed in the urban core transects on 14 May was 2.7 ppbv with only 16% in the particle phase.

[22] The observed dairy facility plume NH_3 and HNO_3 partial pressure product (Figure 2, blue diamonds) was much greater than K_p , even though HNO_3 levels were reduced because of the high NH_3 mixing ratios. The average total

nitrate observed in the dairy facility plumes on 14 May was 2.7 ppbv (western transect) and 2.2 ppbv (eastern transect) with 51% and 68%, respectively, in the particle phase indicating that the additional NH_3 from the dairies caused most of the HNO_3 to partition into the particle phase.

[23] This case study demonstrates that SoCAB NH_3 sources have a significant effect on NH_4NO_3 formation. Because of their spatial concentration and high emission rates, dairy facility NH_3 emissions shift the NH_4NO_3 equilibrium towards the particle phase and result in higher NH_4NO_3 concentrations downwind of the dairies than downwind of the urban core, even though total NH_3 emissions and total ambient nitrate levels were similar. Airborne transects further downwind of the dairies showed that NH_4NO_3 concentrations continues to increase as additional photochemically produced HNO_3 mixed into the still concentrated NH_3 dairy emissions (Figure 1). Increases in NH_4NO_3 concentrations driven by the NH_3 dairy emissions impacts the air quality of 4.2 million people (<http://www.census.gov/>) downwind of the dairy facilities in the eastern portion of the SoCAB.

[24] This suggests that an aerosol precursor control strategy addressing the dairy NH_3 source would have the larger impact on reducing SoCAB NH_4NO_3 formation. Dairy NH_3 emissions cause downwind NH_3 mixing ratios a factor of 10 higher than those from automobile emissions, leading to enhanced gas-to-particle conversion. The airborne data also show that dairy emissions account for roughly half of the total NH_3 mass emitted into the SoCAB atmosphere. While the SoCAB automobile NH_3 emissions also can create favorable conditions for NH_4NO_3 formation, without the dairy NH_3 emissions most of the HNO_3 remained in the gas phase. It was not until the dairy NH_3 emissions were added that most of the HNO_3 was driven to the particle phase.

[25] Even if the dairy NH_3 emissions are effectively addressed in the SoCAB, automobile NH_3 emissions could still lead to NH_4NO_3 formation in the SoCAB. Though the automobile fleet NH_3 emissions are decreasing [Kean *et al.*, 2009], the use of urea-based selective catalytic reduction technology to reduce diesel NO_x emissions is potentially an additional mobile NH_3 source [Heeb *et al.*, 2011] that could contribute to additional NH_4NO_3 formation in the future.

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