Wintertime Spatial Distribution of Ammonia and its Emission Sources in the Great Salt Lake Region

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Abstract

Ammonium-containing aerosols are a major component of winter time air pollution in many densely populated regions around the world. Especially in mountain basins, the formation of persistent cold air pool (PCAP) periods can enhance particulate matter with diameters less than 2.5 μm (PM\textsubscript{2.5}) to levels above air quality standards. Under these conditions, PM\textsubscript{2.5} in the Great Salt Lake Region of northern Utah has been shown to be primarily composed of ammonium nitrate, however, its formation processes and sources of its precursors are not fully understood. Hence, it is key to understand the emission sources of its gas-phase precursor, ammonia (NH\textsubscript{3}). To investigate the formation of ammonium nitrate, a suite of trace gases and aerosol composition were sampled from the NOAA Twin Otter aircraft during the Utah Winter Fine Particulate Study (UWFPS) in January and February 2017. NH\textsubscript{3} was measured using a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS), while aerosol composition, including particulate ammonium (pNH\textsubscript{4}), was measured with an aerosol mass spectrometer (AMS). The origin of the sampled air masses was investigated using the Stochastic Time-Inverted Lagrangian Transport (STILT) model and combined with an NH\textsubscript{3} emission inventory to obtain model-predicted NH\textsubscript{3} (= NH\textsubscript{3} + pNH\textsubscript{4}) enhancements. Comparison of these NH\textsubscript{3} enhancements with measured NH\textsubscript{3} from the Twin Otter shows that modelled values are a factor of 1.6 to 4.4 lower for the three major valleys in the region. Among these, the underestimation is largest for Cache Valley, an area with intensive agricultural activities. We find that one explanation for the underestimation of wintertime emissions may be the seasonality factors applied to NH\textsubscript{3} emissions from livestock. An investigation of inter-valley exchange...
revealed that transport of NH$_3$ between major valleys was limited and PM$_{2.5}$ in Salt Lake Valley (the most densely populated area in Utah) was not significantly impacted by NH$_3$ from the agricultural areas in Cache Valley. We found that in Salt Lake Valley around two thirds of NH$_3$ originated within the valley, while about 30% originated from mobile source and 60% from area source emissions in the region. For Cache Valley, a large fraction of NO$_x$ potentially leading to PM$_{2.5}$ formation may not be locally emitted but mixed in from other counties.

1 Introduction

Ammonia (NH$_3$) is a key atmospheric pollutant, with significant impacts on air quality, climate, and ecosystem nitrogen availability. As the most abundant base in the atmosphere, NH$_3$ is an important precursor gas for secondary aerosol particle formation. As a result, ammonium-containing aerosols may comprise a significant amount of the particulate matter with a diameter of 2.5 µm or less (PM$_{2.5}$) (Pozzer et al., 2017). High levels of PM$_{2.5}$ impact human health by increasing the risk for stroke, heart disease, lung cancer, and both chronic and acute cause respiratory deceases (WHO, 2016). Especially in urban areas, where a mix of pollutants such as nitrogen oxides (NO$_x$), sulfur dioxide (SO$_2$) or volatile organic compounds (VOCs) are present in elevated concentrations alongside NH$_3$, ammonium-containing aerosol can be a major source of PM$_{2.5}$. For example, NH$_3$ emitted from agricultural activities may be transported towards NO$_x$-rich urban centres to form ammonium nitrate (NH$_4$NO$_3$) or ammonium sulfate ((NH$_4$)$_2$SO$_4$) aerosols (e.g., Zhao et al., 2017). This illustrates the importance of the transport and meteorological conditions in mixing the precursors that lead to secondary particle formation.

During the winter season, cold temperatures in combination with high pressure systems result in shallow boundary layers that trap and promote the build-up of pollutants near the surface, leading to enhanced secondary aerosol formation and winter smog. Periods with strong atmospheric stability are referred to as persistent cool air pool (PCAP) periods (Whiteman et al., 2014), typically featuring a temperature inversion below the height of the surrounding terrain. In addition, the topography of mountain basins promotes the evolution of strong PCAP periods and thereby the confinement of pollutants near the surface. Under these conditions, urban areas such as Salt Lake City frequently experience high PM$_{2.5}$ concentrations. In the Great Salt Lake Region in northern Utah, the 24-hr U.S. National Ambient Air Quality Standard (NAAQS) for PM$_{2.5}$ (35 µg m$^{-3}$) is exceeded on average 18 days per winter (Silcox et al., 2012; Whiteman et al., 2014). Previous measurements made in the Salt Lake Valley (Kelly et al., 2013; Kuprov et al., 2014) and recently published analysis of the UWFPS aerosol composition (Franchin et al., 2018) agree that during PCAP periods up to 75% of wintertime PM$_{2.5}$ is ammonium nitrate.

To develop appropriate PM$_{2.5}$ mitigation strategies in such areas where ammonium nitrate is high, it is essential to understand the mechanisms of local ammonium nitrate formation as well as the emission source of its precursor gases NO$_x$ and NH$_3$. While emissions of NO$_x$ are regulated, NH$_3$ is not regulated as a criteria air pollutant (CAP) in the U.S. As a consequence, NH$_3$ emissions are not reported by NH$_3$ emitting industries or sectors to the same extent as other CAPs, resulting in higher
uncertainties of NH₃ emission estimates. In addition, observational networks for NH₃ are sparse compared to those for NOₓ, which is in part related to the challenges in the measurement of NH₃. Therefore, improving the understanding of NH₃ sources is key to making reliable predictions of ammonium-aerosol formation and finding the appropriate mitigation strategies for PM₂.₅.

To understand the sources of NH₃ in the Great Salt Lake Region, which are responsible for ammonium-aerosol formation and high levels of PM₂.₅ in winter, we studied the spatial distribution of NH₃ in the three mountain basins as part of the Utah Winter Fine Particulate Study (UWFPS) (UWFPS report, 2018). The spatial distribution of NH₃ was measured from a Twin Otter aircraft and compared to NH₃ measurements from several ground stations in the region. The main objectives of this study are to identify the sources of NH₃ and the key emission sectors contributing to the regional formation of ammonium-aerosol. To address these objectives, airborne measurements were compared to emission inventory-based NH₃ estimates. A footprint approach based on the Stochastic Time-Inverted Lagrangian Transport (STILT) model was used to estimate contributions from NH₃ source regions, while the results are discussed for the three major valleys in the study region. Finally, the exchange of air masses between valleys is investigated and discussed in respect to its role for ammonium-aerosol formation in the region.

2 Methods

2.1 Study area and the Utah Winter Fine Particulate Study (UWFPS)

The Utah Winter Fine Particulate Study (UWFPS) was carried out in January and February 2017 in the Great Salt Lake Region. The Great Salt Lake Region is located in northern Utah in the U.S. Western Rocky Mountains, comprised of three major mountain valleys (Salt Lake Valley, Utah Valley, and Cache Valley) and the Great Salt Lake (Fig. 1a). Salt Lake City, the most populated urban area in Utah and part of the Salt Lake City metropolitan area (1.2M inhabitants), is situated in the northern part of Salt Lake Valley bordering the Great Salt Lake. Cache Valley (125k inhabitants), north of Salt Lake Valley, is separated by a branch of the Wasatch Range from the North Metropolitan Area and is characterized by its intensive agricultural activities, including concentrated animal feeding operations (CAFOs). The regulatory environment of Cache Valley straddles the states of Utah and Idaho and comes under the jurisdiction of two different US EPA regions (8 and 10). Utah Valley (575k inhabitants) borders Salt Lake Valley to the south via the Traverse Mountains and features Utah Lake, a large freshwater lake in the valley centre, and agricultural and industrial activities, including a major gas-fuelled power plant. The objective of the UWFPS was to investigate wintertime air quality in the Salt Lake region, focusing on PCAP periods when formation of ammonium nitrate leads to high levels of PM₂.₅. NOAA’s Twin Otter aircraft flights and ground site observations in each valley were used to probe the spatial distribution of trace gases and aerosols, with the aim of identifying their importance for PM₂.₅ and its formation mechanisms. A further objective of UWFPS was to investigate key emission sources of aerosol precursors and the role of agricultural, industrial, urban, mobile, home heating and natural emission sectors.
From 16 January to 12 February 2018 a total of 23 research flights were carried out with the Twin Otter aircraft. Flights were performed in a north and south flight pattern, where the north pattern covered the North Metropolitan area, Cache Valley, Bear Valley, the Great Salt Lake, Tooele Valley and the Northern part of Salt Lake Valley. The South leg mainly encompassed Salt Lake Valley and Utah Valley. Figure 1 shows the region and county boundaries as well as a typical distribution of NH$_3$ mixing ratios measured from the aircraft. Measurements were taken from ground level at the Salt Lake International Airport (1288 m, 5225 ft) through 3800 m (12500 ft) a.s.l. when flying over inter-valley mountain ranges (Fig. S1b). The lowest cruising altitude was around 150 m (500 ft) above ground level. To probe vertical profiles near the surface, missed approaches were performed at seven different air fields throughout the region (Fig. S1b).

2.2 Airborne ammonia measurements

A continuous wave Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS, Aerodyne research Inc., MA) (Ellis et al., 2010) was employed on the Twin Otter aircraft for measurements of NH$_3$ (see Fig. 2). The instrument uses a multi-pass absorption cell (0.5 L, 76 m effective path length) which is purged with sample air to measure NH$_3$. Due to its fast time response and high precision compared to other commercially available NH$_3$ analyzers, the instrument is suited for aircraft measurements (Hacker et al., 2016). Prior to installation on the Twin Otter, the weight of the single laser instrument (QC-mini) was further reduced by using a smaller vacuum pump (SH-110, Varian Inc., MA) for generating the sample flow rate. The 4 L min$^{-1}$ flow rate through the sample cell was set by the critical orifice of a PFA (Teflon) virtual impactor, which acted as a particulate matter filter to avoid interferences from thermally dissociated ammonium aerosol and also to protect the cell mirrors. That thermal dissociation of ammonium aerosol was negligible is shown by measurement periods where NH$_3$ was within the instrument’s detection limit despite high levels (> 20 ppbv) of measured particulate ammonium. As adsorption and desorption processes within the inlet system are major challenges for NH$_3$ measurements, the time response of the system was optimized by introducing an additional bypass flow rate of 16 L min$^{-1}$ to purge the inlet line (PFA, 3/8” OD). The winglet that housed the inlet tubing was mounted directly above the QC-TILDAS allowing an inlet length of only 0.5 m. To further, minimize adsorption and desorption effects of NH$_3$ and humidity to the tubing wall, the winglet was heated to 40°C.

Variations in pressure, temperature and instrument vibrations may significantly impact the instrument performance by influencing the absorption spectrum fringe pattern. Fringes are periodic structures in the absorption spectrum which are caused by optical interferences within the laser beam path and can be responsible for signal drift if their pattern changes over time. To account for changing ambient pressures with flight altitude, a pressure controller (PC3P, Alicat Scientific Inc., AZ) was installed downstream of the absorption cell, which was able to keep the cell pressure at a constant value between 36.5 and 38.5 Torr. Inflight background measurements were performed manually approximately every 5 to 15 min to account for potential instrument drifts using zero air from an ultra-zero air cylinders.
The precision of the instrument during the campaign was significantly degraded from its usual performance due to difficulties with the laser source. As a result, NH$_3$ absorption was detected at 965.3 cm$^{-1}$ instead of using the stronger absorption line at 967.3 cm$^{-1}$. A measurement precision at 1 Hz sample frequency of 150 ppt (1σ) could be achieved, which is similar to the background noise (200 pptv) of a QC-TILDAS that was operated by Hacker et al. (2016) on a different aircraft. Accordingly, the limit of detection (3σ) was 450 pptv at 1 Hz and 90 pptv for a 30 s averaging interval. Due to the effect of increased gravitational forces and vibrations on the optical alignment, data during take-off, landings and spiralling ascents and descents were not used in this study.

2.3 Airborne measurements of other trace gases and aerosols

The Twin Otter aircraft was equipped with an Aerosol Mass Spectrometer (AMS, Aerodyne Research Inc., MA) to measure the chemical composition of the non-refractory aerosol particles in the 70 to 800 nm range (NR-PM1) (Drewnick et al., 2005; Jayne et al., 2000). The operation of the AMS during UWFPS is described in detail in Franchin et al. (2018). In brief, ambient aerosol particles are focused in an aerodynamic lens, evaporated, ionized with electron-impact ionization and detected by a mass spectrometer. The AMS measured mass loadings of particulate nitrate (pNO$_3$), ammonium (pNH$_4$), organic species, sulfate (pSO$_4$), chloride (pCl), and total aerosol mass, with detection limits of 0.04, 0.09, 0.33, 0.03, 0.07, and 0.38 μg m$^{-3}$ respectively. The uncertainty on the total AMS mass concentrations is estimated to be 20% (Bahreini et al., 2008). Aerosol mass with the AMS was well-correlated with aerosol volume measured with an Ultra High-Sensitivity Aerosol Spectrometer (UHSAS, Droplet Measurement Technologies, CO) on the same sampling line as the AMS.

Nitrogen oxides (NO$_x$ = NO + NO$_2$), total reactive nitrogen (NO$_y$) and ozone (O$_3$) were measured at 1 Hz using the NOAA nitrogen oxides cavity ringdown instrument (NOxCaRD). The instrument measures NO$_2$ directly by optical absorption at 405 nm, while NO and O$_3$ are measured in two separate channels after quantitative conversion to NO$_2$ by reaction with excess O$_3$ or NO, respectively (Fuchs et al., 2009; Washenfelder et al., 2011). A fourth channel measures NO$_y$ by conversion to NO and NO$_2$ in a heated quartz inlet (650 °C) and subsequent conversion of NO to NO$_2$ in excess O$_3$ (Wild et al., 2014). Accuracies for NO$_x$, NO$_2$ and O$_3$ were 5% and 12% for NO$_y$, based on previous comparison of the NO$_y$ measurement to a standard NO$_y$ instrument (Wild et al., 2014).

A commercial probe (Avantech) measured meteorological parameters (ambient temperature, pressure, relative humidity with respect to liquid water, wind speed, and wind direction), the global positioning satellite (GPS) location including altitude above sea level, and aircraft parameters (heading, pitch, and roll). Wind data were compromised for some flights, making only partial coverage available. The aircraft GPS altitude above sea level was converted into altitude above ground level using USGS data (https://gis.utah.gov/data/elevation-and-terrain/).
2.4 Ground site observations

During UWFPS, a series of ground measurements were conducted to measure the evolution of trace gases, aerosols and meteorology during the pollution episodes in the study region. Data used in this study were taken from the University of Utah ground site (UU) in Salt Lake Valley (40.7663, -111.8477), the Logan ground site (L4) in Cache Valley (41.7589, -111.8151) and the North Provo ground site (NP) in Utah Valley (40.2528, -111.6627) (Fig. 1c). The Logan ground site is referred to as L4 as it is located approximately 3 km north east from the actual downtown federal reference site (named L4).

The UU site is located on the top floor of William Browning Building on the University of Utah campus, which is situated on the north east side of the Salt Lake Valley, and approximately 150 m above the valley floor. A sampling inlet was located on top of a 7 m observation tower, at a height of 40 m a.g.l. Online measurements of ambient air PM$_{2.5}$ composition and gas phase precursors were performed using University of Toronto’s modified Ambient Ion Monitoring System (AIM 9000D, URG Corp., NC) coupled with two ion chromatographs (Dionex ICS-2000, Thermo Fisher Scientific, ON). The system measures water soluble gases (NH$_3$, SO$_2$, HNO$_3$) and particles (pNH$_4$, pSO$_4$, pNO$_3$) at an hourly resolution using parallel wet denuders (Markovic et al., 2012). Continuous PM$_{2.5}$ mass concentrations were determined using the 8500 Filter Dynamics Measurement System (FDMS) coupled with a TEOM 1400ab ambient particulate monitor. Instrumental background measurements were conducted by introducing an overflow of zero air into the AIM-IC inlet and sampled for a 24-hr period. Based on background experiments, the 3σ detection limits were determined to be 0.15 ppb for NH$_3$ and 0.3 µg m$^{-3}$ (at STP) for pNH$_4$.

The L4 ground site was a temporary sampling station during UWFPS, located on the Utah State University campus in Logan, employing an environmentally controlled shelter with the inlet extending through the shelter roof to a height of 5 m a.g.l. Ambient mixing ratios of NH$_3$ were obtained with a Picarro G2508 cavity-ringdown spectroscopy instrument (Picarro Inc., CA). The analyzer collected on a nominal 5 s sampling frequency, which is averaged up to 1 min sample periods. At one minute averaging times the G2508 has a precision of <3 ppbv and measured detection limit (3σ) of 2.3 ppb. A Teledyne API T640 measured continuous mass concentrations of PM$_{2.5}$, PM$_{10}$, and PM$_{10-2.5}$ at the L4 ground site.

At the NP site, mass concentration of PM$_{2.5}$ was monitored by the Utah Division of Air Quality using a 1405-DF TEOM Continuous Dichotomous Ambient Air Monitor (Thermo Fisher Scientific Inc., MA). No NH$_3$ measurements were available from this site.

2.5 The UDAQ emission inventory

To better understand the formation of ammonium nitrate in the study region, it is important to identify and quantify the major sources of NH$_3$. In northern Utah, NH$_3$ from livestock, fertilizer and on-road vehicle emissions are the most dominant NH$_3$ sources, according to the emission inventory provided by the Utah Division of Air Quality (UDAQ). The Utah emissions inventory is created by UDAQ and ultimately informs the emissions estimates found in the U.S Environmental Protection
Agency’s (EPA) National Emission Inventory (NEI). Yearly totals of county-wide emission data for criteria and other significant air pollutants (NO\textsubscript{x}, VOC, direct PM\textsubscript{10}, direct PM\textsubscript{2.5}, NH\textsubscript{3}, SO\textsubscript{2}, CO, and others) are processed in the SMOKE v3.6.5 (Sparse Matrix Operator Kernel Emissions) emissions processing software to obtain higher temporally and spatially resolved emission estimates (Baek and Seppanen, 2018). UDAQ uses two modelling domains: (1) a larger 4 km resolution outer-domain covering the State of Utah and portions of surrounding states and (2) a smaller 1.33 km inner-domain covering the Wasatch Range and Cache Valley, representing the majority of the PM\textsubscript{2.5} non-attainment area in northern Utah. Temporal allocation in SMOKE consists of defining emission distributions through the use of monthly, weekly and hourly profiles, which are applied to the yearly emission totals.

Inventory data are compiled for four distinct emission sectors: area, non-road, mobile and point sources. Total estimated daily NH\textsubscript{3} emissions from each sector are given in Table 1 for the regions in the study area. NH\textsubscript{3} emissions in all regions are dominated by areas sources with the exception of Salt Lake Valley, where NH\textsubscript{3} from mobile sources are thought to be dominant. Area sources include NH\textsubscript{3} emissions from fertilizer applications, livestock and residential wood combustion. Emissions from livestock are the largest portion of area sources in Utah County (71%) and Cache County (81%), while they are only minor in Salt Lake County (11%). The NEI-based NH\textsubscript{3} emissions from livestock are based on county-level animal populations, which are multiplied by daily-resolved emission factors that are representative for each animal type and management practice. These location-specific emission factors are produced by a Farm Emission Model (FEM) for each day of the modelled year by taking meteorological as well as animal type and practice input data (McQuilling and Adams, 2015). For the compilation of NH\textsubscript{3} emissions from fertilizer applications, a bi-directional exchange model uses meteorological and application-based input data. The Environmental Policy Integrated Climate (EPIC) modelling system provides information regarding fertilizer timing, composition, application method, and amount. A bidirectional version of the Community Multiscale Air Quality (CMAQ) is then used to calculate county-level emission factors which are multiplied by county-level total fertilizer estimates to obtain NH\textsubscript{3} emissions. For both, livestock and fertilizer NH\textsubscript{3} emissions annual NEI emission totals are multiplied in SMOKE by monthly, weekly and hourly profiles.

Non-road emissions include emissions from non-stationary sources, except commuter automobiles. For example, non-road sources would include construction equipment, snowmobiles, boats, trains, and aircraft. Similar to mobile emissions, non-road emissions are mainly projected using the MOVES 2014a model. However, the emissions from trains, aircraft, and airport ground support equipment are estimated from specific EPA-provided tools.

Mobile emissions are calculated and projected using the MOVES 2014a model, which are then input into SMOKE as precomputed mobile inventory numbers. Mobile emissions are informed by vehicle population data and vehicle-specific emissions-rate information. Also, various metropolitan planning organizations supply UDAQ with the traffic activity data that goes into MOVES 2014a.
Point sources include large emitters such as oil refineries, power plants, and big mining operations. Since the vertical release height of point stack emissions impact air quality, the 2D SMOKE gridded emissions output is input into the air-quality model (CAMx 6.30), which calculates vertical plume rise from those point source stack parameters using 42 layers matching WRF inputs.

5.6 Modelling of ammonia concentrations using STILT

To account for the atmospheric transport of NH₃ from emission sources to the receptors of the NH₃ measurement observations made during UWFPS, we used the Stochastic Time-Inverted Lagrangian Transport (STILT) model (Lin et al., 2003). STILT simulated the upstream influence by modelling the evolution of ensembles of 200 simulation particles, each representing an air parcel 24 hours back in time. Particle ensembles are considered to be influenced by surface fluxes when they spend time in the vertically well-mixed surface layer (defined as 50% of the boundary layer height). STILT compiles a “footprint”, a flux sensitivity matrix, using the flux sensitivity from each of the 200 trajectories. The flux sensitivity represents the contribution of a grid cell area to the NH₃ mixing ratio per surface flux unit. To obtain footprints for the aircraft measurements, STILT was run for every 2 min of the Twin Otter flight path for all 23 research flights. STILT was driven with gridded meteorological information available from NOAA’s High Resolution Rapid Refresh (HRRR) model (http://ruc.noaa.gov/hrrr/), which covers the entire continental U.S.. HRRR is based upon the widely-used Weather Research and Forecasting (WRF) mesoscale model (Skamarock and Klemp, 2008) and resolves the atmosphere at 3-km grid spacing, assimilating radar observations. Model NH₃ enhancements (in pptv) were estimated by multiplying the flux sensitivity data (in pptv/(μmol m⁻² s⁻¹)) with the NH₃ emissions from the UDAQ emission inventory (in μmol m⁻² s⁻¹) for each grid cell. As STILT was run 24 hrs back in time, the modelled NH₃ enhancements represent the NH₃ mixing ratio contribution from surface emissions within the last 24 hrs. Before multiplying, the NH₃ emissions were resampled to the match the spatial grid of the flux sensitivity data (0.01° x 0.01°). Modelled NH₃ enhancements were then obtained by summing the NH₃ contributions from each grid cell. To account for the large spatial extent of the 24-hr trajectories from the Twin Otter position, the 1.33 km inventory data was inset into the larger 4 km inventory, to have the maximal spatial extent but also make use of the refined NH₃ emissions of the 1.33 km emission inventory.

To account for formation of particle ammonium from emitted NH₃, the modelled NH₃ estimates are compared to measured total NH₄ (= NH₃ + pNH₄). Conversion to particulate ammonium is the dominant reactive sink for gas phase NH₃ as the oxidation of NH₃ by OH is significantly slower. Thus using NH₄ as a passive tracer is reasonable, however, the approach does not account for potential dry and wet deposition of NH₃. As a result of this simplification, modelled NH₄ enhancements could be overestimated. Modelled NH₄ enhancements only account for NH₄ emitted within the past 24 hr in the spatial domain of the produced NH₃ contributions map and do not include NH₄ advected from outside that spatial domain or NH₃ which was present in the air shed before the 24 hr period. Therefore, an estimate of background NH₄ mixing ratios was subtracted from...
measured NH\textsubscript{x} mixing ratios before comparing them to the modelled enhancements. Background mixing ratios were determined separately for each region listed in Sect 2.1 (see Fig. 1a), using the measured NH\textsubscript{x} mixing ratios data from each individual flight in the respective region. To account for varying vertical mixing between flights, the data were split into vertical layers of 50 m depth covering the entire altitude range of the Twin Otter. The background mixing value specific for each layer, region and flight was then determined by the 1\textsuperscript{st} percentile of NH\textsubscript{x} data from the Twin Otter. As shown in Fig. S14, for areas with significant NH\textsubscript{3} surface emissions, the 1\textsuperscript{st} percentile was well above the instrument’s detection limit. If the background mixing ratio was underestimated, this would lead to unrealistically high estimates of the NH\textsubscript{x} enhancements from the measurements.

In the remainder of the text, we refer to modelled NH\textsubscript{3} and measured NH\textsubscript{x} enhancements as modelled and measured dNH\textsubscript{x}, respectively.

3 Results and discussion

3.1 Meteorological conditions and PCAP episodes

Weather conditions in the Great Salt Lake Region in January and February 2017 included episodes of winter storms and above-average precipitation. As storm tracks promote vertical mixing, PCAP periods were less frequent during UWFPS than typically observed. Within the period of the Twin Otter measurements, two major PCAP periods were identified: PCAP#1 from 13 to 20 January 2017 and PCAP#2 from 27 January to 4 February 2017. A third and less intense PCAP period occurred at the end of the campaign on 13 February and lasted until 18 February 2017. The strong atmospheric stability during those PCAP periods lead to the build-up of high PM\textsubscript{2.5}-levels for Salt Lake Valley, Cache Valley and Utah Valley, as shown in Fig. 3. Due to the lack of snow cover and the relatively weak subsidence inversion, the inversion height during PCAP#1 was atypically high, reaching from about 400 m up to 800 m a.g.l., before a strong storm initiated the top-down erosion of the PCAP on 19 January. During PCAP#1, ground-level PM\textsubscript{2.5} reached up to 90 \(\mu\text{g m}^{-3}\) in Cache Valley (L4), and up to 50 \(\mu\text{g m}^{-3}\) in Salt Lake Valley (UU), while the PCAP was only weakly developed in Utah Valley (NP) with PM\textsubscript{2.5} levels below 20 \(\mu\text{g m}^{-3}\) (1-hr averages). In contrast, PCAP#2 was a stronger, classic PCAP period, which was promoted by several inches of fresh snow and cold air left by a storm that was followed by a large high pressure period. This resulted in PM\textsubscript{2.5} values building up in all three major valleys over the course of the PCAP and reaching 104 \(\mu\text{g m}^{-3}\) at the L4, 64 \(\mu\text{g m}^{-3}\) at the UU, and 80 \(\mu\text{g m}^{-3}\) at the NP sites (1-hr averages). As evident in the PM\textsubscript{2.5} data, the PCAP started eroding in Utah Valley first, then in Salt Lake Valley second, whereas it persisted a few days longer in Cache Valley, which is also attributed to the deeper snow cover in Cache Valley during January and February 2017. Compared to PCAP#2, PCAP#3 was moderate with only the onset captured by the aircraft flights.
3.2 Observed NH$_3$ mixing ratios

3.2.1 Evolution of ammonia mixing ratios near the surface

Ammonia mixing ratios measured at the L4 and UU ground sites (Fig. 3), correlates with increasing PM$_{2.5}$ levels during PCAP periods, especially at the L4 site (Fig. 3a), where NH$_3$ reached up to 100 ppbv during PCAP#1 and PCAP#2. The correlation between PM$_{2.5}$ and NH$_3$ indicates the presence of local NH$_3$ sources, and illustrates the strong influence of atmospheric stability on pollutant concentrations during winter. NH$_3$ mixing ratios show a stronger diurnal variation than PM$_{2.5}$. Accumulation of directly emitted NH$_3$ in the nocturnal boundary layer leads to transient enhancements of NH$_3$ mixing ratios, which is for example visible in the short-term (<12 hrs) NH$_3$ peaks observed during night time at the L4 site (e.g. nights of 08/09 and 09/10 February). Although PM$_{2.5}$ formation occurs through both daytime and night-time processes, the nigh-time process is typically fast in the residual layer and suppressed in the surface layer (McDuffie et al., 2019; Womack et al., 2019). At the UU site, ambient NH$_3$ measurements were significantly lower than in Cache Valley, typically below 10 ppbv (Fig. 3b). Measurements are not available for PCAP#1, however, the build-up of NH$_3$ mixing ratios in Salt Lake Valley is evident in the second half of PCAP#2. Increasing PM$_{2.5}$ levels mark the first half of PCAP#2, while NH$_3$ mixing ratios were still low between 1 and 3 ppbv. During that period, NH$_3$ mainly partitioned into pNH$_3$ as it was observed by the simultaneous increase of pNH$_3$ with PM$_{2.5}$ (data not shown).

Near surface mixing ratios were sampled from the Twin Otter aircraft during missed approaches at regional airfields (Fig. S1 and S2). Figure 3a shows NH$_3$ mixing ratios at Logan airport, located about 3 km northwest of the L4 ground site. NH$_3$ mixing ratios from the Twin Otter follow the trend of the ground measurements with (1) high mixing ratios between 45 and 55 ppbv during PCAP#1, (2) medium mixing ratio levels between 20 and 25 ppbv during the first half of PCAP#2, and (3) lower mixing ratios below 20 ppbv towards the end of the measurement campaign. The direct comparison of ground site and Twin Otter measurements was performed by averaging the Twin Otter mixing ratios within a distance of 1 km of the airport runway and obtaining the mean ground site mixing ratios for the same time interval. As shown in Fig. S3b, mean values from the Twin Otter are roughly a factor of two lower than measurements from the L4 ground site. This can be explained by dilution of NH$_3$ mixing ratios from higher altitudes as the averaging window for the Twin Otter values partially includes NH$_3$ measurements from the ascents and descents of the missed approaches. For that reason, maximum values better represent the ground level mixing ratios, which is supported by a closer correspondence with the data from the L4 site. Furthermore, Moore (2007) and Hammond et al. (2017) showed that mean NH$_3$ concentrations can vary spatially across the Cache Valley by as much as an order of magnitude, depending on the strength of adjacent sources and duration of a PCAP event. For Salt Lake Valley, NH$_3$ measured at the UU site compares generally well with the airborne NH$_3$ obtained when the Twin Otter was overflying the ground site (Fig. 3b). The direct comparison of both measurements (Fig. S3a) shows that airborne measurements are on average lower, attributed to the higher altitude of the measurement and the vertical gradient of NH$_3$ away from the surface.
3.2.2 Prevailing NH₃ mixing ratios in different regions from aircraft observations

The frequency distributions of NH₃ mixing ratios measured in Salt Lake Valley, Cache Valley, Utah Valley and over the Great Salt Lake are shown in Fig. 4a and 4b for both PCAP and non-PCAP conditions. Mixing ratios were filtered to only include those from the lowest steady flight level (data between 100 – 500 m a.g.l) for a better comparison between regions. The histograms reveal that during both PCAP and non-PCAP conditions NH₃ mixing above the Great Salt Lake were mostly below 5 ppbv and in Salt Lake Valley mostly below 5 ppbv, with only a few measurements outside of those limits. The majority of NH₃ measurements in both Cache Valley and Utah Valley were also below 5 ppbv, however, higher mixing ratios up to 20 ppbv in Cache Valley and 10 ppbv in Utah Valley were also frequently observed. While the distributions for all regions are similar under PCAP and non-PCAP conditions, during PCAP conditions higher extreme values up to around 70 ppbv in both Cache Valley and Utah Valley were observed at the lowest steady flight level, indicating the presence of local emission sources. Higher levels up to nearly 90 ppbv were only measured during missed approaches at the Logan airport in Cache Valley, marking it as a distinct high NH₃ region. In contrast to NH₃, the frequency distributions of pNH₄ show clear difference between PCAP and non-PCAP periods (Fig. 4c, d), with significantly higher pNH₄ values during PCAP conditions. This can be explained by increased partitioning of NH₃ into the particle phase and build-up of ammonium nitrate over the course of the PCAP periods (Fig. 3).

3.3 Evaluation of NH₃ emission sources

3.3.1 Comparison of modelled and measured enhancements

To investigate NH₃ emissions sources in the different regions, we compare dNH₃ measured on the Twin Otter with dNH₃ derived by the footprint model (see Sect. 2.5 and 2.6). Figure 5 shows an example of a STILT flux sensitivity footprint, and how it is overlaid with the UDAQ emission inventory to obtain dNH₃ estimates for the locations of the Twin Otter. The mean measured and modelled dNH₃ for all regions in the study area are given in Table 1, including a scaling factor which is the ratio of dNH₃_meas/dNH₃_model. Figure 6 shows the frequency distribution for modelled and measured dNH₃ for Salt Lake Valley, Cache Valley and Utah Valley for non-PCAP (a-c) and PCAP (d-f) conditions. The distributions show that the model underestimates dNH₃ in all three valleys, compared to the measurements from the Twin Otter. During non-PCAP conditions, the underestimation is most prominent in Cache Valley. During PCAP conditions the underestimation is in general more pronounced than during non-PCAP conditions. As during PCAP periods NH₃ mainly persists as pNH₄ (see Section 3.2.2), this leads to the high measured dNH₃ over the course of the PCAP period in Salt Lake Valley and Utah Valley. Due to high local NH₃ emissions, in Cache Valley NH₃ and pNH₄ are of similar magnitude, which is why the difference between PCAP and non-PCAP periods is slightly less pronounced (see also linear scale distributions in Fig. S8).
Lower modelled dNH₃ values may suggest an underestimation of NH₃ emissions in the UDAQ inventory. Table 1 lists the mean measured and modelled dNH₃ mixing ratios for the different regions in the study area, which were used to derive a mean scaling factor between measured and modelled values. The mean scaling factor for Cache Valley, Salt Lake Valley and Utah Valley are 4.4, 1.9 and 1.6, respectively, which reflects that modelled dNH₃ are underestimated in all three valleys. Due to the non-Gaussian distribution of both measured and modelled dNH₃ values, the median scaling factors vary but still show the same trend for underestimation of modelled dNH₃, with highest underestimation in Cache Valley (2.7), followed by Salt Lake Valley (1.9) and Utah Valley (1.2).

To further discuss the discrepancies between measured and modelled dNH₃ values, it is important to address the uncertainties of both measured and modelled dNH₃, which we discuss in the following section.

### 3.3.2 Uncertainties in measured and modelled mixing ratio enhancements

Calculations of the trajectories and footprints with the STILT model rely on the accurate representation of meteorological conditions and parameterizations such as the definition of the height of the surface mixed layer, which couples the ground surface emissions to the calculated trajectories. While we do not go in detail on the STILT parameterization and the derived weather model (HRRR), the examination of NOₓ enhancements above background mixing ratios (dNOₓ), which were also measured from the Twin Otter, gives confirmation that the overall representation of the meteorology is reasonable. Figures S12 and S13 show the frequency distributions for measured and modelled dNOₓ. The scaling factors (dNOₓ measured/dNOₓ modelled) for Cache Valley, Salt Lake Valley and Utah Valley were 1.3, 1.0 and 0.9, respectively, which shows agreement of measured and modelled dNOₓ for all of the three valleys. This indicates that on average both meteorological conditions and NOₓ emissions are represented adequately in the model approach we used. This interpretation relies on the assumption that both the NOₓ emission inventory and NOₓ measurements are accurate. As particulate nitrate (pNOₓ) is only quantitatively sampled by the NOxCaRD if it enters the inlet (not designed specifically for aerosol sampling), NOₓ measurements may be biased low. By comparing the NOₓ to the AMS pNOₓ (after subtracting NOₓ and other relevant NOₓ species), we found that inlet sampling was effectively quantitative to within the uncertainty in the AMS (20%) and NOₓ (12%) measurements. Furthermore, since the NOₓ to NOₓ ratio was always fairly large (0.53 ± 0.34), a significant amount of NOₓ was present as NOₓ. While the agreement in the frequency distributions is good, the direct comparison of modelled and measured dNH₃ reveals a relatively poor point-to-point correlation (Fig. S7). A similarly poor correlation was found for dNOₓ (Fig. S11) and also for measured and modelled dNH₃, dNOₓ and dCO₂ at the UU ground site (data not shown), which shows that there is no clear bias in either the STILT footprints from the Twin Otter or in the NH₃ inventory.

Due to the finite extent of the combined UDAQ emission inventory map (Sect. 2.5), fractions of the STILT footprints may be outside of the emissions inventory domain. For both Salt Lake Valley and Utah Valley, more than 50% of the 24-hr footprints lie completely within the inventory domain during PCAP conditions, while only a small number that have a contribution from
outside of the domain of 50% or more. As Cache Valley is located close to the northern border of the UDAQ emission inventory map (Fig. 1), a larger fraction of footprints exceeded the inventory domain, with 18% of footprints completely within the inventory domain and 63% of footprints at least 50% within the domain during PCAP conditions. However, this effect cannot explain the large underestimation of modelled dNH₄ in Cache Valley due to the following reasons: (1) the analysis of the STILT trajectories (Fig. S15) showed that air masses for a majority of the extreme measured dNH₄ values in Cache Valley originated in low NH₄ environments (at high altitudes or areas with low NH₃ emissions), and (2) high mixing ratios were only observed in Cache Valley (see also Fig. 4), providing evidence that measured dNH₄ were dominated by local NH₃ sources. Advection of high amounts of NH₃ from the north would have also strongly affected other regions such as the Great Salt Lake, which the measurements do not show.

Uncertainties of measured dNH₄ values arise from uncertainties in the measurements from the Twin Otter and uncertainties in the background determination (Sect. 2.2 and 2.3). The precision of NH₃ mixing ratios was 0.09 ppbv for a 1 min averaging period, which was used for the comparison. The uncertainty of pH₄ is given as 20%. Given the uncertainty in the measurements and an uncertainty of the background determination method, the distinction between small measured and modelled dNH₄ differences is difficult. As a result, although the scaling factors in Table 1 suggest that NH₃ emissions in Salt Lake Valley are underestimated by 50%, it is possible that part or all of the model-measurement mismatch could be due to method uncertainties rather than due to an underrepresentation of NH₃ emission in the UDAQ inventory. In contrast, the large differences between measured and modelled dNH₄ in Cache Valley, cannot be attributed to measurement errors, and therefore is more likely attributed to an underestimation of NH₃ emission in the UDAQ inventory in Cache Valley.

3.3.3 Modification of modelled dNH₄ using scaling factors

To investigate the effect of a possible underestimation of NH₃ emissions in the UDAQ inventory on the presented dNH₄ distributions, we scaled the modelled dNH₄ by the scaling factors given in Table 1. For Cache Valley, if we assume that all the underestimation in modelled dNH₄ is due to an underestimation in livestock emissions (see Sect. 3.3.4), we can adjust the scaling factors in Table 1 to be solely applied to area source emissions. Accordingly, the area source scaling factor for Cache Valley is 4.55. If we apply this factor to the modelled dNH₄ in Cache Valley, the range of measured and modelled dNH₄ agrees well for non-PCAP conditions (Fig. 7a). As the same factor is applied to all modelled dNH₄, the shape of distribution does not change significantly, and a much larger scaling factor would be necessary to reproduce measured dNH₄ values up to 88 ppbv for the PCAP conditions (Fig. 7c). A Mann-Whitney-Wilcoxon test was used to evaluate the agreement between modelled and measured dNH₄ distribution before and after applying the scaling factor (Table S2). The increase of p-values above the 0.05 significance level indicates that the distributions of modelled and measured dNH₄ show similarity after applying the scaling factor. Assuming a systematic underestimation of livestock emissions, we applied the same scaling factor also to area source emissions in Salt Lake Valley and Utah Valley. As illustrated in Fig. S9, for Salt Lake Valley the modified modelled dNH₄
are not significantly larger, which is due to the fact that emissions from area sources play a less important role in Salt Lake Valley than in Cache or Utah Valley (Table 1). Since the largest emissions source in Salt Lake Valley is the mobile sector, modelled dNH$_3$ for all three valleys were additionally modified by a scaling factor, which was retrieved from the ratio of modelled and measured dNH$_3$ value in Salt Lake Valley (Fig. S10). Applying the factor (= 3) to the mobile emissions of modelled dNH$_3$, yields a better agreement for Salt Lake Valley during non-PCAP conditions, however, the large frequency of measured dNH$_3$ above 10 ppbv during PCAP conditions cannot be explained. This suggests that especially during PCAP conditions either (1) background NH$_3$ mixing ratios used to calculate measured dNH$_3$ are higher than accounted for or (2) the surface influence in STILT is underestimated in Salt Lake Valley.

### 3.3.4 Ammonia emissions in Cache Valley: Uncertainties in livestock emissions

The results presented above suggest that NH$_3$ emissions may be underestimated in the UDAQ emission inventory, with highest underestimation in Cache Valley. According to the inventory, 96.7% of total NH$_3$ emissions in Cache Valley are attributed to emissions from area sources. Cache Valley area sources are dominated by emissions from cattle waste (56.2%) and poultry operations (20.6%). Emissions from fertilizer application only account for 6.8% and from swine production only 3.1% of the total area sources. As cattle waste is by far the largest NH$_3$ source in Cache Valley, it therefore seems most likely that an underrepresentation of cattle waste emissions are at least partially responsible for the gap between measured and modelled dNH$_3$.

In the UDAQ inventory, sources from livestock emissions are treated as areas sources and distributed uniformly over the county or an area in the county. As a result, high NH$_3$ emissions released by CAFOs are spread over a larger area instead of being treated as a point source. This may be another reason why the higher measured dNH$_3$ values are not reproduced by the model. As the UDAQ inventory does not report the location of CAFOs, we modelled dNH$_3$ using a NH$_3$ emission inventory compiled by Utah State University (USU), which reports facility-based emissions from livestock in Cache Valley (see Section S4 for a description of the inventory). The USU inventory compiled emissions from dairy cattle, beef cattle, swine, poultry, automobiles, wastewater treatment facilities, and industry for both Cache and Franklin Counties for the year 2006 (Table S1). In winter time, the largest NH$_3$ emissions source in Cache Valley was dairy cattle (89.6%), while 98.1% of total emissions were from the livestock sector. Figure S5 spatially locates the facility-based livestock, poultry and other area source NH$_3$ emissions in Cache Valley and visually indicates estimated relative source strengths. To derive modelled dNH$_3$ estimates, we replaced the UDAQ NH$_3$ emissions in Cache Valley with these facility-based emissions from the USU inventory. These emissions were embedded into the UDAQ emission inventory map (Fig. S6) before overlaying them with the STILT footprints from the Twin Otter. Compared to the original UDAQ inventory, the USU inventory produces higher modelled dNH$_3$ values, which compare better to dNH$_3$ measured from the Twin Otter. The USU emissions yield a mean modelled dNH$_3$ value of 5.05 (± 8.38) ppbv, as shown in Table 1, whereas using the UDAQ inventory this value was only 1.70 (± 1.47) ppbv. Maximum
modelled dNH₃ values from each inventory are 61.7 and 5.7 ppbv, respectively. Mean dNH₃ mixing ratios from the USU are a factor of 2.55 higher than from the UDAQ inventory, which agrees with the ratio between total emission rates from each inventory in Cache Valley given in Table 1 (12435 kg d⁻¹ ÷ 4757 kg d⁻¹ = 2.61). In comparison to measured dNH₃, the scaling factor (all sectors included) decreases from 4.4 to only 1.5 when using the USU inventory.

Possible reasons for the underestimation of NH₃ emissions in the UDAQ inventory could be differences in the livestock numbers or differences in livestock emission factors used in the inventories. As described in Moore (2007), the USU inventory uses animal counts from 2007, derived from personal discussions with count extension agents, local producers and co-op organizations, with approximately 90,000 dairy cattle in Cache Valley (40,000 in Cache County; 50,000 in Franklin County) and nearly 2,000,000 chickens. The USU inventory is based on a NH₃ emission factor between 152.7 and 161.3 g d⁻¹ AU⁻¹ (AU = animal units), depending on the cattle age and waste disposal method. Dairy cattle emissions in the UDAQ are based on the county wide estimates of the 2014v1 NEI inventory. As mentioned in Sect. 2.5, the FEM used in the NEI inventory produces location specific emission factors for each day of the modelled year (McQuilling and Adams, 2015). In SMOKE, annual NEI emission totals are multiplied by monthly, weekly, and hourly profiles to obtain temporally resolved emissions. The monthly profile redistributes the annual total NEI emissions over the year and is determined through inverse modelling, as described in Gilliland et al. (2006). NH₃ observational data from the National Atmospheric Deposition Program (NADP) is used together with prior seasonal NH₃ emission estimates in the CMAQ model to produce a region specific monthly profile. The monthly profile used in the UDAQ inventory is presented in Fig. S4 showing a clear seasonal cycle of livestock emissions. Emissions peak in summer, with more than 18% of annual emissions in July, while emission are lowest in wintertime. This seasonal profile is typically explained by increases in fertilizer application, a higher fraction of outdoor housing and higher temperatures in summer than in winter. However, a significant month-to-month variation is present. Especially in wintertime, when expected emissions are lower, the percentage variation between months is significant. This suggests uncertainties in wintertime livestock emissions, in particular as the monthly profile is based on the year 2005. Furthermore, as shown in Table S1, the USU inventory suggests nearly similar livestock emissions for both summer and winter. This is supported by on average higher surface NH₃ concentrations observed in winter than summer in Cache Valley by the authors of the inventory in 2006 (Moore, 2007).

It is beyond the scope of this study to evaluate the uncertainties of inventory livestock emissions in detail. A larger measurement dataset and also a more thorough consideration of other processes such as NH₃ deposition are necessary.

### 3.4 Inter-valley exchange of NH₃ and impact on PM formation

Exchange of air masses between valleys or basins in the study region can be a critical factor for air pollution formation. Especially in wintertime when air pollutants accumulate in the valley basins during PCAP periods, the transport of air pollutants or their precursors from adjacent valleys can increase local air pollution. If NH₃ from agriculture in the Cache Valley
is transported to Salt Lake Valley, its equilibrium with HNO$_3$ produced from oxidation of NO$_x$ emitted by mobile and industrial sources may affect the limiting reagent and thus the control strategy for ammonium nitrate PM$_{2.5}$ formation in Utah’s most densely populated region (Franchin et al., 2018). Similarly, NO$_x$ enriched air masses transported from Salt Lake Valley may lead to PM$_{2.5}$ formation in Cache Valley. Utah Valley is connected with Salt Lake Valley via the Jordan Narrows, where exchange of air masses between the two basins is frequently observed. For example, after a mix-out episode at the end of a PCAP period in Salt Lake Valley, Mitchell et al. (2018) observed the transport of PM$_{2.5}$ enriched air from Utah Valley, where the PCAP was still persistent. Similarly, we observed from the Twin Otter the transport of NH$_3$ rich air masses through the Jordan Narrows into Salt Lake Valley, induced by southerly winds during PCAP#1 on 18 January 2017 (mixing ratios in Utah Valley and Salt Lake Valley for that day are shown in Fig. 1c).

To investigate how inter-valley exchange affects air pollution in the Great Salt Lake Region, we examined the origin of air masses through the STILT footprint calculation. The dNH$_3$ contribution from each county to the modelled total dNH$_3$ was determined for the Twin Otter footprints by using emissions from the UDAQ inventory. In addition, we determined the county contribution to dNH$_3$ at the UU site, where hourly STILT emission enhancements were available for the period from 16 to 31 January 2017. Due to the lower elevation of the ground-based UU site compared to the Twin Otter aircraft, the extent of the footprints is typically smaller; however, footprints for UU provide more continuous temporal coverage over the investigated period.

Figure 8a shows the dNH$_3$ contributions for Salt Lake Valley (UU site and Twin Otter), Cache Valley (Twin Otter), and Utah Valley (Twin Otter). Results for the other regions in the study area are presented in Fig. S16. The contributions were segregated by county (e.g. Salt Lake County instead of Salt Lake Valley) as political boundaries are more appropriate divisions for emission control and air pollution regulation. In Salt Lake Valley, the largest portion of dNH$_3$ at the UU site is attributed to emissions from Salt Lake County for both PCAP (66.3%) and non-PCAP (77.2%) conditions. As Twin Otter footprints extend further than those from surface observations, contributions from Salt Lake County NH$_3$ are slightly smaller (47.6 and 40.8%). The second largest contributions are from Davis County adjoining to the North of Salt Lake Valley (13.0 and 24.2% for Twin Otter). Contributions from Utah County are small at the UU site (8.2 and 3.7%), but (16.9%) for the Twin Otter-derived footprints during PCAP periods, as the aircraft also sampled the south section of Salt Lake Valley. This is consistent with frequently observed southerly winds during PCAP periods and shows the importance of inter-valley exchange during these conditions. Contributions from Cache County were only minor (0.5 and 0.0% at UU site, 2.6 and 6.5% for Twin Otter over SLV) and negligible from Franklin County (0.0% at UU site, 0.1 and 1.7% for Twin Otter over SLV). This shows that the impact of the high agricultural emissions in Cache Valley on PM$_{2.5}$ formation in Salt Lake Valley was not significant during the study period. As shown in Fig. S16, the transport of NH$_3$ from Cache County and Franklin County into the medium densely populated North Metropolitan area (Weber County and Davis County) was also minor (<2%) during PCAP periods. Segregating the contributions from each county by emission sector, we found that 55% are from area emissions and about...
30% from mobile sources (Fig. S18). If we account for the observed underestimation of emission sources in the UDAQ inventory by increasing area source and mobile emissions by a factor 4.5 and 3, respectively, (Fig. S19) and take the average values retrieved from the Twin Otter and the UU site, during the study period about 60% of dNH₃ in Salt Lake Valley originated from area source and 30% from mobile source emissions in the region. Future analyses of relationships between NH₃ and tracers for different emission sources, such as CO, CO₂, CH₄, NOₓ and VOCs, will be useful in refining the apportionment of NH₃ emission sources from this campaign.

For Cache Valley, during PCAP conditions 64.2% of dNH₃ contributions were from Cache Valley, while 21.1% were transported from Box Elder County which is connected through a canyon in the west mountain range of Cache Valley. Due to excess NH₃ in Cache Valley, ammonium nitrate formation is mostly nitrate-limited (Franchin et al., 2018). Therefore, the advection of nitrate or NOₓ may be a significant process for PM₃.₅ formation in Cache Valley. Figure 8b, shows the percentage of county contributions for dNOₓ (for all regions see Fig. S17). As they are based on the same STILT footprints, percentages are similar to the dNH₃ contributions, but differ due to a different distribution of NOₓ emission sources. During PCAP conditions, 19.5% of dNOₓ in Cache Valley was emitted in Box Elder County, 16.8% in Davis County, 13.0% in Weber County, and 11% in Salt Lake County. This suggests that a large fraction of NOₓ potentially leading to PM₃.₅ formation in Cache Valley may not be locally emitted but mixed in from other counties.

For Utah Valley, inter-valley exchange seems slightly less important than for Cache Valley as 58.7% of dNH₃ and 57.6% of dNOₓ originated in Utah County during PCAP periods. Nonetheless, transport from Salt Lake County during PCAP conditions is still significant with contributions of 17.5% to dNH₃ and 29.9% to dNOₓ. During non-PCAP conditions the percentage contributions from Salt Lake County to dNH₃ (29.9%) and dNOₓ (49.8%) are even higher, although formation of NH₃NO₄ is less important as demonstrated in lower PM₃.₅ levels observed (Fig. 3).

### 4 Conclusions

Winter air pollution in the Great Salt Lake Region has been shown to be mainly linked to the formation of ammonium nitrate aerosol. Understanding the sources of NH₃ is key to making reliable predictions of ammonium-aerosol formation and identifying the appropriate mitigation strategies for PM₃.₅. To investigate NH₃ emissions in the Great Salt Lake Region, we sampled NH₃ and pNH₄ from a Twin Otter aircraft over the Great Salt Lake Region in Northern Utah and at selected ground sites.

We found that NH₃ (= NH₃+pNH₄) was highest in Cache Valley, which can be attributed to the large number of NH₃ emitting livestock and poultry operations in the Cache Valley. However, NH₃ emissions in the commonly used UDAQ NH₃ emission inventory are not significantly larger in Cache Valley than in Salt Lake Valley or Utah Valley, as the measurements would suggest. Using a STILT footprint model approach, our results suggest that in Cache Valley livestock emissions in the UDAQ
inventory are underestimated by a factor of approximately 4.5 for January and February 2017, based on the following findings: (1) the factor between modelled and measured NH$_x$ enhancements was 4.4, and (2) total UDAQ NH$_3$ emissions in Cache Valley are lower by a factor of 2.61 compared to emissions estimated in the USU inventory. One reason for the discrepancy could be the underestimation of wintertime emissions through the applied monthly profile in the UDAQ emission inventory. This emphasizes the importance of generating year-specific emission factors and temporal profiles that are based on the meteorological conditions of the year for which the inventory is run. Furthermore, our results suggest that in areas with large livestock operations, moving towards facility based inventories for livestock NH$_3$ emissions can yield better NH$_3$ and NH$_x$ predictions in local or regional air quality models. However, more extensive datasets, which also include summertime measurements, would be needed to evaluate the uncertainties of livestock emissions within inventories in more detail.

Our investigation of the inter-valley exchange during the study period revealed that in Salt Lake Valley around two thirds of NH$_x$ originated within the valley, while NH$_x$ transport from Cache Valley was negligible and therefore did not significantly impact the formation of PM$_{2.5}$ in Salt Lake Valley. In contrast, transport of NH$_x$ from Utah Valley can be significant during PCAP period when southerly winds prevail. Furthermore, we found that in Cache Valley a significant fraction (70%) of the NO$_x$ potentially leading to PM$_{2.5}$ formation is not locally emitted and is instead transported from other counties. While nearly 20% of the NO$_x$ in Cache Valley originated in the adjacent Box Elder County, still 11% of the Cache Valley NO$_x$ was transported from Salt Lake County, about 50 km away. Since it was found that the formation of ammonium nitrate in Cache Valley was mostly nitrate limited during the UWFPS campaign, this illustrates the potential effect which regulation of NO$_x$ emissions in Salt Lake County may have on neighbouring regions with higher agricultural NH$_3$ emissions.

**Author contributions**

AM performed the measurements and analysis of airborne NH$_3$ and wrote the manuscript. JGM provided input at all stages of the measurements, the analysis and discussion of results. AF and AMM obtained and analyzed the aircraft based AMS data. DLF, CCW and EEM obtained and analyzed the NOxCaRD data. AH and RM provided the ground site NH$_3$ data. AM performed the model analysis with support from AH and JCL. JCL ran the STILT model and CP, RM and KM provided the emission inventory data. SSB and MB planned and organized the UWFPS measurement campaign. All authors discussed the results and contributed to the final manuscript.
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Tables

Table 1: NH₃ emission estimates and measurements by region. Data include: (1) Total NH₃ emission estimates and their sector-based proportion from the UDAQ emission inventory; (2) NH₃ emission estimates for Cache Valley from the USU emission inventory; (3) measured and modelled NH₃ mixing ratios (mean + standard deviation); (4) the ratio between measured and modelled NH₃ mixing ratios (scaling factor). The regions are: BV = Bear valley (Box Elder County); CV = Cache Valley (Cache County + Franklin County); GSL = Great Salt Lake (Box Elder County, Weber County, Davis County, Salt Lake County + Tooele County); NM = North Metro (Davis County + Weber County); TC = Tooele County, UV = Utah Valley (Utah County).

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Figures

Figure 1: Overview of the study area: a) outlines of sub-regions used for the analysis of Twin Otter measurements, b) borders of counties which are part of the study area, and c) typical NH₃ mixing ratios measured from the Twin Otter combined from a north and south flight leg flight on 17 and 18 January, respectively. Arrows in c) indicate the location of ground site measurements used for this study in North Provo (NP), at the University of Utah (UU) and in Logan (L4). Borders of the sub-regions are shown in c) for reference. Salt Lake City, the most populated area, is situated in the North Eastern part of Salt Lake Valley.

Figure 2: Setup of the QC-TILDAS on the Twin Otter aircraft for NH₃ measurements at 1 Hz sample frequency. The commercially available QC-TILDAS was modified using a smaller vacuum pump, a pressure controller and a custom made PFA aerosol impactor. A bypass system was used to generate a higher flow rate through the inlet line. See text for a detailed description of the setup.
Figure 3: Time series of fine particulate matter (PM$_{2.5}$) and NH$_3$ mixing ratios during PCAP periods over the course of the measurement campaign from Jan 16 to Feb 13 2017. Shown are measurements from the ground sites (a) at the University of Utah (UU), (b) in Logan (L4), and (c) in North Provo (NP). Blue dots represent mean NH$_3$ mixing ratios measured from the Twin Otter during missed approaches (at Logan airport and North Provo airport) or when flying over the UU measurement site. The time frames of the three PCAP periods during the campaign are marked as black bars.
Figure 4: Frequency distribution of NH$_3$ (a, b) and pNH$_4^+$ (c, d) mixing ratios measured from the Twin Otter in Salt Lake Valley (SLV), Cache Valley (CV), Utah Valley (UV) and above the Great Salt Lake (GSL). The distributions are based on mixing ratios from all research flights, segregated into PCAP (a, c) and non-PCAP (b, d) conditions.

Figure 5: Approach used to determine NH$_3$ enhancements by overlaying the emission sensitivity map (in ppmv/(μmol m$^{-2}$ s$^{-1}$), left panel) with the NH$_3$ emissions from the UDAQ emission inventory (in μmol m$^{-2}$ s$^{-1}$, centre panel). The emission sensitivities were derived with STILT for every 2 min of the Twin Otter flight path for all research flights. NH$_3$ enhancement for the Twin Otter location were obtained by summing of all NH$_3$ contributions within the spatial domain of the NH$_3$ contribution map. The NH$_3$ Emission inventory map (centre panel) is a composite of the 1.33 x 1.33 km$^2$ resolution emission inventory in the centre, imbedded into the 4 x 4 km$^2$ emission inventory.
Figure 6: Frequency distribution of measured (blue) and modelled (red) NH$_x$ enhancements (dNH$_x$) for Salt Lake Valley, Cache Valley and Utah Valley on logarithmic scales for (a-c) non-PCAP and (d-f) PCAP conditions.
Figure 7: Frequency distribution of measured (blue) and modelled (red) NH$_3$ enhancements (dNH$_3$) for Cache Valley, using enhanced livestock emissions by a factor of 4.5 and the USU emission inventory for (a+b) non-PCAP and (c+d) PCAP conditions.
Figure 8: Inter-valley exchange of pollutants: Contributions from different counties to (a) dNH\textsubscript{x} and (b) dNO\textsubscript{y} at the UU (Salt Lake Valley) site and Twin Otter locations in Salt Lake Valley, Cache Valley and Utah Valley. The inter-valley exchange was evaluated by segregating contributions from the footprint model (see contributions map in Figure 5) into counties of origin for each run of the footprint model (i.e. every 2 min of Twin Otter flight path, and every hour for UU location).