

1 **Soil-atmosphere exchange of ammonia in a non-fertilized**  
2 **grassland: measured emission potentials and inferred**  
3 **fluxes**

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## 1 **Abstract**

2 A 50-day field study was carried out in a semi-natural, non-fertilized grassland in south-  
3 western Ontario, Canada during the late summer and early autumn of 2012. The purpose was  
4 to explore surface-atmosphere exchange processes of ammonia ( $\text{NH}_3$ ) with a focus on bi-  
5 directional fluxes between the soil and atmosphere. Measurements of soil pH and ammonium  
6 concentration ( $[\text{NH}_4^+]$ ) yielded the first direct quantification of soil emission potential ( $\Gamma_{\text{soil}} =$   
7  $[\text{NH}_4^+]/[\text{H}^+]$ ) for this land type, with values ranging from 35 to 1,850 (an average of 290). The  
8 soil compensation point, the atmospheric  $\text{NH}_3$  mixing ratio below which net emission from  
9 the soil will occur, exhibited both a seasonal trend and diurnal trend. Higher daytime and  
10 August compensation points were attributed to higher soil temperature. Soil-atmosphere  
11 fluxes were estimated using  $\text{NH}_3$  measurements from the Ambient Ion Monitor Ion  
12 Chromatograph (AIM-IC) and a simple resistance model. Vegetative effects were neglected  
13 due to the short canopy height and significant  $\Gamma_{\text{soil}}$ . Inferred fluxes were, on average,  $2.6 \pm 4.5$   
14  $\text{ng m}^{-2} \text{ s}^{-1}$  in August (i.e. net emission) and  $-5.8 \pm 3.0 \text{ ng m}^{-2} \text{ s}^{-1}$  in September (i.e. net  
15 deposition). These results are in good agreement with the only other bi-directional exchange  
16 study in a semi-natural, non-fertilized grassland. A Lagrangian dispersion model (HYSPLIT)  
17 was used to calculate air parcel back trajectories throughout the campaign and revealed that  
18  $\text{NH}_3$  mixing ratios had no directional bias throughout the campaign, unlike the other  
19 atmospheric constituents measured. This implies that soil-atmosphere exchange over a non-  
20 fertilized grassland can significantly moderate near-surface  $\text{NH}_3$  concentrations. In addition,  
21 we provide indirect evidence that dew and fog evaporation can cause a morning increase of  
22  $[\text{NH}_3]_{\text{g}}$ . Implications of our findings on current  $\text{NH}_3$  bi-directional exchange modelling efforts  
23 are also discussed.

# 1 1 Introduction

2 Atmospheric ammonia ( $\text{NH}_{3(\text{g})}$ ) is the most abundant alkaline gas and is important for many  
3 biogeochemical and atmospheric processes (Seinfeld and Pandis, 2006). It neutralizes acidic  
4 aerosol, leading to increased mass loadings of fine atmospheric particulate matter ( $\text{PM}_{2.5}$ )  
5 which reduces visibility and can cause adverse health effects (Pope et al., 2002). In addition,  
6 deposition of  $\text{NH}_3$  and other forms of reactive nitrogen (i.e.  $\text{NO}_x$ ,  $\text{HNO}_3$ ) can lead to  
7 eutrophication, soil acidification, and loss of biodiversity in sensitive ecosystems (Krupa,  
8 2003).  $\text{NH}_3$  is primarily emitted through agricultural activities (i.e. fertilization, animal waste)  
9 with minor contributions from transportation and chemical industries (Reis et al., 2009).

10  $\text{NH}_{3(\text{g})}$  exists in equilibrium with aqueous ammonia ( $\text{NH}_{3(\text{aq})}$ ) in surface reservoirs (i.e.  
11 apoplastic tissues of plants or soil pore water) that, at least in theory, can be described by the  
12 Henry's law constant ( $K_H$ ). The  $\text{NH}_{3(\text{aq})}$  is also in equilibrium with aqueous-phase ammonium  
13 ( $\text{NH}_4^+(\text{aq})$ ), governed by the acid dissociation constant ( $K_a$ ) of  $\text{NH}_4^+$  and the pH of the solution.  
14 The gas-phase concentration above this aqueous phase at thermodynamic equilibrium is  
15 known as the compensation point ( $\chi$ ) and can, to a first approximation, be predicted according  
16 to:

$$17 \quad \chi = \frac{K_a \cdot [\text{NH}_4^+(\text{aq})]}{K_H \cdot [\text{H}^+]} \quad (1)$$

18 where  $[\text{H}^+]$  is the concentration of the hydronium ion in solution. If the atmospheric mixing  
19 ratio of  $\text{NH}_3$  over a surface is below this value, net emission from the surface pool is expected  
20 until the equilibrium  $\text{NH}_3$  value (i.e.  $\chi$ ) is reached and vice versa. In order to account for the  
21 temperature dependence of the equilibrium constants, the van't Hoff equation must be applied  
22 so Eq. (1) can be updated to:

$$23 \quad \chi = 13,587 \cdot \Gamma \cdot e^{\frac{-10,396K}{T}} \cdot 10^9 \quad (2)$$

24 where T is the temperature of the surface reservoir in K,  $\Gamma$  is the emission potential equal to  
25 the ratio between  $[\text{NH}_4^+]$  and  $[\text{H}^+]$  in the surface reservoir ( $\Gamma = [\text{NH}_4^+]/[\text{H}^+]$ ), and  $\chi$  is given in  
26 ppb, or  $\text{nmol mol}^{-1}$  (Nemitz et al., 2001; Nemitz et al., 2004). A large  $\Gamma$  indicates the surface  
27 has a high propensity to emit  $\text{NH}_3$  since it is directly proportional to  $\chi$ . Values for  $K_H$  ( $10^{-1.76}$   
28  $\text{atm M}^{-1}$ ) and enthalpy of vaporization ( $34.18 \text{ kJ mol}^{-1}$ ) at  $25^\circ \text{C}$  were obtained from Dasgupta

1 and Dong (1986). The  $K_a$  and enthalpy of dissociation of  $\text{NH}_4^+$  at 25 °C are  $10^{-9.25}$  M and  
2 52.21 kJ mol<sup>-1</sup>, respectively (Bates and Pinching, 1950).

3 This conceptual model of a compensation point for  $\text{NH}_3$  was first suggested by Farquhar et al.  
4 (1980). Over the subsequent decades, numerous laboratory and field studies over a wide  
5 range of land types have been undertaken to validate and improve this framework. Single-  
6 layer exchange models were developed in the 1990s to account for bi-directional exchange  
7 with plant stomata and deposition to the cuticle (e.g. Sutton et al. 1993, 1995, 1998). A two-  
8 layer model was developed by Nemitz et al. (2001) that also included exchange with the soil.  
9 Nemitz et al. (2000) were able to create a multi-layer model that allowed for exchange with  
10 different layers within the canopy (i.e. inflorescences, bottom leaves) of oilseed rape. The flux  
11 of  $\text{NH}_3$  ( $F_{\text{NH}_3}$ ) above a surface reservoir can be calculated from  $\chi$  with an exchange velocity  
12 ( $v_{\text{ex}}$ ) using the following:

$$13 \quad F_{\text{NH}_3} = v_{\text{ex}} \cdot (\chi - [\text{NH}_{3(g)}]) \quad (3)$$

14 The  $v_{\text{ex}}$  (units of m s<sup>-1</sup>) can be parameterized by applying resistances in either a series and/or  
15 parallel schematic. These resistances represent physical barriers to mass transfer and are  
16 analogous to electrical resistances. The number of resistances applied is dependent on how  
17 many surface reservoirs are incorporated into the field-scale model. In all cases, aerodynamic  
18 ( $R_a$ ) and quasi-laminar ( $R_b$ ) resistances must be considered to account for the turbulence  
19 between the surface reservoir and  $\text{NH}_{3(g)}$  measurement height.

20 Numerous pathways are present for bi-directional exchange over land: via plant stomata, soil  
21 pore water, and ground litter. For each compartment there exists a  $\chi$  which is dependent on the  
22 surface properties given in Eqs. (1) and (2). Significant effort has gone into measuring and  
23 modelling  $\text{NH}_3$  fluxes over a wide variety of land types to provide a more thorough  
24 understanding of this framework (Massad et al. 2010; Zhang et al., 2010, and references  
25 therein). Canopy-scale resistance models of varying complexity have been developed and  
26 successfully employed to mechanistically describe  $\text{NH}_3$  fluxes (e.g. Nemitz et al. 2001;  
27 Personne et al. 2009; Sutton et al. 1995). A detailed list of these models is available in  
28 Flechard et al. (2013).

29 While extremely useful, these mechanistic canopy-scale models are often too complex to be  
30 directly incorporated into regional or global chemical transport models. As a result, recent

1 efforts have focused on simplifying previous models by empirically parameterizing certain  
2 components (usually  $\Gamma$ ), with either a constant for each land type or a function using  
3 parameters (i.e. fertilizer application, regional long-term  $\text{NH}_3$  concentration) that are easily  
4 assimilated into the regional and global models (Bash et al. 2013; Cooter et al. 2010, 2012;  
5 Pleim et al. 2013; Wen et al. 2013; Wichink Kruit et al. 2010, 2012). Incorporating bi-  
6 directional  $\text{NH}_3$  exchange in these large scale atmospheric models generally improves model  
7 performance. For instance, Bash et al. (2013) reduced the biases and error in both  $\text{NH}_x$   
8 deposition and aerosol concentration by coupling CMAQ (Community Multiscale Air-  
9 Quality) to an agroecosystem model and allowing for bi-directional exchange over the  
10 continental United States. Wichink Kruit et al. (2012) incorporated bi-directional exchange in  
11 the chemical transport model LOTOS-EUROS and found better agreement between measured  
12 and modelled  $\text{NH}_3$  mixing ratios across Europe, although some domains were still biased low  
13 by up to a factor of 2. Large uncertainties still exist for the parameterizations of  $\Gamma$  for both  
14 stomata and soil over most land types as a result of sparse measurements. Field measurements  
15 of soil and vegetation  $[\text{NH}_4^+]$  and  $[\text{H}^+]$ , along with atmospheric  $\text{NH}_3$  mixing ratios are  
16 required to evaluate the performance of regional air quality models attempting to parameterize  
17 bi-directional exchange.

18 Reviews by Massad et al. (2010) and Zhang et al. (2010) have summarized the studies to date  
19 that have explored bi-directional surface-atmosphere  $\text{NH}_3$  fluxes over a wide variety of  
20 different land types. The majority have focused on biosphere-atmosphere (i.e. stomatal) or  
21 canopy-atmosphere (i.e. sum of stomatal, litter and soil) exchange. In the former, both  
22 stomatal and cuticular resistances are incorporated (Massad et al., 2010 and references  
23 therein). Indeed, there have been a limited number of studies strictly examining soil-  
24 atmosphere bi-directional exchange. One reason is that if a significant canopy (i.e. forest or  
25 crops) is present, a significant fraction of soil  $\text{NH}_3$  emissions are expected to be recaptured by  
26 the canopy before leaving it (Nemitz et al., 2000). For instance, Walker et al. (2013) estimated  
27 that ~76 % of soil  $\text{NH}_3$  emissions are recaptured by the canopy in a fertilized corn field during  
28 peak leaf area index (LAI).

29 Agricultural fields and fertilized croplands have traditionally been the focus of  $\text{NH}_3$  bi-  
30 directional exchange studies due to their high propensity to emit  $\text{NH}_3$  (Massad et al. 2010;  
31 Zhang et al. 2010 and references therein). Semi-natural and non-fertilized ecosystems have

1 been examined less often. Although these areas are much less likely to be large sources of  
2  $\text{NH}_3$ , they account for a large land fraction and have the potential to impact the quality of  
3 atmospheric ammonia predictions from these updated regional scale models. In particular,  
4 there have been fewer studies measuring  $\text{NH}_3$  fluxes over grasslands (e.g. Mosquera et al.  
5 2001; Spindler et al., 2001). Several studies (David et al. 2009; Herrmann et al. 2009; Milford  
6 et al. 2001; Sutton et al. 2001, 2009) have explored how different grassland management  
7 practices (cutting and fertilization) affect  $\text{NH}_3$  fluxes; however, all of these studies were  
8 performed in fields that had received some degree of fertilization within the last 10 years. To  
9 our knowledge, only Wichink Kruit et al. (2007) have investigated  $\text{NH}_3$  bi-directional  
10 exchange over a non-fertilized grassland. The authors used several denuders and the  
11 aerodynamic gradient method to measure fluxes above the canopy and then infer both a  
12 canopy  $\chi$  and  $\Gamma$ .

13 Motivated by a lack of measurements in non-fertilized grasslands, this present study aims to  
14 measure  $\chi$  and  $\Gamma$  to provide a better constraint on these values since they are directly  
15 employed in current air quality models that represent bi-directional exchange. Atmospheric  
16 measurements are then used to estimate a soil-atmosphere flux based on a simple resistance  
17 model that has been utilized in the past (e.g. Nemitz et al., 2001). Furthermore, we present  
18 evidence that bi-directional exchange over a non-fertilized grassland can significantly impact  
19 near-surface  $\text{NH}_3$  concentrations, and that evaporation of dew can release large quantities of  
20  $\text{NH}_3$ .

## 21 **2 Methods and Materials**

### 22 **2.1 Field Site**

23 Measurements were obtained from August 12 to October 2, 2012 at a rural site near Egbert,  
24 ON located approximately 70 km north of Toronto. The long-term sampling site, Centre for  
25 Atmospheric Research Experiments (CARE,  $44^\circ 13' 51''\text{N}$ ,  $79^\circ 46' 58''\text{W}$ , 251 m above sea-  
26 level), is operated by Environment Canada and situated in an agricultural area. Figure 1 shows  
27 the location of CARE in relation to major Canadian cities and is coloured according to annual  
28  $\text{NH}_3$  emissions from 2008 (NPRI, 2008). Canada's National Pollutant Release Inventory  
29 (NPRI) does not include soil or vegetative emissions from non-managed ecosystems. The site  
30 is located on a sharp transition with high  $\text{NH}_3$  emissions to the south and negligible emissions

1 to the north. Air masses originating from the south are typically polluted since they pass over  
2 urban, industrial and agricultural areas of southern Ontario and the northeastern United States,  
3 whereas cleaner air usually arrives from the north (e.g. Rupakheti et al., 2005). As a result,  
4 soil-atmosphere exchange of  $\text{NH}_3$  can be examined under a wide range of atmospheric  
5 pollution regimes.

6 The site itself is surrounded by 60 hectares of semi-natural, non-fertilized grassland with no  
7 overlying canopy. The month of August was relatively dry with cumulative precipitation  
8 totalling 8 mm, whereas September had 75 mm of precipitation. The soil sampling area is  
9 contained within a radius of 10 m as this is the approximate flux footprint of the air sampling  
10 instrumentation explained in section 2.4. Fertilizer has not been applied to the soil in at least  
11 15 years. Grass at the site was cut on June 27 but remained uncut for the duration of the study.  
12 Over the course of the study, the grass grew from about 10 cm to a final height of 20 cm. The  
13 soil is sandy loam with an organic carbon content of roughly 5 % and a cation exchange  
14 capacity (CEC) of  $22.7 \text{ cmol kg}^{-1}$ . The CEC reflects the soil's ability to retain cations  
15 (including  $\text{NH}_4^+$ ) and at this site is an intermediate value relative to other soils.

## 16 **2.2 Bi-directional exchange framework**

17 For surfaces with minimal vegetation and a high soil emission potential ( $\Gamma_{\text{soil}}$ ), the exchange  
18 between the soil and atmosphere is expected to dominate the bi-directional flux (Personne et  
19 al., 2009; Sutton et al., 2009). In these environments, it should be reasonable to estimate the  
20  $v_{\text{ex}}$  by only considering resistances affecting the exchange across the soil-atmosphere  
21 interface. As such,  $v_{\text{ex}}$  in this paper is approximated using Eq. (4) which was derived from Su  
22 et al. (2011) who parameterized HONO soil fluxes in a similar fashion. This method is also  
23 the same as the two-layer resistance model developed by Nemitz et al. (2001) but neglects the  
24 stomatal and cuticular components.

$$25 \quad v_{\text{ex}} = \frac{1}{R_a + R_b + R_{\text{inc}} + R_{\text{soil}}} \quad (4)$$

26 The aerodynamic ( $R_a$ ) and quasi-laminar ( $R_b$ ) resistances reflect the macro and molecular-  
27 scale turbulence, respectively, between the soil and measurement height of  $\text{NH}_{3(\text{g})}$ . The in  
28 canopy ( $R_{\text{inc}}$ ) and soil ( $R_{\text{soil}}$ ) resistances account for processes within the canopy and at the

1 soil interface that hinder the exchange of gases. According to the theory outlined in Hicks et  
2 al. (1987),  $R_a$  and  $R_b$  can be calculated as such:

$$3 \quad R_a = \frac{\ln(z_{ref}) - \ln(z_0)}{\kappa \cdot u_*} \quad (5)$$

$$4 \quad R_b = \frac{2}{\kappa \cdot u_*} \cdot \left(\frac{Sc}{Pr}\right)^{2/3} \quad (6)$$

5 where  $z_{ref}$  is the height of the  $NH_3$  measurement (2.7 m),  $z_0$  the roughness length, equal to  
6 0.05 m for uncut grass (Seinfeld and Pandis, 2006), and the von Karman constant  $\kappa = 0.4$ . The  
7 Schmidt number ( $Sc = 0.58$ ) and Prandtl number ( $Pr = 0.72$ ) are taken from Hicks et al.  
8 (1987) and account for the diffusivity of  $NH_3$  and heat transfer, respectively. The friction  
9 velocity,  $u_*$ , can be calculated by:

$$10 \quad u_* = \sqrt[4]{\overline{u'w'^2} + \overline{v'w'^2}} \quad (7)$$

11 where  $u'$  and  $v'$  are the deviations from the streamline corrected half-hour mean of the  
12 horizontal component of wind velocity and  $w'$  is the vertical component (Wilczak et al.,  
13 2001).

14 Parameterizations for  $R_{inc}$  and  $R_{soil}$  vary and are empirically determined through  
15 measurements of net vertical flux above a given bulk surface. The former is found to be  
16 dependent on the canopy height, season and land use whereas the latter is primarily dictated  
17 by the Henry's law constant and reactivity of the pollutant. For the present study, values of  
18  $R_{inc} = 100 \text{ s m}^{-1}$  and  $R_{soil} = 60 \text{ s m}^{-1}$  are employed based on the work by Wesely (1989). These  
19 values correspond to resistances for a range land in midsummer with lush vegetation and a  
20 soil pH of 6.

21 It should be reiterated that using Eqs. (3) to (7) to estimate soil-atmosphere  $NH_3$  fluxes  
22 neglects any vegetative effects (e.g. recapture of  $NH_3$ , stomatal emission) and that this serves  
23 only as an approximation of  $NH_3$  fluxes between the soil and the atmosphere.

## 24 **2.3 Soil Measurements**

25 Measurements of soil  $[NH_4^+]$ , pH and temperature were necessary to calculate the  $\chi$ . Soil  
26 cores were collected in triplicate on six days during the campaign, all within 30 feet of the



1 atmospheric measurement inlet. The sampling methodology outlined below is based on work  
2 done by Li et al. (2012) and van Miegruet (1995). Samples were collected six times  
3 throughout the campaign on the days listed in Table 1. Sites 1, 2 and 3 correspond to small  
4 ( $\sim 1 \text{ m}^2$ ) areas 10 m west, directly below, and 10 m east of the sonic anemometer, respectively.  
5 The soil was sampled more frequently towards the end of the campaign since meteorology  
6 (i.e. precipitation, air temperature) was more variable and was expected to perturb the  $\Gamma_{\text{soil}}$  to  
7 a greater extent than in August when meteorological conditions were more consistent.  
8 Specifically, the ranges in air and soil temperature were larger in September than in August.  
9 After removing grass and any residual litter (of which there was very little), a PVC tube (2”  
10 inner diameter) was inserted into the ground to a depth of 10 cm and a soil core was removed  
11 by pulling out the tube with a soil core intact. Each core was thoroughly mixed and an  $\sim 8 \text{ g}$   
12 subsample was immediately placed into a pre-weighed extract solution (50 mL of 0.25 % KCl  
13 w/w) and transported on ice back to the lab for analysis. After shaking for 30 minutes,  
14 extracts were gravity filtered (ashless filter #40, Whatman Ltd., Maidstone, UK) then sent  
15 through a  $0.2 \mu\text{m}$  PES membrane syringe filter (Pall Ion Chromatography Acrodisc®, VWR  
16 International, Mississauga, ON). Ammonium, nitrate, and nitrite were then quantified using  
17 two Ion Chromatograph (IC) ICS-2000 systems (Dionex Inc., Sunnyvale, CA) operated with  
18 suppressed conductivity detection and reagent-free eluent (potassium hydroxide for anions,  
19 methanesulphonic acid for cations). Gradient elution schemes were optimized so that analyte  
20 peaks were baseline resolved. CS12A analytical and CG12A guard columns were used for  
21 the cation IC, and AS19 analytical and AG19 guard columns for the anion IC. In both cases,  
22  $25 \mu\text{L}$  loops were used. ICs were calibrated by injection of commercially available (Dionex  
23 Corp., Sunnyvale, CA) mixed standards of 7 anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) and  
24 6 cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ). Serial dilutions of the standards in matrix-matched  
25 0.25 % KCl allowed for a five-point calibration which yielded reasonable calibration curves  
26 (slope of  $R^2 > 0.99$ ) for all analytes. Extraction with a 0.25 % KCl solution proved sufficient  
27 to desorb all accessible ions in the soil matrix, yet dilute enough to allow for quantification of  
28  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in every sample. The inherent assumption is that the extract solution  
29 sufficiently mimics the ability of soil pore water to liberate  $\text{NH}_4^+$  ions from the soil matrix to  
30 participate in soil-air exchange. An additional extraction into deionized water (DIW) was  
31 performed on one set of soil samples. The  $[\text{NH}_4^+]$  measured in the DIW extract was between  
32 30-45% of that measured with the KCl extraction. Extraction into DIW is an absolute lower

1 bound on soil  $[\text{NH}_4^+]$  since higher ionic strength solutions will desorb more  $\text{NH}_4^+$ , and soil  
2 pore water has a much higher ionic strength than DIW. Flechard et al. (2013) and Cooter et al.  
3 (2010) have suggested fundamental analytical research is required to assess the validity of this  
4 assumption, but this is outside the scope of this current study. A field blank was run with  
5 every triplicate to account for any contamination (always less than 1 % of the measured soil  
6  $[\text{NH}_4^+]$ ) from sample handling and extraction.

7 Soil pH was measured by mixing ~10 g of soil with an equal mass of deionized water (1:1  
8 soil:DIW slurry). A standard pH electrode (SympHony 14002-782, VWR International,  
9 Mississauga, ON) was immediately immersed in the slurry until a stable pH reading was  
10 obtained. This was done in triplicate for each soil core and an average pH for each was  
11 calculated. Performing the pH measurements in a saline solution of 0.25 % KCl desorbs more  
12  $\text{H}^+$  and was found to lower the pH reading by up to 1 unit relative to extraction into deionized  
13 water, which has been reported previously (e.g. Walker et al., 2014). Soil temperature was  
14 logged hourly using 5 *in situ* sensors (iButtons, Maxim Integrated, San Jose, CA) placed 10  
15 cm deep dispersed across the 30 foot radius of the soil sampling area. Moisture content was  
16 determined gravimetrically for a subsample (~3 g) of each core by drying in an oven at 105 °C  
17 for at least 24 hours.

## 18 **2.4 Atmospheric Measurements**

19 Ambient  $\text{NH}_{3(\text{g})}$  mixing ratios were needed to infer both the direction and magnitude of soil-  
20 atmosphere fluxes. Measurements of  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  in  $\text{PM}_{2.5}$  and their precursor gases  
21 ( $\text{SO}_2$ , and  $\text{HNO}_3$ ) were also important to aid in interpretation of air mass trajectory. These  
22 water-soluble gases and ions in  $\text{PM}_{2.5}$  were measured continuously on-line every hour with  
23 the Ambient Ion Monitor-Ion Chromatographs (AIM-IC) system (Model 9000D, URG,  
24 Chapel Hill, NC). The set-up has been explained in detail elsewhere (Markovic et al., 2012)  
25 and is described here only briefly. Ambient air is pulled at  $3 \text{ L min}^{-1}$  through a  $\text{PM}_{2.5}$  impactor  
26 to remove coarse particles. Gases are stripped from the sample flow by a liquid parallel plate  
27 denuder with a 2 mM  $\text{H}_2\text{O}_2$  solution continuously flowing over the surface. Particles have  
28 sufficient inertia to pass through the denuder assembly and enter a supersaturated steam  
29 condensation coil where they are grown hygroscopically and collected as an aqueous solution.  
30 The aqueous sample then travels through a 22 m sample line to the IC systems where the ~5

1 mL aliquots (collected over an hour) are separately injected and quantified for water soluble ions. The inlet box was mounted on a tower 3 m above the ground.

3 The AIM-IC was deployed using CS17 and AS19 analytical columns, CG17 and AG19 guard columns and TCC-ULP1 and TAC-ULP1 concentrator columns. Suppressed conductivity detection and reagent-free gradient elution were used. Five-point calibrations were performed at the beginning, middle and end of the campaign. Standard solutions of known concentration were made by serial dilution of commercially available standards of mixed anions and cations discussed in the previous section.

9 Backgrounds were acquired by overflowing the inlet with high purity zero air for 24 hours and averaging the peak area signal acquired. This average peak area was subtracted from the peak areas obtained while sampling ambient air. Detection limits were determined by taking 3 times the standard deviation of the peak area during the final twenty hours of the zero air experiment and converting it to either a mixing ratio or mass loading using the calibration curves and assuming a flow of  $3 \text{ L min}^{-1}$ , pressure of 760 mmHg and temperature of 298 K.

15 Atmospheric species of primary interest for this study are  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  in  $\text{PM}_{2.5}$  and their precursor gases ( $\text{NH}_3$ ,  $\text{SO}_2$ , and  $\text{HNO}_3$ ), for which the limits of detection were 0.2, 0.003 and 0.008 ppb for  $\text{NH}_3$ ,  $\text{SO}_2$ , and  $\text{HNO}_3$ , respectively. For  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in the particle phase the detection limits were 0.025, 0.04 and  $0.04 \mu\text{g m}^{-3}$ , respectively.

19 Friction velocity ( $u_*$ ) parameters were calculated from wind velocity measured with a 3-D sonic anemometer (model CSAT3, Campbell Scientific, Logan, UT) operating at 10 Hz. Hourly relative humidity (RH) and air temperature (in  $^\circ\text{C}$ ) at CARE were measured by an Environment Canada weather station located 20 m north of the sonic anemometer. This data was obtained from the Environment Canada website ([http://climate.weather.gc.ca/data\\_index\\_e.html](http://climate.weather.gc.ca/data_index_e.html)).

25 The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to compute 48-hour back trajectories throughout the campaign in order to assess air parcel history (Draxler and Rolph, 2013). The model was run four times per day with parcels arriving at a height of 100 m above CARE at 2:00, 8:00, 14:00 and 20:00 local time. Resolution of the meteorology model (EDAS) was set to 40 by 40 km.

## 1 3 Results and Discussion

### 2 3.1 Soil Emission Potential Measurements

3 Figure 2 shows the measured  $\Gamma_{\text{soil}}$  for the six soil sampling dates in this study. Soil  $[\text{NH}_4^+]$  and  
4 pH measurements used to determine the  $\Gamma_{\text{soil}}$  are shown in Table 1. The variation in  $\Gamma_{\text{soil}}$  was  
5 up to an order of magnitude on some days (August 13<sup>th</sup> and September 20<sup>th</sup>) yet was more  
6 consistent on others (i.e. September 13<sup>th</sup> and 25<sup>th</sup>). Both August dates have the highest  $\Gamma_{\text{soil}}$   
7 suggesting there might be some seasonal variability, as has been observed for stomatal  
8 emission potentials ( $\Gamma_{\text{stom}}$ ) (Loubet et al., 2002). However, a similar trend cannot be  
9 confirmed for this study due to the relatively short time frame and the inherent heterogeneity  
10 of soil. Also shown in Fig. 2 is the range of ground emission potentials ( $\Gamma_{\text{g}}$ ) in grasslands  
11 suggested by Zhang et al. (2010).  $\Gamma_{\text{g}}$  includes both soil and litter, but during this study there  
12 was a negligible amount of litter on the ground, therefore  $\Gamma_{\text{g}}$  and  $\Gamma_{\text{soil}}$  should be analogous.  
13 The suggested range in  $\Gamma_{\text{g}}$  (2,000 to 200,000) is based on 14 values from six studies, all of  
14 which were in fertilized grasslands. Of these studies, only two (David et al. 2009; Mattsson et  
15 al. 2009) directly measured  $\Gamma_{\text{g}}$ , whereas the other four either inferred it from measurements of  
16 dead or dying leaves (Herrmann et al. 2009; Mattsson and Schjoerring, 2003) or modelled it  
17 (Burkhardt et al. 2009; Personne et al. 2009). All the  $\Gamma_{\text{soil}}$  values (35 to 1,850) measured in  
18 this study are below the range from Zhang et al. (2010) review, likely because the field at  
19 CARE is non-fertilized and so has a lower N-content. Suggested ranges of  $\Gamma_{\text{g}}$  from Zhang et  
20 al. (2010) for various land types were recently incorporated into a regional air quality model  
21 (STILT-Chem) by Wen et al. (2013) to allow for bi-directional exchange. The authors found  
22 the updated model, using  $\Gamma_{\text{g}} = 2,000$  over grasslands, overestimates  $\text{NH}_{3(\text{g})}$  in sites with lower  
23  $\text{NH}_{3(\text{g})}$  concentrations (i.e. CARE). This could be a consequence of overestimating  $\Gamma_{\text{g}}$  in these  
24 regions, as implied by the  $\Gamma_{\text{soil}}$  measurements given here.

25 Massad et al. (2010) have carried out a similar review and suggest that  $\Gamma_{\text{g}}$  be parameterized as  
26 500 in non-fertilized, semi-natural environments without vegetation. To our knowledge, the  
27 results presented here represent the first values of  $\Gamma_{\text{soil}}$  directly measured in a non-fertilized  
28 grassland. These measurements underscore the importance of distinguishing between fields  
29 that receive fertilization and those that do not. The  $\Gamma_{\text{g}}$  range from Zhang et al. (2010) is not

1 applicable to the field at CARE, whereas the estimation ( $\Gamma_g = 500$ ) from Massad et al. (2010)  
2 is more suitable.

3 It is worth comparing  $\Gamma_{\text{soil}}$  to the range of stomatal emission potentials ( $\Gamma_{\text{stom}}$ ) in grasslands  
4 proposed by Zhang et al. (2010) (Fig. 2, green line).  $\Gamma_{\text{stom}}$  values (300 to 3,000) are based on  
5 roughly 50 measurements from over two dozen studies which reflect the narrower range in  
6  $\Gamma_{\text{stom}}$  compared to  $\Gamma_g$ . Massad et al. (2010) also parameterized  $\Gamma_{\text{stom}}$ , but did so by empirically  
7 fitting measurements to total annual N input instead of using a constant value for each land  
8 use type. These suggested  $\Gamma_{\text{stom}}$  values from each review are on the same order as the  $\Gamma_{\text{soil}}$   
9 measured in this study, suggesting that in a non-fertilized field the soil and vegetation might  
10 have a very similar propensity to either emit or uptake  $\text{NH}_3$  (i.e. they likely have similar  $\chi$ ).

### 11 **3.2 Inferred Soil Compensation Point and Fluxes**

12 A linear interpolation of  $\Gamma_{\text{soil}}$  between the six sampling dates in combination with hourly soil  
13 temperature measurements were used to generate a time series of soil compensation point  
14 ( $\chi_{\text{soil}}$ , black trace in Fig. 3a) according to Eq. (2). The shaded region around  $\chi_{\text{soil}}$  was  
15 calculated from a linear interpolation of  $\pm 1\sigma$  in  $\Gamma_{\text{soil}}$  measurements and therefore reflects the  
16 uncertainty in  $\chi_{\text{soil}}$  attributed to variability in soil pH and  $[\text{NH}_4^+]$ . Hourly gas-phase  $\text{NH}_3$   
17 measured by the AIM-IC (orange trace) is also shown. These two traces frequently cross  
18 meaning that repeated switching between soil emission and atmospheric deposition is  
19 predicted. There is a clear decline in  $\chi_{\text{soil}}$  throughout the campaign that is mostly attributable  
20 to a decrease in soil temperature ( $T_{\text{soil}}$ ) as shown by the grey trace at the top of Fig. 3a.  
21 Precipitation can also be important factor for  $\text{NH}_3$  fluxes – both Cooter et al. (2010) and  
22 Walker et al. (2013) observed emission “pulses” of  $\text{NH}_3$  over agricultural soils within 24  
23 hours after rainfall. Elevated  $[\text{NH}_3]$  levels are seen on August 13, August 28, and September  
24 22 following 0.4 mm, 5.0 mm and 10.9 mm of rain. Reasons for this could include increased  
25 soil  $\text{NH}_4^+$  available for exchange, increased diffusion of  $\text{NH}_3$  through soil, and/or increased N  
26 inputs to the surface as a result of wet deposition.

27 There is a diurnal trend in  $\chi_{\text{soil}}$  with lower values during the night time that is a consequence  
28 of  $T_{\text{soil}}$  and has been observed before for stomatal compensation points (Van Hove et al.,  
29 2002). It is possible there is a diurnal trend in  $\Gamma_{\text{soil}}$  that is not captured by the periodic soil  
30 sampling regime. However, this is unlikely since additional measurements from a nearby site

1 found that spatial heterogeneity in soil  $[\text{NH}_4^+]$  was much larger than the temporal variability  
2 in 24 soil grabs taken 6 hours apart (soil grabs were in triplicate) over the course of two days.

3 The  $\chi_{\text{soil}}$  diurnal trends are more evident in Figs. (3b) and (3c), which show time-of-day plots  
4 for August and September, respectively. During both months,  $\text{NH}_3$  peaks between 8:00-10:00  
5 in the morning and is typically at a minimum during the evening where it plateaus at around 2  
6 ppb, which has been observed previously in the region (e.g. Ellis et al. 2011). Mixing ratios  
7 were fairly similar in both months, although the morning peak in August was larger than in  
8 September. On the other hand,  $\chi_{\text{soil}}$  values were significantly lower in September as a result of  
9 lower soil temperatures. Accordingly, the diurnal profiles of the difference between  $\chi_{\text{soil}}$  and  
10  $[\text{NH}_3]$  (red trace) in Figs. (3b) and (3c) are distinct. In August, the difference between  $\chi_{\text{soil}}$  and  
11  $[\text{NH}_3]$  is positive throughout the majority of the day (excluding 7:00-11:00 in the morning)  
12 indicating a net flux from the soil to the atmosphere. On the other hand, in September the  
13 difference is negative throughout the entire day meaning the soil is a continuous sink for  
14 atmospheric  $\text{NH}_3$ . This suggests a clear transition from the soil being a net source to a net sink  
15 for  $\text{NH}_3$  due to lower soil temperatures. It should be noted that grass senescence had not yet  
16 begun and that there was no appreciable accumulation of litter, which has been shown to act  
17 as a strong source of  $\text{NH}_3$  (e.g. David et al. 2009; Mattsson et al. 2009; Mattsson and  
18 Schjoerring, 2003).

19 In order to determine the magnitude of this exchange, the  $v_{\text{ex}}$  was estimated using Eqs. (4) to  
20 (7) and the flux was calculated from Eq. (3). The diurnal profile of  $\text{NH}_3$  fluxes (in  $\text{ng m}^{-2} \text{s}^{-1}$ )  
21 for both months is shown in Fig. 4. Throughout August there is an average net  $\text{NH}_3$  emission  
22 from the soil of  $2.6 \pm 4.5 \text{ ng m}^{-2} \text{ s}^{-1}$ . In September, there was an average net deposition of  $5.8$   
23  $\pm 3.0 \text{ ng m}^{-2} \text{ s}^{-1}$  from the atmosphere to the surface. Average fluxes measured by Wichink  
24 Kruit et al. (2007) were  $4 \text{ ng m}^{-2} \text{ s}^{-1}$  in summer and  $-24 \text{ ng m}^{-2} \text{ s}^{-1}$  in autumn, which are on the  
25 same order of the flux values estimated in this study. Wichink Kruit et al. (2007) used their  
26 measured fluxes to infer a canopy emission potential ( $\Gamma_{\text{canopy}}$ ) using data points where  
27 cuticular deposition can be neglected (dry conditions) and stomatal exchange is dominant  
28 (daytime). Exchange with the soil is neglected in their study due to the low soil pH (about pH  
29 = 5); however, this would not be a valid assumption in this study as the soil pH at CARE is  
30 about 7, as shown in Table 1. Nonetheless, the inferred  $\Gamma_{\text{canopy}}$  was 2,200 and is higher than  
31 the  $\Gamma_{\text{soil}}$  measured in this study. At least to a first approximation, it appears that  $\text{NH}_3$  fluxes in

1 both these non-fertilized fields are comparable. The larger deposition in the autumn in  
2 Wichink Kruit et al. (2007) is likely attributable to higher  $\text{NH}_3$  mixing ratios ( $\sim 9$  ppb average  
3 versus  $\sim 2$  ppb September average in this study). It is noteworthy that both sites are considered  
4 the same land type but likely have very different canopy-level processes driving  $\text{NH}_3$  fluxes.  
5 Specifically, the soil in Wichink Kruit et al. (2007) had a sufficiently low pH ( $\sim 5$ ) to suppress  
6 appreciable soil-to-atmosphere exchange, which is not the case at CARE. Furthermore, a  
7 review by Schlesinger and Hartley (1992) estimate volatilization rates of  $\text{NH}_3$  from  
8 undisturbed grasslands are between  $0.3$  and  $30 \text{ ng m}^{-2} \text{ s}^{-1}$ , which encompasses the values from  
9 this work and that of Wichink Kruit et al. (2007).

10 It is also important to consider wet deposition when assessing net exchange of  $\text{NH}_3$  between  
11 the atmosphere and an ecosystem. The Canadian Air and Precipitation Monitoring Network  
12 (CAPMoN) collects daily precipitation samples at CARE and reports the results on line  
13 (<http://www.on.ec.gc.ca/capmon/login/login.aspx>). The average  $\text{NH}_4^+$  wet deposition rates  
14 from 2001-2011 for August and September are  $12.4 \pm 4.6 \text{ ng m}^{-2} \text{ s}^{-1}$  and  $11.3 \pm 5.4 \text{ ng m}^{-2} \text{ s}^{-1}$ ,  
15 respectively. . In the context of our results (fluxes of  $2.6 \pm 4.5 \text{ ng m}^{-2} \text{ s}^{-1}$  in August and  $-5.8 \pm$   
16  $3.0 \text{ ng m}^{-2} \text{ s}^{-1}$  in September), the site at CARE has net  $\text{NH}_3$  deposition in both months when  
17 one considers both wet deposition and bi-directional exchange. In other words, the magnitude  
18 of wet deposition fluxes is roughly 2-5 times larger than the magnitude of bi-directional  
19 exchange. However, it is important to note that wet deposition occurs in discrete events,  
20 whereas dry exchange is continuous.

### 21 **3.3 Evidence for Bi-directional Exchange**

22 Since CARE lies on a sharp gradient between high  $\text{NH}_3$  emissions to the south and low  
23 emissions to north (Fig. 1), one might expect air masses from the north to be lower in  $\text{NH}_3$   
24 relative to air masses from the south. Similarly, the greater level of anthropogenic activity  
25 south of CARE suggests an enrichment of anthropogenic pollutants (i.e.  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{HNO}_3$   
26 and  $\text{NO}_3^-$ ) in air masses from the south. In order to interrogate this hypothesis, 2-day back  
27 trajectories were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory  
28 (HYSPLIT) model for every six hours throughout the study. Each 6-hour time stamp was then  
29 classified as having had the air mass pass through Toronto (a box defined from  $43.5$ - $44.0^\circ\text{N}$   
30 by  $79.0$ - $80.0^\circ\text{N}$ ), or having originated from the North (spent more than half its time above

1 44.23°N) or the South (spent more than half its time below 44.23°N and not passing through  
2 Toronto). Results from this analysis are shown in Fig. 5 and yield a distinct directional bias  
3 for all species except NH<sub>3</sub>; air masses passing through Toronto are clearly enhanced in SO<sub>2</sub>,  
4 HNO<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> but not NH<sub>3</sub>. A lack of directional bias for NH<sub>3</sub> could be  
5 explained by proximity to a large NH<sub>3</sub> source, but as seen in Fig. 1 there is a sharp regional  
6 (tens of kilometres) gradient in the emissions inventory suggesting that no such local source  
7 exists. A more likely explanation is that bi-directional exchange of NH<sub>3</sub> between the surface  
8 and atmosphere modulates near-surface NH<sub>3</sub> mixing ratios sufficiently to eliminate any  
9 directional bias that would result from traditional emission sources.

10 Considering the relatively low  $\Gamma_{\text{soil}}$  and small magnitude of soil fluxes, it is reasonable to ask  
11 whether such an exchange could have a noticeable effect on observed NH<sub>3</sub> mixing ratios.  
12 First, a simple calculation was performed to see if the soil reservoir contained enough NH<sub>4</sub><sup>+</sup> to  
13 sustain fluxes during the month of August. To do this, the following assumptions were made:  
14 NH<sub>3</sub> exchange occurs in the top 10 cm of soil, the soil is equilibrating a 1000 m atmospheric  
15 boundary layer and soil density is 1.5 g cm<sup>-3</sup>. Figure 6 shows that even during peak soil  
16 emission in the afternoon, less than 1 % of the soil NH<sub>4</sub><sup>+</sup> pool is required to equilibrate the  
17 entire boundary layer. Furthermore, much of this lost soil NH<sub>4</sub><sup>+</sup> would be regained during the  
18 inferred morning deposition event. Considering that the turnover time for most soil NH<sub>4</sub><sup>+</sup>  
19 pools is on the order of a day (Booth et al., 2005) it is safe to assume that there is sufficient  
20 NH<sub>4</sub><sup>+</sup> in non-fertilized grasslands to maintain fluxes to the atmosphere.

21 Second, this exchange could only sufficiently impact NH<sub>3</sub> mixing ratios if it occurs quickly  
22 enough. To test this, fast (0.005 m s<sup>-1</sup>, at 14:00) and slow (0.003 m s<sup>-1</sup>, at 1:00) average  
23 exchange velocities from August were used to calculate the time it would take the system  
24 (soil and atmosphere) to arrive halfway to equilibrium with an atmospheric height of 1000 m  
25 as well as with the height at which AIM-IC measurements were made (3 m). For 1000 m, the  
26 timescale is calculated to be between 40 and 62 hours for the fast and slow  $v_{\text{ex}}$ , respectively.  
27 However, for a height of 3 m, only 7 and 11 minutes are required to get halfway to  
28 equilibrium. Although this calculation neglects vertical mixing beyond 3 m (which will  
29 occur), these short timescales suggest soil-atmosphere exchange is an important component of  
30 observed negative [NH<sub>3(g)</sub>] gradients with height. In other words, soil-atmosphere exchange  
31 over non-fertilized grasslands has the ability to strongly influence near-surface NH<sub>3</sub> despite



1 the low  $\Gamma_{\text{soil}}$  (relative to fertilized fields) whereas the impact on  $\text{NH}_3$  levels throughout the  
2 boundary layer is dampened due to slower exchange.

### 3 **3.4 Morning Increase of $\text{NH}_3$**

4 A morning increase in  $\text{NH}_{3(\text{g})}$  between 8:00-10:00 is clearly evident in Figs. (3b) and (3c) and  
5 has been observed elsewhere (e.g. Bash et al., 2010; Ellis et al., 2011; Flechard et al., 2013;  
6 Nowak et al., 2006; Wichink Kruit et al., 2007). The factors contributing to this phenomenon  
7 at CARE are not entirely clear but may include one or more of: dew evaporation,  
8 volatilization of particulate  $\text{NH}_4\text{NO}_3$ , emission from plants/soil, and/or mixing down of  $\text{NH}_3$   
9 rich air entrained above the nocturnal boundary layer. Wichink Kruit et al. (2007) observed a  
10 similarly timed increase that coincided with a decrease in leaf wetness. Furthermore, Flechard  
11 et al. (1999) and Bussink et al. (1996) found that water layers sorbed on leaves can store  
12 significant quantities of  $\text{NH}_3$  even at an RH below 100%. Although no leaf wetness sensor  
13 was employed during this study, we use night time RH as a surrogate for dew and fog  
14 formation. Figure 7 shows the difference between the morning  $\text{NH}_x$  ( $\equiv \text{NH}_{3(\text{g})} + \text{NH}_4^+_{(\text{particle})}$ )  
15 and the average overnight  $\text{NH}_x$  concentration.  $\text{NH}_x$  was chosen to eliminate any bias caused  
16 by volatilisation of  $\text{NH}_4\text{NO}_{3(\text{p})}$  to  $\text{NH}_{3(\text{g})}$  and  $\text{HNO}_{3(\text{g})}$  as temperatures rise. Mornings  
17 following a night during which RH was above 0.9 had an average  $\Delta \text{NH}_x$  of  $207 \pm 37 \text{ nmol m}^{-3}$ ,  
18 whereas increases during mornings following drier nights ( $\text{RH} < 0.9$ ) were about half that  
19 with an average  $94 \pm 16 \text{ nmol m}^{-3}$ . Although the RH benchmark of 0.9 only serves as a  
20 surrogate for dew formation, this finding does suggest that pools of surface water (i.e. dew or  
21 fog), which form on nights that have a high RH, can act as significant  $\text{NH}_x$  reservoirs that  
22 release  $\text{NH}_3$  upon evaporation in the mid-morning. This is corroborated by measurements  
23 from Burkhardt et al. (2009) who report an approximate water film thickness of 0.1 mm  
24 during dew events and an average dew  $[\text{NH}_4^+]$  of  $3.5 \text{ mg kg}^{-1}$  in a grassland canopy. If all of  
25 the  $\text{NH}_4^+$  were to be released as  $\text{NH}_{3(\text{g})}$  upon dew evaporation, this reservoir would release  
26 about  $20 \text{ } \mu\text{mol m}^{-2}$  of  $\text{NH}_{3(\text{g})}$  into the atmosphere, which corresponds to an increase of  $20$   
27  $\text{nmol m}^{-3}$  throughout a 1000 m boundary layer, equivalent to an increase in mixing ratio of 0.5  
28 ppb. Such a release could have a significant impact on near surface  $\text{NH}_{3(\text{g})}$  measurements and  
29 manifest itself as a large morning increase of  $\text{NH}_{3(\text{g})}$ . The role of dew and fog as a night-time

1 reservoir definitely merits further investigation and could be an important process within this  
2 bi-directional framework.

3 Since  $\text{NH}_x$  morning increases plateau at  $\sim 100 \text{ nmol m}^{-3}$  at an RH below 0.85, there are likely  
4 other contributing factor(s) that lead to this morning enhancement of  $\text{NH}_3$ . Bash et al. (2010)  
5 observed a similar morning rise over a fertilized corn field and attributed it to plant and/or soil  
6 processes. However, CARE contains significantly less vegetation and is non-fertilized.  
7 Walker et al. (2013) suggest surface-air  $\text{NH}_3$  exchange is impacted by ions that can  
8 accumulate in dew as well as the pH of the dew. In addition, Fig. 4 reveals there are predicted  
9 deposition fluxes to the soil during the morning. It is highly unlikely that a substantial rise in  
10  $\Gamma_{\text{soil}}$  could occur over the span of a few hours. Stomatal emission cannot be conclusively ruled  
11 out as a significant contribution. However, if this were an important factor one would expect  
12 sunrise (when stomata open) and the spike to coincide, but given that sunrise at CARE was  
13 between 6:00 and 7:15 throughout the campaign, stomatal emission is not likely the driving  
14 factor behind this trend at CARE. It is also possible this morning increase is linked to the  
15 break-up of the nocturnal boundary layer, as observed by Walker et al. (2006) who measured  
16 surface  $\text{NH}_3$  fluxes over a fertilized soy bean field. Observations from this study rule out soil  
17 emissions and suggest that dew/fog evaporation plays a key role in enhancing morning  $\text{NH}_3$   
18 mixing ratios.

#### 19 **4 Conclusions**

20 Measurements of  $\Gamma_{\text{soil}}$  and  $T_{\text{soil}}$  in a non-fertilized grassland were used to construct a time  
21 series of  $\chi_{\text{soil}}$  over a 50-day period.  $\Gamma_{\text{soil}}$  ranged from 35 to 1,850 with an average value of 290  
22 which is well below the  $2,000 < \Gamma_g < 200,000$  suggestion by Zhang et al. (2010) for  
23 grasslands. Zhang et al. (2010) recommended this range based on field studies exclusively in  
24 fertilized grasslands, which is likely the reason  $\Gamma_g$  values in this study are lower. Indeed the  
25 distinction between fertilization and non-fertilization is critical in accurately assessing bi-  
26 directional exchange. Our findings are more in line with the parameterizations of Massad et  
27 al. (2010) who suggest a  $\Gamma_g$  of 500 for semi-natural, non-fertilized areas without vegetation.  
28 Seasonal and diurnal trends in  $\chi_{\text{soil}}$  were observed with lower values at night and in September  
29 due to decreases in  $T_{\text{soil}}$ .

30 Fluxes of  $\text{NH}_3$  between the soil and atmosphere were estimated using  $[\text{NH}_{3(\text{g})}]$  measurements  
31 and a simple resistance scheme that neglects the influence of vegetation. August fluxes were

1 primarily upwards, except between 7:00-11:00, and resulted in an average emission of  $2.6 \pm$   
2  $4.5 \text{ ng m}^{-2} \text{ s}^{-1}$  from the soil. September was characterized by exclusive deposition from the  
3 atmosphere at a rate of  $5.8 \pm 3.0 \text{ ng m}^{-2} \text{ s}^{-1}$ . These values are fairly similar to fluxes measured  
4 by Wichink Kruit et al. (2007) who reported fluxes of 4 and  $-24 \text{ ng m}^{-2} \text{ s}^{-1}$  in the summer and  
5 autumn, respectively.

6 HYSPLIT analysis revealed that air masses passing through Toronto were enriched in  
7 atmospheric pollutants, except  $\text{NH}_3$ . Since CARE lies on a sharp gradient of high emissions to  
8 the south and low emission to the north, this lack of directional bias implies that bi-directional  
9 exchange efficiently modulates  $\text{NH}_3$  mixing ratios. Back-of-the-envelope calculations confirm  
10 that: (1) the reservoir of  $\text{NH}_4^+$  in soil of non-fertilized grasslands is large enough to sustain  
11 fluxes to the atmosphere, and (2) fluxes are rapid enough to impact surface concentrations on  
12 a relevant timescale.

13 Figure 7 suggests that dew and fog evaporation can enhance the frequently observed morning  
14 increase in  $\text{NH}_3$ . It is unlikely that soil emissions contribute to this increase as deposition to  
15 the soil is predicted during the morning.

16 More research is needed to explore seasonal and annual trends in  $\Gamma_{\text{soil}}$ ,  $\Gamma_{\text{stomata}}$  and  $\chi_{\text{canopy}}$   
17 across all land types, particularly those lacking in measurements. Since regional scale models  
18 require these parameters as direct inputs there is great utility in taking a “bottom-up”  
19 approach (i.e. measuring  $\Gamma$  instead of inferring it from flux data). Even though non-fertilized  
20 fields have lower nitrogen content, evidence provided here suggests surface-atmosphere  
21 exchange can still affect near-surface concentrations and that this process should be  
22 considered when measuring ambient  $\text{NH}_3$  over non-fertilized surfaces. The role of fog and  
23 dew as a night-time reservoir for water-soluble gases also requires further attention as it may  
24 greatly enhance morning  $\text{NH}_3$  concentrations and is currently not incorporated in models.

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- 3

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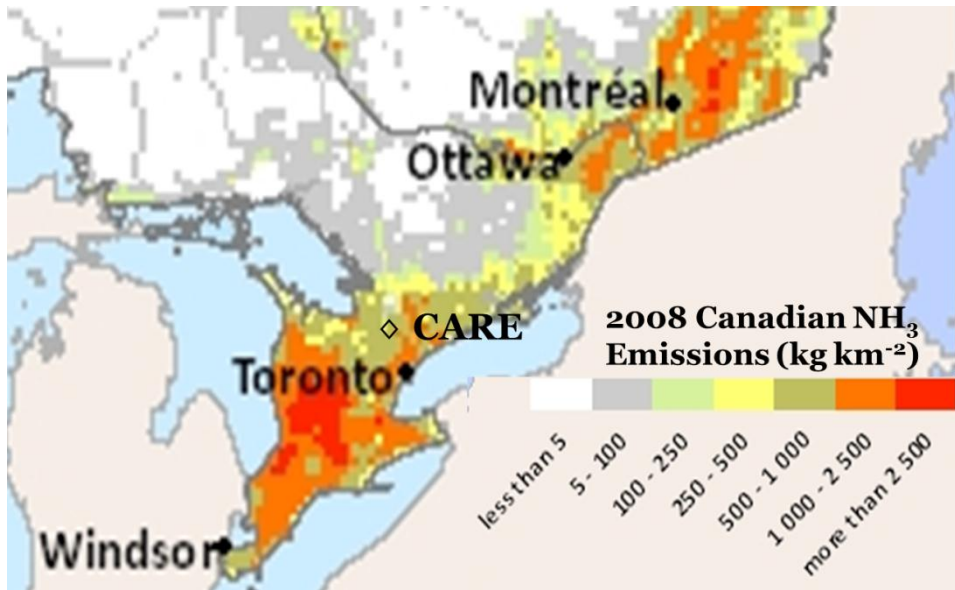
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4

1 Table 1. Soil parameters measured in this study

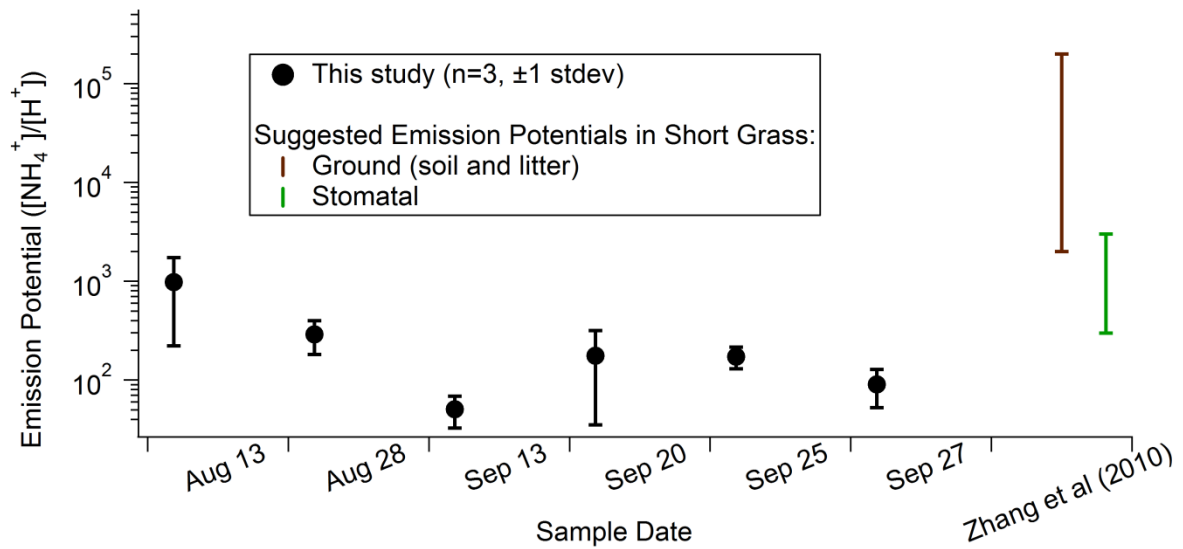
Date	Site	[NH <sub>4</sub> <sup>+</sup> ] (mg/kg wet soil)	pH (1:1 slurry soil:deionized water)	Average $\Gamma_{\text{soil}} (\pm 1\sigma)$
August 13	1	1.4	6.9	978 ± 750
	2	1.67	7.3	
	3	0.85	7	
August 28	1	1.43	6.6	290 ± 110
	2	0.31	7	
	3	0.87	6.9	
September 13	1	1.31	5.81	51 ± 20
	2	0.17	6.87	
	3	0.51	6.09	
September 20	1	1.01	5.8	176 ± 140
	2	0.89	6.81	
	3	0.94	6.53	
September 25	1	2.1	6.22	172 ± 43
	2	0.6	6.57	
	3	0.93	6.59	
September 27	1	0.61	6.16	91 ± 40
	2	0.46	6.59	
	3	0.25	6.95	

2

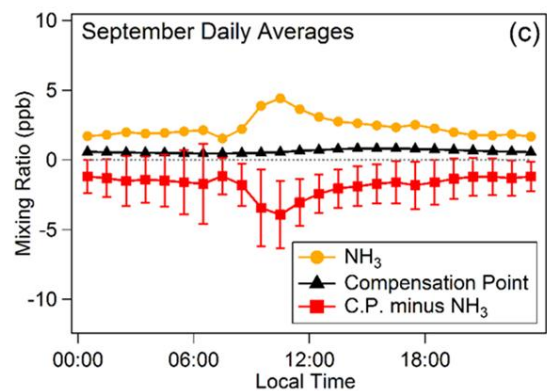
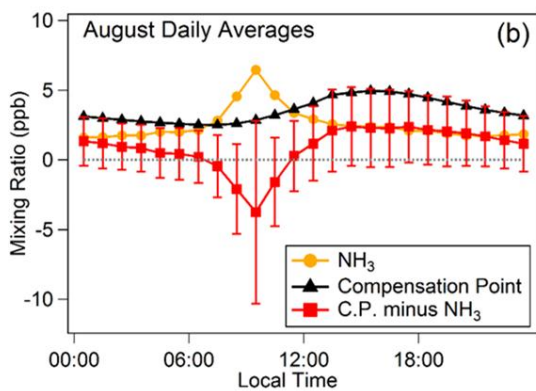
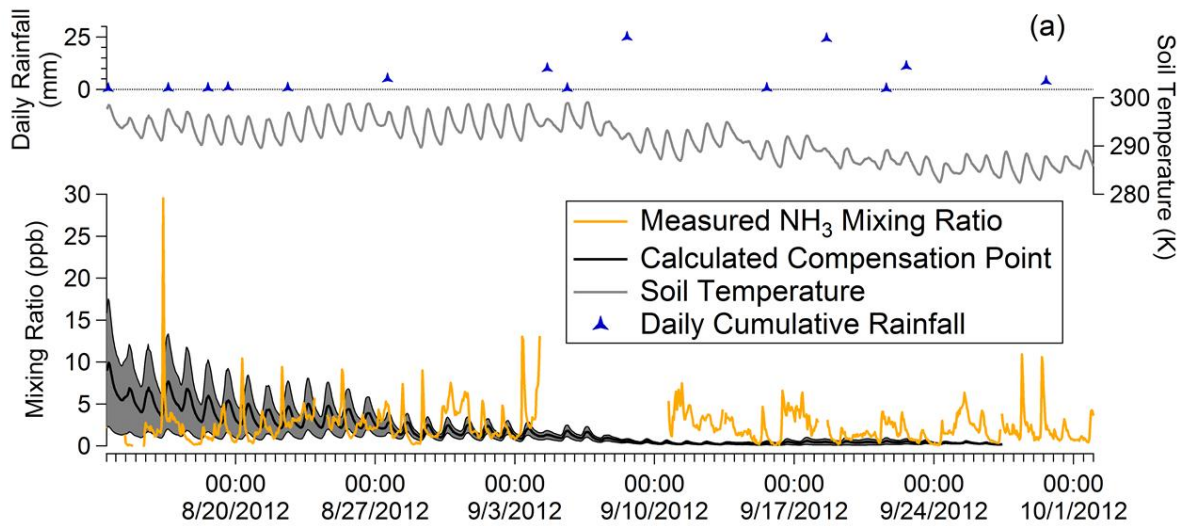


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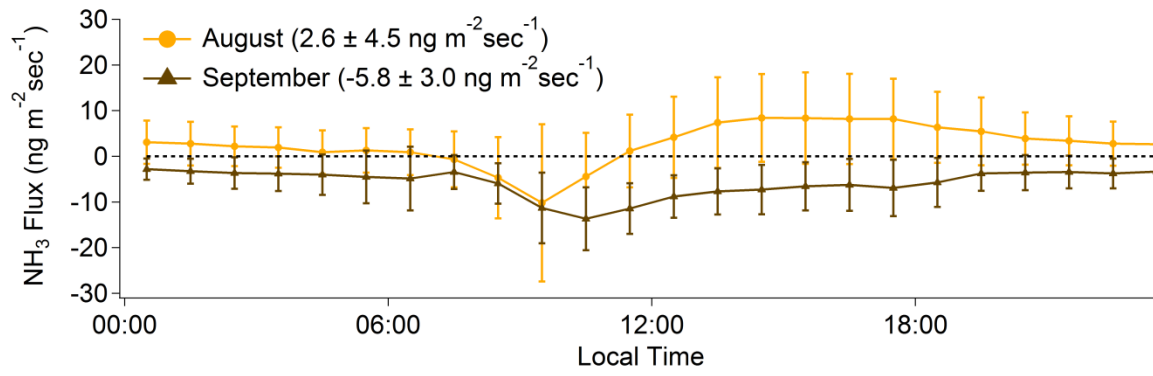
2 Figure 1. Location of CARE (◇) and major cities in the surrounding area. The map is  
3 coloured by annual NH<sub>3</sub> emissions according to the 2008 emission inventory.



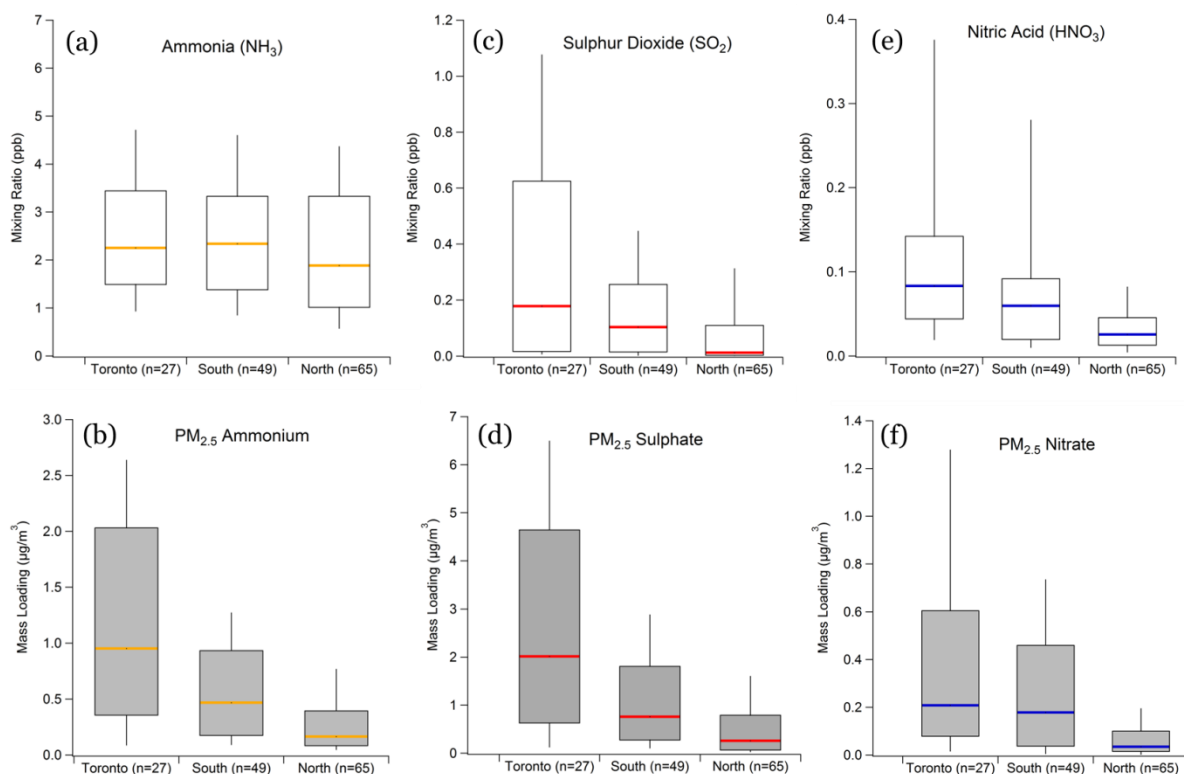
1  
 2 Figure 2. Soil emission potentials ( $\Gamma_{\text{soil}}$ ) measured throughout this study. Black circles  
 3 represent the average of three measurements  $\pm 1\sigma$ . A review by Zhang et al. (2010) suggests  $\Gamma$   
 4 ranges for ground ( $\Gamma_{\text{g}}$ ) and stomata ( $\Gamma_{\text{stom}}$ ) for low and high nitrogen input grasslands. These  
 5 ranges are shown in brown ( $\Gamma_{\text{g}}$ ) and green ( $\Gamma_{\text{stom}}$ ).



1  
 2 Figure 3. (a) Time series of  $\text{NH}_3$  mixing ratio ( $[\text{NH}_3]$ , orange trace),  $\chi_{\text{soil}}$  (black trace), daily  
 3 cumulative rainfall (blue markers) and soil temperature ( $T_{\text{soil}}$ , grey trace) throughout the  
 4 campaign.  $\chi_{\text{soil}}$  was calculated using a linear interpolation of  $\Gamma_{\text{soil}}$  and hourly soil temperature  
 5 measurements. The shaded region around  $\chi_{\text{soil}}$  was calculated by linear interpolation of  $\pm 1\sigma$  of  
 6  $\Gamma_{\text{soil}}$  and reflects the uncertainty in  $\chi_{\text{soil}}$  as a result of uncertainty in  $\Gamma_{\text{soil}}$  measurements. (b) and  
 7 (c) show time of day plots for the average  $[\text{NH}_3]$ ,  $\chi_{\text{soil}}$ , and difference between the two ( $\chi_{\text{soil}} -$   
 8  $[\text{NH}_3]$ , red trace) for August and September, respectively. Errors bars in (b) and (c) represent  
 9  $\pm 1\sigma$ , and are only included for the difference trace for clarity.

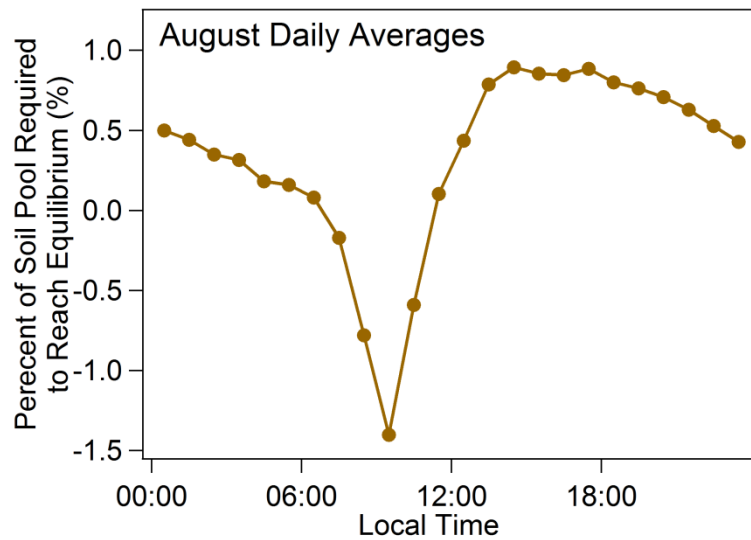


1  
 2 Figure 4. Time of day plot showing the average hourly  $\text{NH}_3$  flux in August (orange trace) and  
 3 September (brown trace). A positive flux indicates emission from the soil, whereas a negative  
 4 flux indicates deposition from the atmosphere.



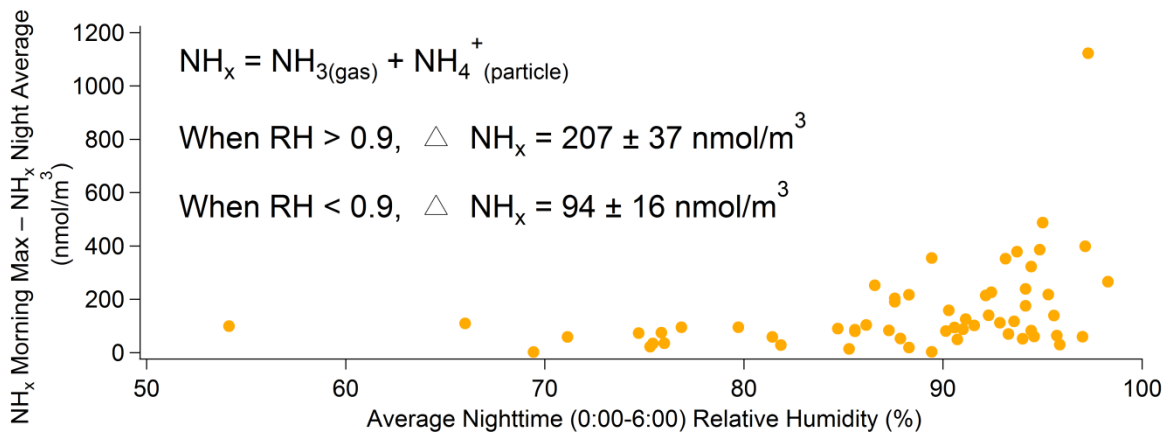
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 2 Figure 5. Atmospheric concentrations of various (a)  $\text{NH}_3$ , (b) particulate  $\text{NH}_4^+$ , (c)  $\text{SO}_2$ , (d)  
 3 particulate  $\text{SO}_4^{2-}$ , (e)  $\text{HNO}_3$ , and (f) particulate  $\text{NO}_3^-$  binned by air mass origin calculated  
 4 from HYSPLIT back trajectories every 6 hours throughout the campaign. The line denotes the  
 5 median value, the interquartile range is encompassed within the box, and the end of the  
 6 whiskers are the 10<sup>th</sup> and 90<sup>th</sup> percentiles. The number of back trajectories in each bin is given  
 7 on the x-axis in brackets.





1

2 Figure 6. Estimated percent of the soil  $\text{NH}_4^+$  pool required to equilibrate with the boundary  
 3 layer (assumed to be 1000 m) using the average fluxes during August. It was assumed that the  
 4 top 10cm of soil exchanges and the density of soil is  $1.5 \text{ g cm}^{-3}$ . Positive values indicate  
 5 fluxes are from the soil to the atmosphere (i.e. the soil is losing  $\text{NH}_4^+$ ).



1  
 2 Figure 7. The magnitude of the morning  $NH_x$  ( $\equiv NH_{3(g)} + NH_{4^+ (particle)}$ ) peak subtracted by the  
 3 night time (0:00-6:00)  $NH_x$  average versus the average night time relative humidity. The latter  
 4 was used as a surrogate for dew formation. The average  $\Delta NH_x$  ( $\pm 1\sigma_{\text{mean}}$ ) both above and  
 5 below  $RH = 0.9$  are shown inset in the figure.