1 The role of dew as a nighttime reservoir and morning

2 source for atmospheric ammonia

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12 Abstract

13 Several field studies have proposed that the volatilization of NH_3 from evaporating dew is

14 responsible for an early morning pulse of ammonia frequently observed in the atmospheric

15 boundary layer. Laboratory studies conducted on synthetic dew showed that the fraction of

16 ammonium (NH_4^+) released as gas-phase ammonia (NH_3) during evaporation is dependent on

17 the relative abundances of anions and cations in the dew. Hence, the fraction of NH_3 released

18 during dew evaporation (Frac(NH_3)) can be predicted given dew composition and pH. Twelve

19 separate ambient dew samples were collected at a remote high elevation grassland site in

20 Colorado from 28 May to 11 August, 2015. Average $[NH_4^+]$ and pH were 26 μM and 5.2,

21 respectively, and were on the lower end of dew $[NH_4^+]$ and pH observations reported in the

22 literature. Ambient dew mass (in g m^{-2}) was monitored with a dewmeter, which continuously

23 measured the mass of a tray containing artificial turf representative of the grass canopy to track

24 the accumulation and evaporation of dew. Simultaneous measurements of ambient NH_3

25 indicated that a morning increase in NH_3 was coincident in time with dew evaporation, and that

26 either a plateau or decrease in NH_3 occurred once the dew had completely evaporated. This

27 morning increase in NH_3 was never observed on mornings without surface wetness (neither

28 dew nor rain, representing one-quarter of mornings during the study period). Dew composition

29 was used to determine an average Frac(NH_3) of 0.94, suggesting that nearly all NH_4^+ is released

back to the boundary layer as NH_3 during evaporation at this site. An average NH_3 emission of 6.2 ng m^{-2} s^{-1} during dew evaporation was calculated using total dew volume (V_{dew}) and evaporation time (t_{evap}), and represents a significant morning flux in a non-fertilized grassland. Assuming a boundary layer height of 150 m, the average mole ratio of NH_4^+ in dew to NH_3 in the boundary layer at sunrise is roughly 1.6 ± 0.7. Furthermore, the observed loss of NH_3 during nights with dew is approximately equal to the observed amount of NH_4^+ sequestered in dew at the onset of evaporation. Hence, there is strong evidence that dew is both a significant night-time reservoir and strong morning source of NH_3. The possibility of rain evaporation as a source of NH_3, as well as dew evaporation influencing species of similar water solubility (acetic acid, formic acid, and HONO) is also discussed. If release of NH_3 from dew and rain evaporation is pervasive in many environments, then estimates of NH_3 dry deposition and NH_x ($\equiv NH_3 + NH_4^+$) wet deposition may be overestimated by models that assume that all NH_x deposited in rain and dew remains at the surface.

1   Introduction

Ammonia (NH_3) is the most prevalent alkaline gas in the atmosphere and has important implications for both climate and air quality (Seinfeld and Pandis, 2006). For instance, NH_3 partitions to acidic fine particulate matter (PM$_{2.5}$, aerosol with diameter < 2.5 μm) to form particulate-phase ammonium (NH_4^+), which alters aerosol properties such as hygroscopicity (Petters and Kreidenweis, 2007) and scattering efficiency (Martin et al., 2004). High atmospheric loadings of PM$_{2.5}$ can lead to adverse health effects (Pope et al., 2002) as well as reduced visibility. NH_3 is primarily emitted to the atmosphere through agricultural activities (e.g. fertilization, animal husbandry) in addition to natural sources (e.g. soil, vegetation, oceans, volcanoes, wildfires) and other anthropogenic sources (vehicles and industry) (Reis et al., 2009). Deposition of atmospheric NH_x ($\equiv NH_3 + NH_4^+$) can cause eutrophication and soil acidification in sensitive ecosystems (Krupa, 2003). Hence, there is great interest in being able to accurately model sources, sinks and reservoirs of NH_x.

A common feature in the diurnal cycle of atmospheric NH_3 mixing ratios is a morning increase or "spike" that typically occurs around 7:00-10:00. Frequently observed in many environments, current hypotheses to explain the morning NH_3 increase include dew evaporation (Gong et al., 2011; Wentworth et al., 2014; Wichink Kruit et al., 2007), plant and/or soil emissions (Bash et al., 2010; Ellis et al., 2011), mixing down of NH_3-rich air during the break-up of the nocturnal boundary layer (Walker et al., 2006) and automobile emissions during morning rush hour (Gong

et al., 2011; Löflund et al., 2002; Nowak et al., 2006; Whitehead et al., 2007). Several field studies have indicated that NH_3 desorption from microscopic water films on leaf surfaces can yield significant fluxes (Burkhardt et al., 2009; Flechard et al., 1999; Neirynck and Ceulemans, 2008; Sutton et al., 1998); therefore, it is reasonable to suggest that macroscopic dew droplets have the same effect. Wentworth et al. (2014) observed a larger morning increase following nights with high relative humidity (RH, a surrogate for dew) and Wichink Kruit et al. (2007) found increasing upward fluxes as soon as the canopy began to dry as measured by a leaf wetness sensor.

Dew generally forms during calm, clear nights when radiative cooling of the surface favours the condensation of water (Richards, 2004). Formation typically starts shortly after sunset and lasts until sunrise when surface heating and a drop in RH initiate evaporation. Over the last five decades, several dozen studies have characterized dew composition and have found that NH_4^+ is a ubiquitous constituent of dew and, in some environments, can be the most abundant cation (e.g. Polkowska et al., 2008; Wagner et al., 1992; Yaalon and Ganor, 1968; Yadav and Kumar, 2014). Average $[NH_4^+]$ reported in dew ranges from 25 μM (Lekouch et al., 2010) to 1600 μM (Yadav and Kumar, 2014). The composition of dew is primarily controlled by dissolution of water soluble gases (e.g. NH_3, HNO_3, CO_2, SO_2) and deposition of coarse mode particles (larger than $PM_{2.5}$ but smaller than 10 μm in diameter) (Takeuchi, 2003).

Field-scale models typically allow NH_3 to only deposit on leaf cuticles (i.e. it cannot desorb) and use an empirically-derived function of RH and cuticle acidity to calculate a cuticle deposition velocity. This parameterization accounts for enhanced deposition to acidic water films on leaf surfaces. There are only a handful of field-scale NH_3 models that allow for desorption of NH_3 from drying water films on leaf cuticles (Burkhardt et al., 2009; Flechard et al., 1999; Neirynck and Ceulemans, 2008; Sutton et al., 1998). Three of these studies (Flechard et al., 1999; Neirynck and Ceulemans, 2008; Sutton et al., 1998) compared models with and without cuticle desorption and found that allowing for NH_3 emission from water films on cuticles agrees better with observed fluxes during the morning. Other field-scale measurements attribute discrepancies between measured and modelled morning fluxes to NH_3 emission during the drying of canopies (e.g. Bash et al., 2010; Walker et al., 2013; Wyers and Erisman, 1998). Most larger scale (regional or global) chemical transport models (CTMs) still employ highly simplified deposition schemes for NH_3 using look-up tables for deposition velocity and canopy resistance terms (Wesely, 1989). In other words, they treat deposition and emission of NH_3

independently despite abundant field evidence that these processes are often highly coupled. However, some recent studies have successfully incorporated a bi-directional NH_3 exchange framework into regional and global CTMs (Bash et al., 2013; Wichink Kruit et al., 2012; Zhu et al., 2015).

Although most NH_3 surface-air exchange studies account for enhanced deposition to microscopic water films and several even model NH_3 desorption, far fewer have attempted to assess the role that macroscopic dew has on influencing NH_3 fluxes. This partly stems from the inherent difficulty in measuring dew amount, composition, and pH. Only a few NH_3 surface-air exchange studies have attempted to measure dew composition and pH, and did so by manually collecting enough individual droplets in pipettes to perform bulk analyses (Bash et al., 2010; Burkhardt et al., 2009; Walker et al., 2013). To constrain dew amount, Burkhardt et al. (2009) used an empirically-derived relationship to approximate water film thickness from a leaf wetness sensor. Walker et al. (2013) estimated dew amount by difference in water mass between wet and dried leaves. Both studies acknowledge the large uncertainties associated with these methods for estimating total dew amount in the canopy. Regardless, Walker et al. (2013) estimated a maximum flux of 17.6 ng NH_3 m^{-2} s^{-1} from dew evaporation in a fertilized corn canopy. One key assumption in this calculation is that all of the NH_4^+ present in dew is released as NH_3 during evaporation.

Few studies have examined the fate of semi-volatile solutes (e.g. NH_4^+/NH_3, NO_2^-/HONO, acetate/acetic acid etc…) in rain, cloud, fog or dew during droplet evaporation. Takenaka et al. (2009) studied the chemistry of drying aqueous salts in a series of lab experiments and found that the fraction of "volatile" anions (which they operationally defined as NO_2^-, acetate, and formate) remaining on the surface as a salt upon evaporation depends on the relative equivalents of "non-volatile" cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) and "non-volatile" anions (Cl^-, NO_3^-, and SO_4^{2-}). The fraction of volatile anion (X^-) that is released during evaporation (as $HX_{(g)}$) can then be predicted using the following equation (Takenaka et al., 2009):

$$Frac(X) = \frac{[X]_i - (\Sigma cations - \Sigma anions)}{[X]_i} \qquad (1)$$

where Frac(X) is the fraction of the initial anion released to the atmosphere during evaporation, $[X]_i$ is the initial equivalents of "volatile" anion X, and Σcations and Σanions are the sums of "non-volatile" cations and anions, respectively. The authors performed numerous experiments for NO_2^-, acetate, and formate under a wide range of solute concentrations and pH values and

found that Eq. (1) was consistently able to predict the fraction of each constituent liberated during evaporation of aqueous salt solutions. Although not the focus of the work, Takenaka et al. (2009) also performed some evaporation experiments on solutions containing NH_4^+ and were able to predict $Frac(NH_3)$ with an analogous equation:

$$Frac(NH_3) = \frac{[NH_4^+]_i - (\Sigma anions - \Sigma cations)}{[NH_4^+]_i} \qquad (2)$$

where $[NH_4^+]_i$ is the initial ammonium concentration in the solution.

Few field studies have simultaneously quantified both dew and atmospheric composition. He et al. (2006) observed HONO emission from a drying forest canopy and performed lab studies to show that, on average, ~90% of NO_2^- was released as HONO during droplet evaporation. Rubio et al. (2009, 2012) found positive correlations between formaldehyde, phenols and HONO in dew and the atmosphere. However, none of these studies, or those mentioned earlier for NH_3, accurately measured dew amount (in g m^{-2}) on the surface, so the relative abundances of the analyte in the dew and gas-phase could not be reliably calculated.

Therefore, great uncertainty exists regarding the influence of dew on boundary layer composition, particularly with respect to NH_3 mixing ratios. Motivated by the paucity of data on dew-atmosphere NH_3 fluxes, as well as uncertainties about the origin(s) of the frequently observed yet currently unexplained morning NH_3 spike, the specific goals of this study are to:

1) Determine the fate of NH_4^+ during dew evaporation (Section 3.1). What is the ratio of NH_x released as NH_3 versus NH_4^+ remaining on the surface as a non-volatile salt? What factor(s) govern this ratio?

2) Simultaneously quantify dew amount, NH_3 mixing ratio, and dew composition at the onset of evaporation at a field site (Section 3.2).

3) Use measurements from 1) and 2) to calculate the relative abundance of NH_4^+ in dew and NH_3 in the boundary layer, as well as NH_3 fluxes from dew evaporation (Section 3.3). Is dew a significant night-time sink or reservoir for NH_3? Is NH_3 release from dew an important morning source?

4) Evaluate if NH_3 is also released during rain evaporation (Section 3.4).

5) Assess the impact of dew evaporation for other water-soluble gases (Section 3.5).

2 Materials and Methods

2.1 Drying Chamber

A drying chamber was used to determine the fraction of NH_4^+ lost as NH_3 during droplet evaporation and was based on the set-up used by Takenaka et al. (2009). The set-up consists of a zero air cylinder (AI Z300, Airgas) and mass flow controller which deliver zero air at a controlled flow rate into a drying chamber (URG-2000-30H, URG Corp.) containing droplets of synthetic dew. Downstream of the drying chamber is an annular denuder (URG-2000-30, URG Corp.) coated with a phosphorous acid solution (10 g H_3PO_3 in 100 mL deionized water and 900 mL HPLC grade methanol) to capture any NH_3 emitted during dew drying.

At the beginning of each experiment, 26 droplets (20 μL each) of synthetic dew were deposited in the drying chamber and dried over the course of several hours by exposure to a flow of 2 L min^{-1} of zero air. Immediately after the last droplet had dried, the residue remaining in the chamber was extracted twice using two separate 10 mL aliquots of deionized water (18.2 MΩ cm^{-1}) and vigorous washing. The second aliquot always contained <10% of each analyte relative to the first aliquot. The annular denuder was extracted by adding 10 mL of deionized water and rotating for 10 minutes. Concentrations of ions in all three extracts were quantified using ion chromatography (IC) systems (DX-500, Dionex Inc.) and an isocratic elution scheme (1.8/1.7 mM Na_2CO_3/$NaHCO_3$ solution for anions and 0.020 mM methanesulphonic acid solution for cations). The pH of the dew was determined using a commercial pH meter (Orion Model 250A, Thermo Scientific). The fraction of each analyte remaining in the salt residue was then calculated, as well as the fraction of ammonium lost as NH_3 based on the total NH_x amount measured in the three aliquots.

Experimental parameters (composition, pH and drying time) were varied to determine the factor(s) responsible for the fraction of NH_3 that is released from dew as it dries. Synthetic dew was prepared by dissolving salts in deionized water to the desired concentration. All salts were reagent grade, obtained from Sigma Aldrich and used without further purification. The pH was then adjusted with either concentrated acid (HCl) or base (NaOH). A total of nine different synthetic dews were prepared to mimic ambient dew composition reported from previous studies (e.g. Lekouch et al., 2010; Takenaka et al., 2003; Yadav and Kumar, 2014). The pH and concentrations of the nine synthetic dews are listed in supplemental Table S1.

Synthetic dew was deposited as 20 μL droplets, which corresponds to a hemi-spherical diameter of ~4.25 mm. Takeuchi et al. (2002) found that the diameter of most dew droplets range from 0.8 to 1.0 mm in diameter; however, applying such small droplets would bring the concentration of the extracts below detection limit. In order to maintain solute concentrations relevant to ambient dew, but generate sufficient signal for analysis, it was necessary to use 20 μL droplets. The impact of larger droplet size on NH_3 liberation was tested by performing several drying experiments on four 140 μL drops (~8.1 mm in diameter). These larger droplets had no effect on the fraction of NH_3 emitted relative to the 20 μL droplets.

2.2 Field Site

Ambient measurements of dew composition, dew volume and gas-phase NH_3 were obtained at a field site situated on the eastern edge of Rocky Mountain National Park (RMNP) in Northern Colorado (40.2783° N, 105.5457° W; 2784 m a.s.l.) from 28 May to 31 August, 2015. The field site is remote with the nearest town (Estes Park, CO, population ~6,000) located approximately 14 km north. This site is also used by the Interagency Monitoring of Protected Visual Environments (IMPROVE) and EPA Clean Air Status and Trends Network (CASTNet) programs for air quality monitoring and has been the location of extensive studies on nitrogen deposition (Beem et al., 2010; Benedict et al., 2013a) and atmospheric reactive nitrogen (Benedict et al., 2013b). The field site is a grassland clearing approximately 150 m in diameter surrounded by a mixed aspen and pine forest (average summertime maximum leaf area index of 1.5). In addition, excessive nitrogen deposition at RMNP has been linked to ecological impacts including changes in diatom assemblages (Baron, 2006; Wolfe et al., 2003) and shifts in a dry alpine meadow community (Bowman et al., 2012). Recently, Nanus et al. (2012) suggested that the critical load for nitrogen deposition (a value beyond which negative ecological impacts are observed) has been exceeded in ~21% of the Rocky Mountains. The existing body of knowledge regarding reactive nitrogen at RMNP makes this site ideal to examine how dew-atmosphere interactions affect NH_3 in the boundary layer as well as its deposition.

2.3 Atmospheric Measurements

NH_3 was measured using a Picarro G1103 Analzyer, a cavity ringdown spectroscopy instrument. The inlet line was 3.56 cm diameter Teflon tubing located approximately 2.5 m above ground level. The entire length of the 0.61 m inlet line was insulated and heated to 40°C

to minimize wall losses. A filter (Picarro P/N S1021) was placed on the end of the inlet to prevent particles from entering the instrument. The filter was also heated which may have caused NH_4NO_3 to volatilize from the filter or air stream resulting in an overestimation of the ammonia concentration. However, a previous study at the site found that, on average, only a small fraction of particulate NH_4^+ exists as NH_4NO_3 during the summer (Benedict et al., 2013b). Furthermore, the same study found that NH_3 was the majority of the NH_x ($\equiv NH_3 + NH_4^+$) loading. Hence, it is unlikely that there is a large interference from NH_4NO_3 volatilization.

Calibrations were performed twice during the field deployment using MKS mass flow controllers, a certified 2 ppm NH_3 cylinder (AirGas), and a zero air source (Teledyne Zero Air Generator Model 701). The calibration gas was split between the Picarro and a phosphorus acid (10% w/v) coated denuder to act as a check of the concentration. The denuder was sampled at 2 L min^{-1} and the total volume was recorded using a dry gas meter. The concentration determined by the denuder was used as the "true" concentration in the calibration curve.

Meteorological measurements were made at the site by a 10 m tower operated by the National Park Service. Measurements are reported at 1 hour intervals for solar radiation, temperature, wind speed, wind direction, standard deviation of the wind direction over the period, relative humidity, and rainfall.

2.4 Dew Measurements

Ambient dew samples at RMNP were gathered using a dew collector with a design similar to Guan et al. (2014). The collector was built in-house and consists of a wooden base that supports a 7 cm-thick polystyrene foam block with an area of 48 x 60 cm. The top surface of the polystyrene block is covered by a 0.2 mm-thick polytetrafluoroethylene (Teflon®) sheet. The Teflon® sheet is parallel to the ground at a height of 30 cm. During the night the Teflon® sheet undergoes radiative cooling while the polystyrene insulates the sheet from below. This results in dew formation on the Teflon® surface which can be manually collected into clean sample bottles the following morning using a pre-cleaned scraper and funnel. The emissivity of Teflon® is 0.94 (Baldridge et al., 2009) and is very similar to that of vegetation (0.95) (Guan et al., 2014).

The dew collector was deployed before dusk on nights that had a forecast favourable for dew formation (high relative humidity, light winds, and clear skies). The Teflon® surface was cleaned immediately before deployment in a two-step process: 1) splashing ~1 L of deionized

water across the surface, followed by 2) squirting ~30 mL of deionized water on the surface and scraping it off using a plastic scraper. The latter step was repeated 10 times, and the 10th rinse was collected and used as a field blank for dew collected the following morning. Prior to dew collection, the funnel and scraper were rinsed 10 times with deionized water. This cleaning procedure proved sufficient and is similar to prior studies using a similar collector (e.g. Okochi et al., 2008; Wagner et al., 1992). Dew samples were collected into 15 mL polypropylene sample bottles in order to minimize headspace during transport and storage.

If rain had occurred during the night, then rain samples were also collected off of the dew collector in a similar fashion the following morning. Rain samples were unambiguously identified using data from the dewmeter described below.

Chemical analyses of all dew samples were performed within 6 hours of collection, with the exception of one sample which was stored at 4 °C and analysed 48 hours later. The concentration of ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, acetate, formate and oxalate) in dew samples was determined through ion chromatography and pH was measured with a pH meter, as outlined in section 2.1. The total organic carbon (TOC) and inorganic carbon (IC) were quantified with a commercial TOC analyser (TOC-V$_{CSH}$, Shimadzu Corp.) equipped with a total nitrogen (TN) analyser (TNM-1, Shimadzu Corp.) for quantification of TN. Concentrations of analytes in ambient dew samples were background corrected by subtracting the volume-weighted concentration in the tenth rinse collected the prior evening which is likely an upper bound for the background signal given that some volatile solutes will be scavenged from the air during application and collection of the rinse.

It was also necessary to quantify the volume of dew (V_{dew}) that formed each night. The dew collector is not suitable since V_{dew} obtained from the collector is not necessarily representative of V_{dew} that forms naturally on the grassland canopy at RMNP. Numerous methods and instruments exist to measure V_{dew}; for instance, the cloth-plate method (Ye et al., 2007), lysimeter-related instruments (Grimmond et al., 1992; Price and Clark, 2014), and eddy-correlation techniques (Moro et al., 2007). Although there is no standard method to measure V_{dew}, Richards (2004) provides a detailed overview of various techniques that have been used to collect and quantify dew.

For this study, we constructed a dewmeter similar to that of Price and Clark (2014). The design consists of a circular collection tray (diameter of 35 cm) that is attached to the top of an analytical balance (HRB 3002, LWC Measurements). The balance has a resolution of 0.01 g

1 and a maximum load of 3000 g. The tray contains artificial turf that is intended to be

2 representative of the grass at the RMNP field site during the early part of the growing season.

3 The balance was contained in a weatherproof box with a hole cut in the lid to accommodate the

4 tray/turf. The mass on top of the balance was recorded to a laptop at a rate of 5 Hz so that the

5 mass of dew was continuously monitored as it formed and evaporated. The data were averaged

6 to 10 min to achieve better signal-to-noise.

7 Price and Clark (2014) performed an extensive characterization of the dewmeter and compared

8 dew formation/evaporation on co-located dewmeters containing real turf and artificial turf. The

9 authors found that V_{dew} and the dew deposition rate were identical between the two turfs. In

10 other words, the radiative properties and surface area of artificial turf sufficiently mimic real

11 turf such that artificial turf can be used as a surrogate to quantify V_{dew} and its temporal

12 evolution. The advantage of using artificial turf is that there are no changes in mass due to

13 evapotranspiration during the daytime. The dewmeter is also capable of quantifying rainfall and

14 its evaporation. However, if the rainfall is too intense (≥ 2 mm) then the tray becomes flooded

15 and must be replaced with a dry tray/turf.

2.5 Flux Calculation

17 NH_3 fluxes from dew evaporation were calculated using the following equation:

$$F_{NH3} = \frac{[NH_4^+] \cdot V_{dew}}{t_{evap}} \cdot Frac(NH_3) \cdot 17{,}031 \tag{3}$$

19 where F_{NH3} is the average emission flux (in ng m^{-2} s^{-1}) during dew drying, $[NH_4^+]$ is the

20 concentration of ammonium in dew (in μM), V_{dew} is the volume of dew in the canopy (in L m^{-}

21 ^{2}), t_{evap} is the time it takes for dew to evaporate (in s), $Frac(NH_3)$ is the fraction of NH_4^+ in the

22 dew that is released as NH_3, and 17,031 is to convert μmol to ng. It is important to note that Eq.

23 (3) yields the average F_{NH3} during evaporation and cannot account for any variations in F_{NH3}

24 over the evaporation period. The dewmeter was used to record V_{dew} and t_{evap}, whereas sample

25 from the dew collector was used to quantify $[NH_4^+]$ and calculate $Frac(NH_3)$. The dewmeter is

26 automated and was deployed continuously from 22 June until 31 August (and intermittently

27 between 27 May and 21 June), whereas the dew collector requires manual cleaning and

28 collection so was only deployed when forecasts were favourable for dew formation.

3   Results and Discussion

3.1   Fraction of NH_3 that evaporates from drying dew

We tested the validity of Eq. (2) by performing a series of drying experiments similar to Takenaka et al. (2009) but specifically targeting conditions relevant for dew (i.e. composition and drying time). Takenaka et al. (2009) used solutions in the mM range with drying times of ~9 h, whereas natural dew is typically less concentrated (μM range) and usually dries within a few hours. The composition of synthetic dew (Table S1) and drying time (~2.5 h) in this work are a better representation of natural dew.

Figure 1 shows the measured Frac(NH_3) versus predicted Frac(NH_3) from an updated form of Eq. (2) (see below for details) for the nine synthetic dews. Drying experiments were performed three times per dew composition, and error bars in Fig. 1 denote the standard deviation between experiments. The amount of NH_x ($\equiv NH_4^+ + NH_3$) recovered was always within 20% of the amount of NH_4^+ added at the beginning of the experiment. There is good agreement between the measured and predicted Frac(NH_3) which is mostly consistent with the findings of Takenaka et al. (2009) with a few key differences: 1) the majority of acetate and formate remained as a salt after evaporation, 2) HCO_3^- was an important constituent in the anion balance, and 3) the pKa of each substance must be considered. Although acetic acid, formic acid, and carbonic acid are relatively volatile, the conjugate bases can (and do) form non-volatile salts upon evaporation if there is an excess of cations. Furthermore, if the pH is near or less than the pKa of the acids then a significant fraction will be neutral (protonated) and unable to form a salt. Hence, we update the definition of Σanions in Eq. 2 to include acetate, formate, and bicarbonate (also reflected in Fig. 1) which yields much better agreement in predicted versus measured Frac(NH_3).

Since ion chromatography quantifies the total amount of each species (i.e. both charged and neutral forms) it is necessary to use pH and the acid dissociation constant (K_a) for each species to calculate the ionic fraction of each. Furthermore, Takenaka et al. (2009) recommend including carbonate/bicarbonate in the ion balance for field samples. The authors did not account for CO_2-equilibria since their lab experiments were performed under strict CO_2-free conditions, whereas our synthetic dew samples had sufficient exposure to lab air to equilibrate with atmospheric CO_2 (~500 ppm in the lab) as verified by subsequent inorganic carbon measurements (section 2.4). Hence, we calculated the amount of HCO_3^- and CO_3^{2-} in synthetic

1   dew using pH and carbonate equilibria assuming P_{CO_2} = 500 ppm. Charge imbalance calculated

2   in Eq. (2) is a result of CO_2 dissolving (or outgassing if a large quantity of bicarbonate/carbonate

3   salt was added) as well as the addition of HCl or NaOH.

3.2   Dew Parameters

5   A total of 12 dew samples for chemical analysis were collected at RMNP over the study period.

6   The equivalent concentrations of ions are given in Fig. 2 and TOC, IC, TN, pH and Frac(NH_3)

7   in Table 1. Average values of [NH_4^+] in dew found in the literature span several orders of

8   magnitude ranging from 25 μM in coastal Croatia (Lekouch et al., 2010) to 1600 μM in urban

9   India (Yadav and Kumar, 2014). Dew at RMNP is at the lower end of this range with median

10   [NH_4^+] = 28 μM. In general, the concentrations of all species in RMNP dew are lower than most

11   previous studies (e.g. Singh et al., 2006; Takenaka et al., 2003; Wagner et al., 1992). This is

12   due to the remoteness of RMNP resulting in low levels of coarse mode aerosol and water-

13   soluble gases which tend to control the composition of dew via deposition and dissolution

14   (Takeuchi, 2003; Wagner et al., 1992). The dominant cations in dew at RMNP are Ca^{2+} and

15   NH_4^+. The former is likely from the deposition of coarse mode soil and/or dust particles and the

16   latter from gas-phase dissolution of NH_3. Acetate and formate are the major anions and may be

17   the result of dissolution of acetic and formic acid (Wagner et al., 1992) and/or the products of

18   aqueous-phase oxidation of semi-volatile organics (SVOCs, e.g. aldehydes) which has been

19   observed in cloud and fog water (Herckes et al., 2007, 2013; Munger et al., 1989). The area

20   surrounding the field site is heavily forested and the boundary layer is likely rich in biogenic

21   SVOCs which could explain the high TOC content in the dew (average = 6.23 mg C L^{-1}). The

22   ability for dew to act as a medium for aqueous-phase oxidation of SVOCs is outside the scope

23   of this paper but warrants further investigation.

24   The average pH of dew at RMNP was 5.19 (median = 5.34) which is on the lower range of what

25   has been reported for dew. For instance, Yaalon and Ganor (1968) and Xu et al. (2015) found

26   median dew pH of 7.7 and 6.72 in Jerusalem and Changchun, China, respectively. Whereas

27   Pierson et al. (1986) reported an average dew pH of 4.0 at a rural site in Pennsylvania in a

28   region containing several coal-fired power plants. Given the remoteness of RMNP and low

29   ionic concentrations, CO_2 dissolution plays an important role in governing dew pH. Acidic

30   dews are considered to enhance deposition of NH_3 and hinder that of certain weakly acidic

31   gases (e.g. SO_2, organic acids) (Chameides, 1987; Okochi et al., 1996). In addition, the average

32   summertime NH_3 mixing ratio at RMNP is about a factor of 3 higher than that of HNO_3

1 (Benedict et al., 2013b) which is roughly the same ratio as $NH_4^+:NO_3^-$ in dew measured in this
2 study.

3 Figure 2 reveals a persistent ion imbalance for ambient dew samples. On average, about 25%
4 more anion is needed to achieve ion balance with the measured cations. This implies that some
5 anions are unaccounted for in the system. Possible explanations include: 1) longer chain organic
6 acids (e.g. succinate, maleate, malonate, and pyruvate) and/or 2) silicates from wind-blown
7 dust.

8 Equation (2) was used to calculate $Frac(NH_3)$ for ambient dew samples (average = 0.94). Only
9 three of the twelve samples had a $Frac(NH_3)$ less than 1 meaning that, in most cases, all of the
10 NH_4^+ present is predicted to volatilize as NH_3 during dew evaporation. It is important to note
11 that acetate, formate, and HCO_3^- were included in the $\sum$anion budget in contrast to Takenaka et
12 al. (2009). If the aforementioned anions were not included in the $Frac(NH_3)$ calculation then all
13 dew samples would have $Frac(NH_3) = 1$.

14 The high $Frac(NH_3)$ has an important implication for N-deposition: NH_3 that is dry deposited
15 onto a surface wetted with dew does not necessarily contribute to N-deposition. In other words,
16 NH_3 deposited into dew overnight should not necessarily be counted towards the total N-
17 deposition budget for a given ecosystem. The consequence of this implication likely extends
18 beyond RMNP and merits additional field measurements of dew to calculate $Frac(NH_3)$ in other
19 environments (e.g. agricultural, urban, and rural). To our knowledge, this is the first field study
20 to quantify the extent to which NH_4^+ is released as NH_3 during dew evaporation. Additional
21 research is needed to examine the effects of: 1) salts already present on vegetative surfaces on
22 dew composition, 2) dew transfer from leaf to soil prior to evaporation, and 3) different
23 canopies (e.g. forest, tall grass) on the amount and timing of dew accumulation and evaporation.

24 ## 3.3 Dew-Atmosphere NH_3 Fluxes

25 In this section we examine how the formation and evaporation of dew impacts NH_3 in the
26 boundary layer. Figure 3 shows time series (from 19:00 to 11:00 the following day) of dew
27 mass (g m^{-2}), air temperature (°C) and NH_3 mixing ratio (ppbv) on four separate nights with
28 dew. One feature common to all four panels is the increase of NH_3 at the onset of dew
29 evaporation followed by a plateau or decrease of NH_3 once the surface had dried completely.
30 The features in Fig. 3 are representative of the other 29 nights on which dew formed during the
31 study period (27 May to 31 August). It should be noted that in Fig. 3c and 3d, the start of the

1 morning NH_3 increase is slightly delayed from the onset of dew evaporation. This may be

2 attributed to canopy growth over the course of the campaign – during May and June (Figs. 3a

3 and 3b) the grassland canopy was relatively short (~5 cm) and roughly the same height as the

4 artificial turf on the dewmeter. However, during July (Fig. 3c) and August (Fig. 3d) the canopy

5 had grown significantly (up to ~30 cm) providing significant shade to lower parts of the grass

6 such that dew finished evaporating off the dewmeter prior to complete drying of the canopy.

7 This would also cause an underestimation of dew amount by the dewmeter towards the end of

8 the measurement period.

9 The consistent timing between dew evaporation and the increase in NH_3 mixing ratio is strong

10 evidence that dew evaporation and the early morning NH_3 increases are linked, but other

11 phenomena must be considered. For instance, it is well known that NH_3 emissions from plant

12 stomata and soil are heavily temperature dependent and increase at higher temperatures

13 (Massad et al., 2010; Sutton et al., 2013; Zhang et al., 2010). However, NH_3 decreases after

14 dew evaporation ceases, despite a continued increase in temperature, suggesting that this

15 morning increase is not from stomata or soil emissions. Another possible explanation is reduced

16 deposition after dew evaporation since wet canopies provide a lower resistance to deposition

17 for water-soluble gases (e.g. NH_3) relative to dry canopies (Fowler et al., 2009; Neirynck and

18 Ceulemans, 2008); however, this scenario requires other continuous source(s) of NH_3. If this

19 were the mechanism responsible for morning NH_3 increases then one would expect a plateau

20 in NH_3 after canopy drying. However, Figs. 3a, 3b, and 3d all show NH_3 decreases after dew

21 evaporation. In addition, RMNP is sufficiently remote that morning NH_3 increases cannot be

22 from rush-hour traffic or industrial sources.

23 It is also useful to consider the behaviour of NH_3 on mornings without dew. Of the 72 nights

24 on which the dewmeter was deployed and functioning, there was night-time rain on 23 of the

25 nights, and no surface wetness (neither rain nor dew) at sunrise on 16 nights. Typically, dew

26 formation began around 20:30 and it had completely evaporated by 9:00 the following morning.

27 Figure 4 compares NH_3 mixing ratios from 4:00 to 11:00 on mornings with dew (Fig. 4a) and

28 without dew or rain (Fig 4b). The clear morning NH_3 increase only happens on mornings with

29 dew, further supporting the hypothesis that dew evaporation has a significant influence on near-

30 surface NH_3 mixing ratios. The traces in Fig. 4 are coloured according to the average NH_3

31 mixing ratio the previous night (from 19:00 to 21:00). The magnitude of the morning increase

32 is related to the amount of NH_3 present the previous night suggesting that most of the NH_4^+ in

1 dew is a result of NH_3 dissolution. This is additional evidence that NH_3 deposited in dew

2 overnight at RMNP is recycled back to the atmosphere the following morning upon

3 evaporation, and should not be counted towards total N-deposition. In other words, the dew

4 acts as a temporary reservoir for atmospheric ammonia and the cycle of dew formation and

5 evaporation has a strong influence on boundary layer NH_3 concentrations.

6 Table 1 shows the calculated NH_3 fluxes from dew during evaporation (average = 6.2 ng m^{-2} s^{-}

7 ^{1}) as well as the relevant parameters required for flux calculations (t_{evap}, Frac(NH_3), and V_{dew}).

8 To our knowledge, only two studies to date have reported NH_3 fluxes in a non-fertilized

9 grassland. Wichink Kruit et al. (2007) used the aerodynamic gradient method to measure a daily

10 average summertime NH_3 flux of 4 ng m^{-2} s^{-1} in a field in the Netherlands, whereas Wentworth

11 et al. (2014) inferred a daily average soil emission flux of 2.6 ng m^2 s^{-1} during August in a rural

12 field near Toronto, Canada using simultaneous soil and atmospheric measurements and a simple

13 resistance model. In the context of these previous studies over the same land type, the dew-

14 related NH_3 fluxes at RMNP are significant. Furthermore, it is likely that dew-related NH_3

15 fluxes would be substantially larger at the other field sites given that NH_3 mixing ratios were a

16 factor of 3-10 higher which would result in higher dew [NH_4^+].

17 It is likely that during some periods the emission/deposition footprint of the atmospheric and

18 dew measurements extends beyond the grassland clearing and into the surrounding forest.

19 While we did not find that the overnight loss rate of ammonia depended on dew amount, the

20 deposition rate of ammonia likely depends on surface type, so estimates of moles of NH_3

21 deposited per m^2 from the dew collector may not be representative of the surrounding forest.

22 Upslope and downslope flow conditions could also explain some of the variability in nocturnal

23 NH_3 since the latter is prevalent during the nighttime and delivers cleaner air from the west of

24 RMNP. Subsequent work should be performed to examine the representativeness of grassland

25 dew measurements to the larger surrounding ecosystem.

26 For the 12 dew samples listed in Table 1, a simple calculation was performed to estimate the

27 moles of NH_4^+ contained in dew relative to the moles of NH_3 in the boundary layer. Particulate

28 NH_4^+ is not considered due to its low mass loadings at RMNP (Benedict et al., 2013b). The

29 μmol m^{-2} of NH_4^+ in dew at the onset of evaporation was calculated by multiplying V_{dew} by

30 dew [NH_4^+]. One inherent assumption is that [NH_4^+]$_{dew}$ on the collector is representative of the

31 dew on the dewmeter. An equivalent mole loading (also in μmol m^{-2}) of NH_3 in the boundary

32 layer was calculated by first converting the measured mixing ratio from ppbv to μmol m^{-3}, and

then multiplying by an assumed boundary layer depth of 150 m. The average ratio of $NH_4^+{}_{,dew}$:$NH_{3,BL}$ is 1.6 ± 0.7 for the 12 dew samples collected. In other words, on a per mole basis there is nearly double the NH_4^+ in dew than there is NH_3 in a 150 m deep boundary layer. Unfortunately, there are no measurements at RMNP that allow a better constraint of the boundary layer height. Assuming a smaller (larger) boundary layer height would increase (decrease) the $NH_4^+{}_{,dew}$:$NH_{3,BL}$ ratio.

The measured loss of NH_3 (in ppbv) during dew nights was used to estimate the sink of NH_3 (in μmol m^{-2}) between the onset of dew formation and evaporation. This loss was estimated in a similar fashion as above assuming: 1) 150 m nocturnal boundary layer, 2) no reactive sinks (e.g. NH_4NO_3 formation), 3) no exchange with the free troposphere, and 4) no influence from horizontal advection (i.e. upslope/downslope flow) on NH_3. Figure 5 shows a correlation plot of estimated NH_3 lost on dew nights versus the observed NH_4^+ accumulated in dew. The good correlation and near-unity slope (0.71) show that there is approximate mass closure between NH_3 lost overnight and NH_3 sequestered by dew. Although these calculations are simplistic it is evident that, on average, dew sequesters a significant portion (estimated at nearly two-thirds) of NH_3 over the course of the night. Subsequent studies on dew-atmosphere interactions should include measurements of boundary layer height so a more thorough mass balance calculation can be performed.

The loss rate of NH_3 on dew nights versus dry nights was examined by fitting the NH_3 mixing ratio to an exponential decay function between 20:00 and 9:00 (or dew evaporation) on the 46 nights in Fig. 4. The fit function used was:

$$[NH_3]_t = [NH_3]_{sunset}e^{-kt} + [NH_3]_{overnight} \qquad \text{Eq. (4)}$$

where $[NH_3]_t$ is the mixing ratio of NH_3 at time t, $[NH_3]_{sunset}$ is the mixing ratio at 20:00, $[NH_3]_{overnight}$ is the plateau in nocturnal NH_3 mixing ratio, and k is an empirical fit parameter representing the apparent first-order loss rate constant of NH_3. An example of the fit is shown by the black trace in Fig. 3b.

The average NH_3 loss rate constant on dew nights was $1.33 \pm 0.5 \times 10^{-4}$ s^{-1} compared to $1.35 \pm 0.3 \times 10^{-4}$ s^{-1} on dry nights. In other words, there is no significant difference in the rate of NH_3 loss on dew versus non-dew nights. This implies that dew does not actually enhance NH_3 deposition under these conditions, suggesting that the aerodynamic and quasi-laminar resistances dominate over surface resistances. The average nocturnal wind speed on dew nights

1 was lower than on dry nights (1.3 m s^{-1} versus 2.2 m s^{-1}). Lower wind speeds typically result in

2 a higher R_a and R_b. It is possible that increased aerodynamic and quasi-laminar resistances on

3 dew nights are partially compensated for by a lower surface resistance due to dew, such that the

4 overall canopy resistance is similar on dew nights and dry nights. Average nocturnal wind

5 direction was from the NW (i.e. downslope flow) on both dew nights (307º) and dry nights

6 (313º). The average nocturnal maximum for RH was 75% on dew nights and only 53% on dry

7 nights. The lower wind speeds and higher RH on dew nights are consistent with the

8 meteorological conditions favourable for dew formation.

9 Deposition of NH_3 on dry nights could be to either leaf cuticles and/or soil pore water. However,

10 it is not possible to unambiguously attribute the nocturnal NH_3 loss solely to deposition.

11 Enhanced downslope flow of cleaner air on dry nights cannot be ruled out as a contributor to

12 nocturnal NH_3 loss. Since NH_3 deposition is independent of dew amount, there could be a large

13 discrepancy between [NH_4^+] for dew on the dewmeter versus the dew collector if V_{dew} is

14 significantly different on the two surfaces. However, the campaign averages of V_{dew} on the

15 dewmeter (Table 1) and are within 10% of dew volume obtained off the collector (data not

16 shown) so [NH_4^+] is likely similar for dew on both platforms.

17 Since most of the NH_4^+ in dew volatilizes and the presence of dew does not affect NH_3

18 deposition overnight, the net impact is a reduction in the overall removal of NH_3. As a result,

19 the atmospheric lifetime and range of NH_3 transport will be extended.

3.4 Potential Influence from Rain Evaporation

21 Numerous studies have reported rapid increases of near-surface NH_3 within 1-2 h after some

22 rain events (e.g. Cooter et al., 2010; Walker et al., 2013; Wentworth et al., 2014). Given the

23 findings discussed in the previous section, one possible explanation is the emission of NH_3 from

24 drying rain droplets. However, unlike dew, some difficult-to-predict fraction of rain will

25 permeate through the soil thus preventing or delaying the release of NH_3. Nonetheless, we

26 attempt to qualitatively explore this hypothesis by examining the Frac(NH_3) of four rain

27 samples collected at RMNP as well as the behaviour of NH_3 during rainfall evaporation. Rain

28 samples were collected with the same procedure used to collect dew, which differs from the

29 usual method of capturing precipitation via an automated precipitation bucket (e.g. Benedict et

30 al., 2013a). The precipitation bucket is normally equipped with an O-ring and lid to prevent dry

31 deposition and dissolution of water-soluble gases when it is not precipitating. On the other hand,

1 precipitation on the dew collector surface was left exposed and its composition is influenced by

2 dry deposition and gas-phase dissolution until it was collected at the onset of evaporation.

3 Supplementary Table S2 gives the concentration of ions measured in rain samples. In general,

4 concentrations of ions are comparable between dew and rain samples, with the exception of

5 NH_4^+, SO_4^{2-} and NO_3^-, which are a factor of 2-4 times more concentrated in rain samples. The

6 enhancement of these species in rain may reflect additional in-cloud and below-cloud

7 scavenging of gases (NH_3, HNO_3 and SO_2) and $PM_{2.5}$ aloft. Another possibility is that rain

8 generally forms during upslope conditions which coincide with more polluted air masses from

9 east of RMNP, whereas dew typically forms during downslope (cleaner) conditions. Numerous

10 studies have compared dew composition to rain composition and, in general, have found that

11 concentrations are enhanced in dew relative to rain (e.g. Polkowska et al., 2008; Wagner et al.,

12 1992). However, Pierson et al. (1986) reported dew composition to be similar to, but more

13 dilute than rain at a rural site in Pennsylvania.

14 Table S3 shows the TOC, IC, TN, pH and calculated Frac(NH_3) for the four rain samples. Rain

15 samples were more acidic (average pH = 4.54) than dew samples (average pH = 5.19). The

16 average Frac(NH_3) for rain samples was 0.66 suggesting that, on average, roughly two-thirds

17 of NH_4^+ contained in precipitation on surfaces should be liberated as NH_3 upon evaporation.

18 This could pose a significant flux of NH_3 to the boundary layer; however, since the fraction of

19 rain that remains on surfaces after rainfall where it can readily evaporate is not constrained,

20 only an upper estimate on NH_3 fluxes from drying rain can be calculated (21.2 ± 13 ng m^{-2} s^{-1}).

21 This value was calculated in same manner as the dew samples and assumes all rainfall

22 evaporates.

23 Figure 6 shows time series of rain accumulation (g m^{-2}), air temperature (°C) and NH_3 mixing

24 ratio (ppbv) on four separate days with observed rainfall. The rain accumulation was measured

25 with the dewfall meter; 1000 g m^{-2} of accumulation is equivalent to 1 mm of rainfall. Rainfall

26 in excess of 2000 g m^{-2} flooded the collection tray and could not be reliably recorded by the

27 dewmeter. On 24 June (Fig. 6a) there were three light rainfalls at 15:00, 16:00 and 19:00. The

28 first event at 15:00 was accompanied by a rapid decrease in NH_3 likely due to scavenging by

29 rain droplets; however, this was not observed for the other two rainfalls that day. For the second

30 rain event in Fig. 6a (at 16:00) a substantial increase in NH_3 (from 0.5 to 1.5 ppbv) was observed

31 during evaporation and is consistent with NH_3 liberation from evaporating rain. However,

32 evaporation of the other rain events on 24 June (Fig. 6a) as well as those on 27 June (Fig. 6b)

1   and 11 July (Fig. 6c) are not associated with concomitant increases in NH_3, implying that these

2   rain evaporation events did not release NH_3. The evaporation of a more substantial rainfall on

3   13 August (Fig. 6d) is associated with a temporary rise in NH_3 until evaporation ceases at

4   sundown. The instances of rain evaporation not associated with NH_3 increases could be due to

5   rain with a low Frac(NH_3), an insignificant amount of NH_4^+ in the rain, more atmospheric

6   dilution than dew mornings due to higher turbulence, and/or significant rain penetration into

7   the soil.

8   The results from Fig. 6 are consistent with previous literature showing NH_3 increase

9   immediately following only some rainfall events (Cooter et al., 2010; Walker et al., 2013;

10   Wentworth et al., 2014). The timing of some rain evaporation events with NH_3 increases, as

11   well as the high Frac(NH_3) (average = 0.66) of the four measured rain samples suggests it is

12   possible for rain evaporation from surfaces to be a substantial source of NH_3. Neirynck and

13   Ceulemans (2008) reported NH_3 increases concomitant with a drying forest canopy (after

14   rainfall) as measured by a leaf wetness sensor.

15   Currently, all NH_4^+ collected in precipitation samples is counted towards N deposition.

16   However, if a fraction of NH_4^+ in rainfall is emitted as NH_3 during evaporation then N-

17   deposition could be overestimated. At RMNP, wet deposition of NH_x and dry deposition of

18   NH_3 account for 35% and 18%, respectively, of total reactive nitrogen deposition to the site

19   (Benedict et al., 2013a). This budget does not take into account any re-emission of NH_3 from

20   drying rain. This budget also does not explicitly account for ammonia uptake or emission during

21   dew formation and evaporation. A more extensive suite of dew and rainfall measurements is

22   necessary to quantify the impact of evaporation on annual N-deposition budgets at RMNP.

23   **3.5   Implications for other Gases**

24   Other water-soluble gases with similar or larger effective Henry's law constants (K_H^{eff}) to NH_3

25   are likely influenced by dew and rain evaporation as well, provided that the relative abundance

26   of counter-ions allows for volatilization during evaporation. K_H^{eff} is the equilibrium constant

27   for describing gas-aqueous partitioning and accounts for chemical equilibria in solution. Since

28   acid-base equilibria are pH dependent, then the K_H^{eff} for acidic and basic species is also pH

29   dependent (Sander, 2015). K_H^{eff} of NH_3 was calculated for the twelve dew samples using data

30   from Sander (2015) to determine the temperature-dependent Henry's law constant (K_H) and

31   from Bates and Pinching (1950) for the temperature-dependent acid dissociation constant (K_a)

1   of NH_4^+ required for the calculation of K_H^{eff}. During the study, dew K_H^{eff} spanned two orders

2   of magnitude and ranged from $4.5x10^5$ to $2.7x10^7$ M atm^{-1}. These high values are indicative of

3   the high water solubility of NH_3 at the observed pHs and temperatures. Chameides (1987) used

4   a simple resistance model to show that deposition of gas-phase species with $K_H^{eff} > 10^5$ M atm^{-1}

5   to wetted surfaces (i.e. dew) will be limited by the aerodynamic resistance since the surface

6   resistance is negligible for such highly water-soluble species. In other words, it is likely that

7   dew will be a significant night-time sink for other trace gas species with $K_H^{eff} > 10^5$ M atm^{-1}

8   since the dissolution into dew is controlled by aerodynamic processes independent of the

9   identity of the gas.

10   Table 1 shows the ratio of $[NH_4^+]$ measured in dew to the concentration predicted from

11   equilibrium calculations using K_H^{eff} and measured NH_3 mixing ratio at the onset of evaporation.

12   The average ratio is low (0.04), consistent with a significant aerodynamic resistance that

13   prevents NH_4^+ saturation in dew droplets overnight.

14   It has been suggested that dew can act as a reservoir for phenol, nitrophenols, formaldehyde

15   and HONO based on observations of these species in dew in Santiago, Chile (Rubio et al., 2009,

16   2012). Zhou et al. (2002) found a correlation between high night-time RH (a surrogate for dew

17   formation) and HONO increases the following morning coincident with a decrease in RH. A

18   follow-up study (He et al., 2006) confirmed aqueous solutions mimicking dew can release

19   >90% of NO_2^- as HONO upon evaporation and observed similar HONO pulses during canopy

20   drying at a rural forest site in Michigan. Indeed, there is some evidence in the literature that

21   water-soluble gases (primarily HONO) exhibit a similar behaviour to NH_3 during dew

22   formation and evaporation observed in this study.

23   Table 2 shows the calculated K_H^{eff} (at 10 °C) for common water-soluble gases that could be

24   influenced by dew formation/evaporation. This table is by no means exhaustive, but highlights

25   the important role dew may have as a night-time reservoir and morning source for gases other

26   than NH_3. Formic acid (HCOOH), acetic acid (CH_3COOH), nitrous acid (HONO) and nitric

27   acid (HNO_3) all have increasing K_H^{eff} with increasing pH since a more basic solution will

28   promote dissociation of the acid into its conjugate base. The average pH of dew at RMNP (~5.2)

29   is likely sufficiently acidic for HONO to experience a surface resistance ($K_H^{eff} << 10^5$ M atm^{-1})

30   which would limit its transport across the dew-air interface. This is consistent with the low

31   average $[NO_2^-]$ (0.2 μM) in dew at RMNP, although this might simply reflect low HONO

32   mixing ratios at the remote RMNP site.

Future field studies on these species should include simultaneous measurements of dew composition, dew amount, and gas phase mixing ratios to determine whether dew is an important night-time reservoir and morning source. The latter will be dependent on the fraction of gas released upon dew evaporation, which requires further investigation specific to each gas. Based on the findings in this work and Takenaka et al. (2009) it is likely that acidic semi-volatiles (e.g. acetic acid, formic acid, HONO) will be retained as salts during dew evaporation at RMNP due to the excess of cations.

4 Conclusions

Laboratory experiments involving synthetic dew were performed to determine the factor(s) controlling the fraction of NH_4^+ released as NH_3 upon dew evaporation. Results were mostly consistent with Takenaka et al. (2009) who found that the amount of NH_3 that volatilized from drying aqueous solutions is governed by the relative abundances of NH_4^+ and excess "non-volatile" anions ($\sum$anions - $\sum$cations). However, our findings suggest that acetate, formate and HCO_3^- should also be counted towards the anion budget. Hence, the Frac(NH_3) released from a drying dew sample can be predicted given the ionic composition and pH.

A dewmeter (for dew amount, deployed continuously from 22 June to 31 August) and dew collector (for dew composition, deployed successfully on 12 occasions) were set up at a remote field site in Colorado. Dew was relatively dilute compared to previous studies and had an average [NH_4^+] of 26 μM and pH of 5.2 at sunrise. Simple calculations revealed that dew can act as a significant night-time reservoir of NH_3. At the onset of dew evaporation there was, on average, roughly twice as much NH_4^+ in dew as NH_3 in the boundary layer. Furthermore, the observed NH_3 loss overnight was roughly equivalent to the amount of NH_4^+ that accumulated in dew by sunrise. Dew composition was used to calculate an average Frac(NH_3) of 0.94 suggesting that the vast majority of NH_3 sequestered in dew overnight is emitted during evaporation shortly after sunrise. Mornings with dew experience a large increase in NH_3 coincident with dew evaporation. Once the dew has completely evaporated, NH_3 mixing ratios either plateau or decrease. Fluxes of NH_3 from dew averaged 6.2 ± 5 ng m^{-2} s^{-1} during evaporation and were calculated using measured [NH_4^+], V_{dew}, t_{evap} and Frac(NH_3). These fluxes are substantial compared to previously reported fluxes in non-fertilized grasslands (Wentworth et al., 2014; Wichink Kruit et al., 2007). Mornings without any surface wetness (neither dew nor rain) never experienced a sharp increase in NH_3. Dew-related NH_3 fluxes are

1 likely much more substantial in urban and agricultural areas where NH_3 and [NH_4^+] in dew are

2 significantly higher than at RMNP.

3 Morning increases of NH_3 frequently observed at RMNP (and other sites) are very likely the

4 result of NH_3 emissions during dew evaporation. This hypothesis is supported by: 1) coincident

5 timing of morning NH_3 increases/decreases at the start/completion of dew evaporation, 2) lack

6 of NH_3 morning increase on every non-dew morning, 3) significant NH_3 fluxes calculated from

7 dew, 4) relative abundances of NH_4^+ in dew and NH_3 in the boundary layer, and 5) approximate

8 mass balance closure between NH_3 lost overnight and NH_4^+ accumulated in dew. The

9 phenomenon of dew "recycling" atmospheric NH_3 could lead to an overestimation of NH_3 dry

10 deposition in some ecosystems since dew formed overnight can take up much of the near-

11 surface ammonia and then release most of it again in the morning upon evaporation. Such

12 phenomena are generally not considered in current models of NH_3 dry deposition. In addition,

13 nocturnal loss rates of NH_3 were unaffected by the presence of dew. Our results suggest the net

14 effect of dew is to reduce the overall removal of NH_3 and prolong its atmospheric lifetime as

15 long as the dew composition yields a high Frac(NH_3).

16 Similar behaviour (coincident timing of NH_3 increases and evaporation) was occasionally

17 observed for rain. Analysis of four rain samples yielded an average Frac(NH_3) of 0.66

18 suggesting NH_3 can be released from evaporation of rain in RMNP as well. However, due to

19 the limited number of samples and lack of constraint for amount of rain sequestered below

20 ground it is currently impossible to be even semi-quantitative about potential NH_3 fluxes from

21 rain evaporation. This uncertainty merits further research since NH_x wet deposition does not

22 account for re-release of NH_3 from evaporation. Subsequent studies should also examine: 1)

23 the role of biological processes on surface water composition (e.g. stomatal exchange,

24 modification via microbes) and 2) influence of guttation (leaf exudate) on surface-air NH_3

25 exchange.

26 Additional field measurements quantifying NH_3 release from dew and rain evaporation are

27 needed to determine how relevant these phenomena are for modulating NH_3 mixing ratios and

28 N-deposition in different environments (e.g. urban, rural, agricultural). Although the majority

29 of NH_4^+ in dew was released back to the atmosphere at RMNP, this is not necessarily the case

30 at other locations. For instance, environments with HNO_3 deposition exceeding NH_3 deposition

31 to dew would cause a low (or zero) Frac(NH_3). In addition, a tall canopy can recapture near-

32 surface NH_3 emissions and might modulate emissions from dew drying in the lower canopy

(Walker et al., 2013). Regardless, the ability for dew to act as a morning source of NH_3 is currently absent from atmospheric models, with the exception of a few field-scale models based on the work of Flechard et al. (1999). The observations from this study suggest dew imparts a large influence on boundary layer NH_3; hence, future work should also focus on developing model parameterizations for NH_3 uptake during dew formation and release from evaporating dew.

To our knowledge, this is the first study to quantitatively examine the influence of dew on any water-soluble gas by simultaneously measuring dew amount, dew composition and atmospheric composition. Although NH_3 is the focus of this work, gases with similar K_H^{eff} ($>10^5$ M atm^{-1}) might be influenced by dew formation and evaporation in a comparable manner. Such species include, but are not limited to, acetic acid, formic acid, HONO and HNO_3. Methodology similar to this study should be used to conduct quantitative field studies for the aforementioned species to better understand the dynamic influence of dew on boundary layer composition.

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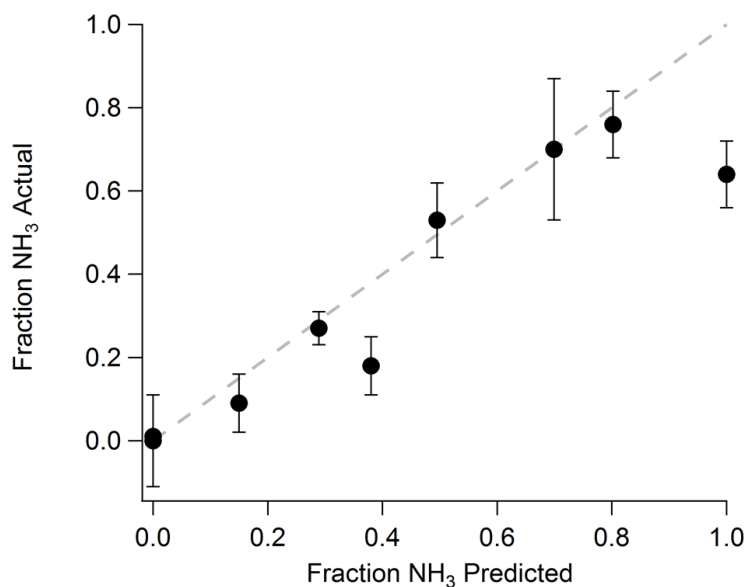
1   Table 1. Total Organic Carbon (TOC), Total Nitrogen (TN), Inorganic Carbon (IC), pH, the

2   ratio of measured to predicted [NH_4^+] in dew, and parameters pertinent to NH_3 flux calculations

3   in the field dew samples

Date	TOC (mg C L⁻¹)	IC (mg C L⁻¹)	TN (mg N L⁻¹)	pH	Frac(NH₃)	V_dew (mL m⁻²)	t_evap (s)	Flux (ng m⁻² s⁻¹)	[NH₄⁺]_meas: [NH₄⁺]_eqm
05/28	0.65	0.52	0.05	5.46	1.0	79.8	6000	2.4	0.02
06/01	2.05	1.21	0.32	5.65	0.68	97.0	6600	4.9	0.08
06/23	6.10	0.58	0.61	5.35	1.0	167.2	10800	7.3	0.02
06/27	6.13	0.59	0.62	5.70	0.85	195.6	9000	11.0	0.05
06/28	9.69	0.56	0.95	5.16	1.0	161.6	8400	17.9	0.04
06/29	5.27	0.19	0.46	4.83	1.0	60.9	3000	7.3	0.01
06/30	6.71	0.22	0.32	4.99	1.0	163.4	7800	3.3	0.01
07/04	6.78	0.23	1.40	5.32	1.0	206.8	16800	2.5	0.02
07/19	6.53	0.11	1.47	5.85	1.0	188.2	24600	1.0	0.08
07/29	10.04	0.31	2.59	5.80	1.0	92.2	8400	5.4	0.09
08/10	7.54	0.38	0.80	5.34	1.0	96.9	7200	6.9	0.07
08/11	7.28	0.17	0.85	4.67	0.74	108.4	14400	4.2	0.02
Avg	6.23	0.42	0.85	5.19	0.94	134.8	10250	6.2	0.04

1   Table 2. K_H^{eff} of NH_3 and other water-soluble gases at 10°C and various pHs

Gas	pH	K_H^{eff} (M atm^{-1})
NH_3 (ammonia)	4.5	2.1×10^7
	6	6.7×10^5
	7.5	2.1×10^4
HCOOH (formic acid)	4.5	1.1×10^5
	6	2.8×10^6
	7.5	8.9×10^7
CH_3COOH (acetic acid)	4.5	1.9×10^4
	6	2.3×10^5
	7.5	7.0×10^6
HONO (nitrous acid)	4.5	1.3×10^3
	6	3.9×10^4
	7.5	1.2×10^6
HNO_3 (nitric acid)	4.5	5.3×10^{12}
	6	1.7×10^{14}
	7.5	5.3×10^{15}

2 Figure 1. Fraction of NH$_3$ liberated during drying experiments versus the fraction predicted

3 according to an updated Eq. (2) to include acetate, formate, CO_3^{2-} and HCO_3^- in the anion

4 balance. Excluding these anions significantly reduces the correlation. Error bars represent $\pm\sigma$

5 from three experiments per synthetic dew. The dashed line is the 1:1 line.

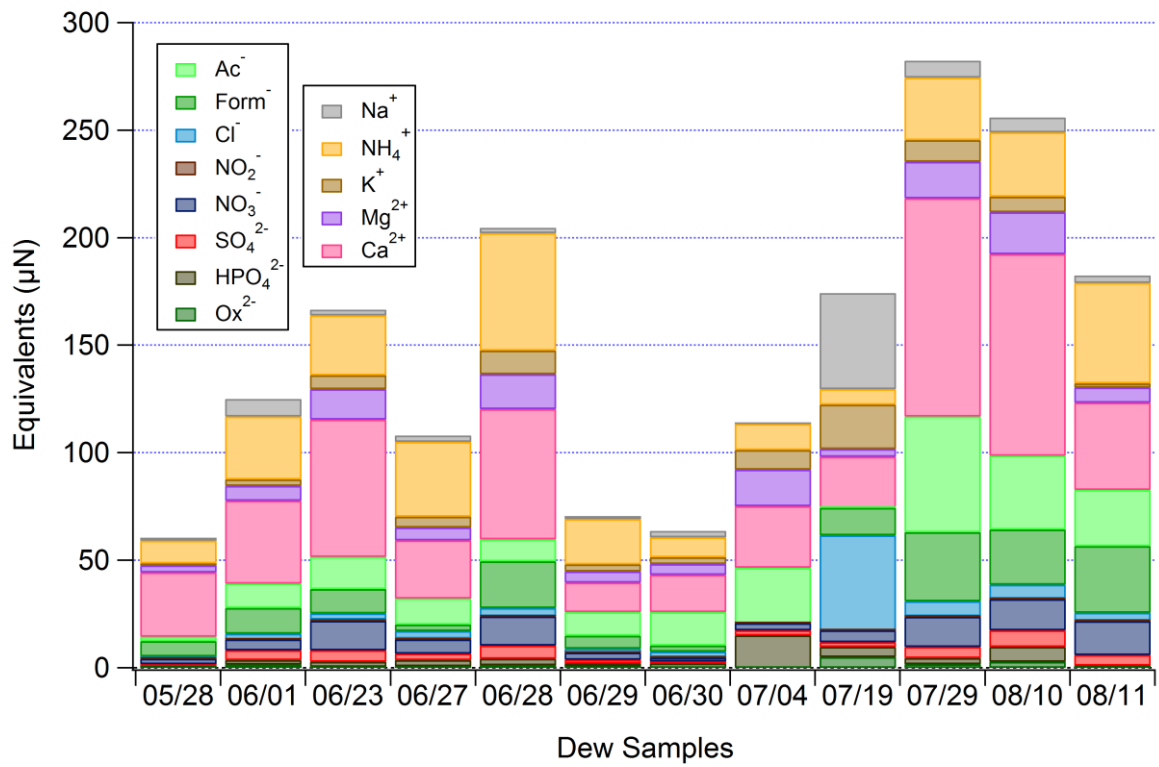
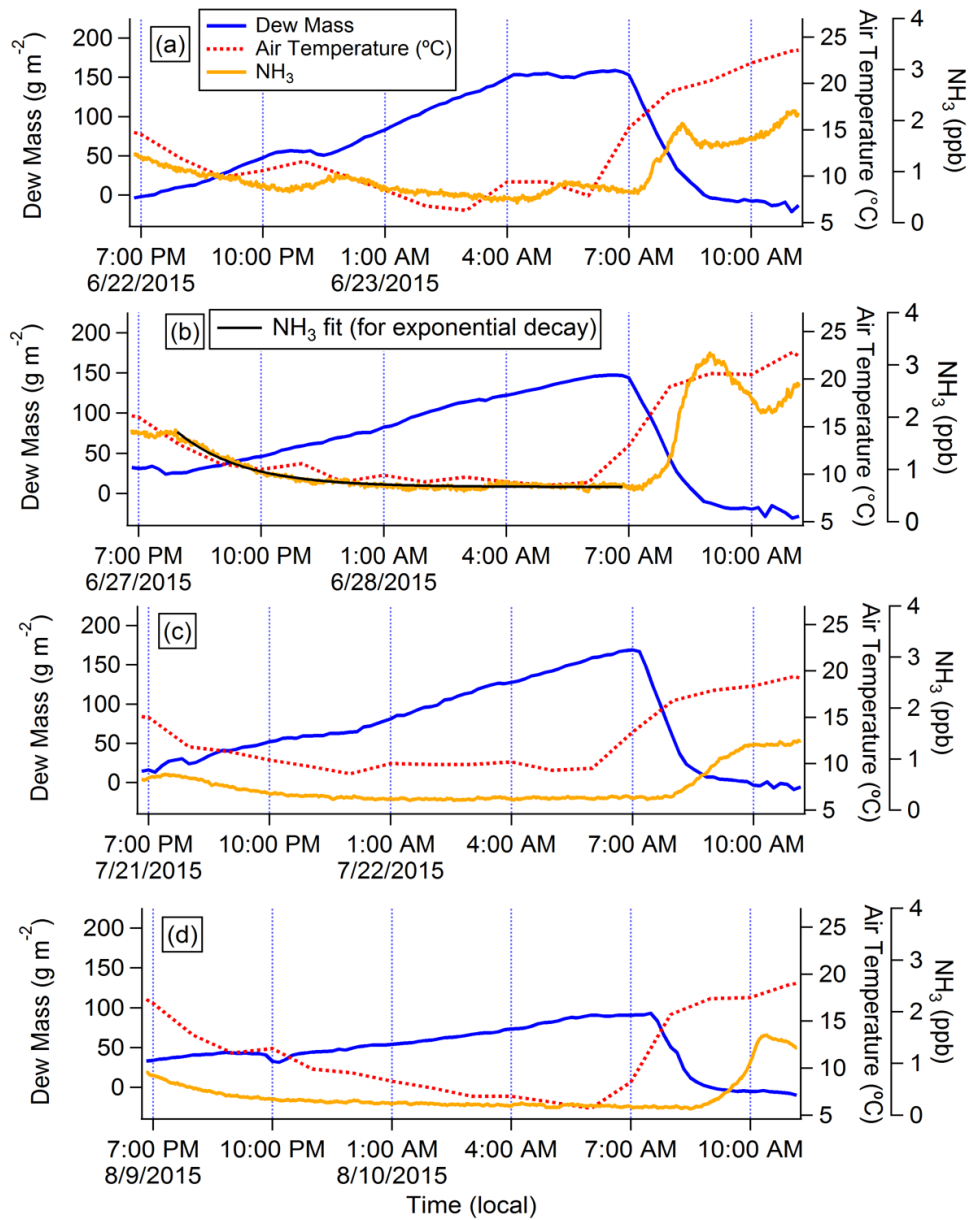
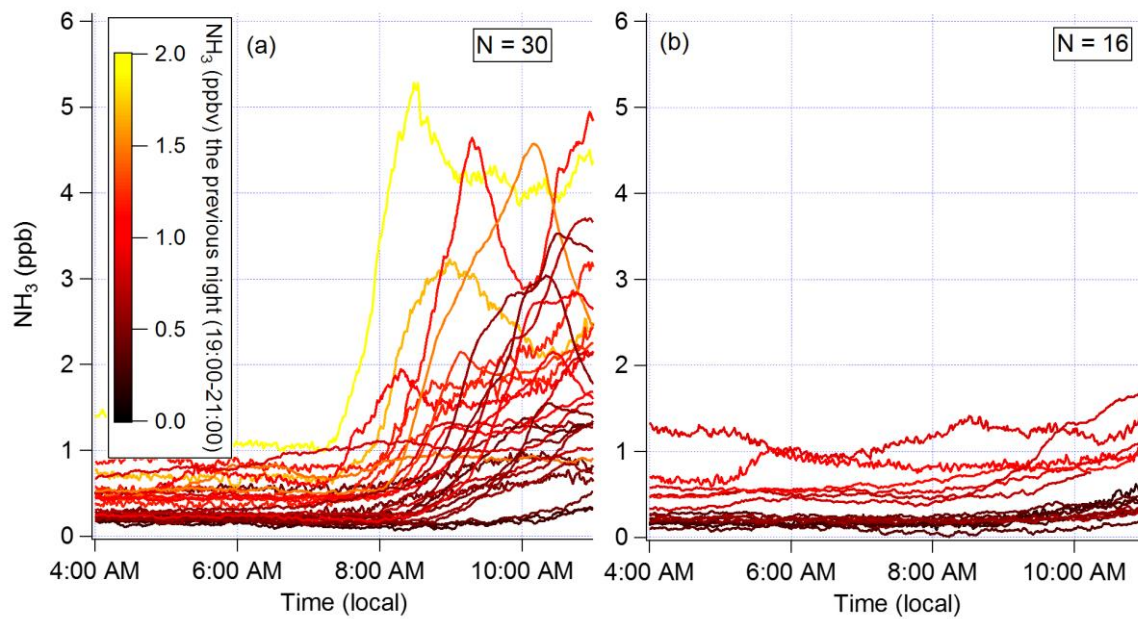



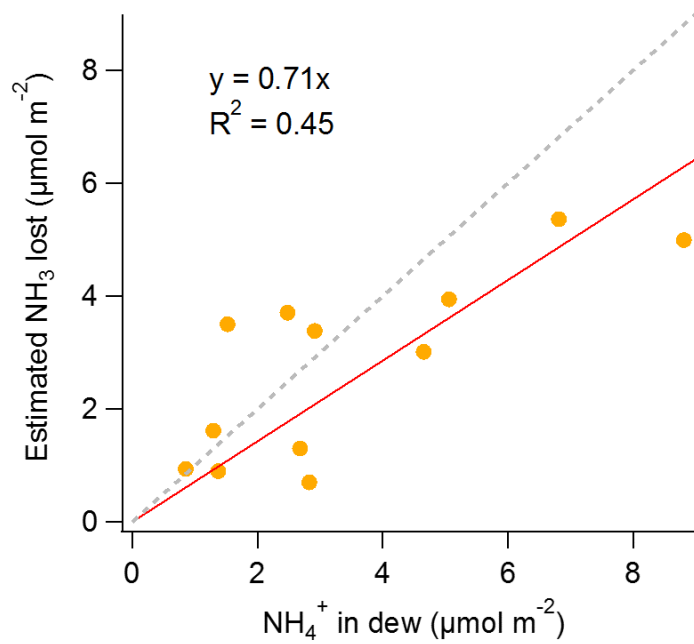
Figure 2. Ionic composition (in µN) of ambient dew collected at RMNP.

2   Figure 3. Dew accumulation (blue, g m^{-2}), NH$_3$ mixing ratio (orange, ppbv) and air

3   temperature (red, °C) overnight on a) 22 June, b) 27 June, c) 21 July and d) 9 August 2015.

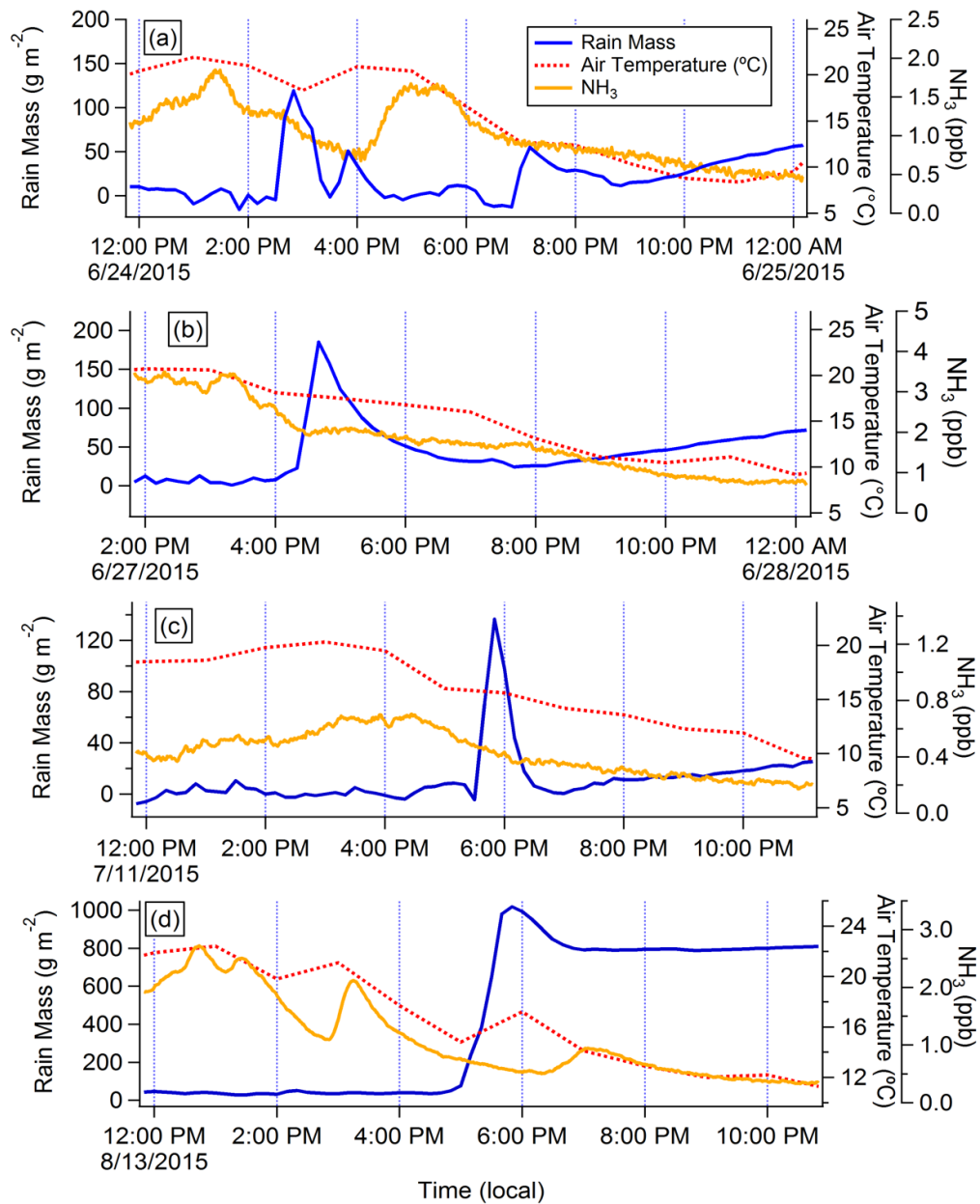
4   The black line in (b) is the best fit for the NH$_3$ mixing ratio to an exponential decay function

5   (see Eq. 4) between 20:00 and the onset of dew evaporation.

2 Figure 4. Time series of NH_3 mixing ratio (in ppb) from 4:00 to 11:00 on (a) mornings with

3 dew and (b) mornings with no surface wetness. Traces are coloured according to the average

4 NH_3 mixing ratio measured the previous night between 19:00 to 21:00.

2   Figure 5. Estimated NH_3 lost overnight assuming a 150 m boundary layer versus measured

3   NH_4^+ accumulated in dew by the onset of evaporation. The red line is the best fit line (forced

4   through the origin) and the dashed grey line is the 1:1 line.

2   Figure 6. Rain accumulation (blue, g m^{-2}), NH$_3$ mixing ratio (orange, ppbv) and air

3   temperature (red, °C) during the afternoon and evening on a) 24 June, b) 27 June, c) 11 July

4   and d) 13 August 2015. 100 g m^{-2} is equivalent to 0.1 mm of rain.