Soil–atmosphere exchange of ammonia in a non-fertilized grassland:
measured emission potentials and inferred fluxes

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Abstract. A 50-day field study was carried out in a semi-natural, non-fertilized grassland in south-western Ontario, Canada during the late summer and early autumn of 2012. The purpose was to explore surface–atmosphere exchange processes of ammonia (NH$_3$) with a focus on bi-directional fluxes between the soil and atmosphere. Measurements of soil pH and ammonium concentration ([NH$_4^+$]) yielded the first direct quantification of soil emission potential ($\Gamma_{\text{soil}} = [\text{NH}_3^+] / [\text{H}^+]$) for this land type, with values ranging from 35 to 1850 (an average of 290). The soil compensation point, the atmospheric NH$_3$ mixing ratio below which net emission from the soil will occur, exhibited both a seasonal trend and diurnal trend. Higher daytime and August compensation points were attributed to higher soil temperature. Soil–atmosphere fluxes were estimated using NH$_3$ measurements from the Ambient Ion Monitor Ion Chromatograph (AIM-IC) and a simple resistance model. Vegetative effects were ignored due to the short canopy height and significant $\Gamma_{\text{soil}}$. Inferred fluxes were, on average, 2.6 $\pm$ 4.5 ng m$^{-2}$ s$^{-1}$ in August (i.e. net emission) and $-5.8 \pm 3.0$ ng m$^{-2}$ s$^{-1}$ in September (i.e. net deposition). These results are in good agreement with the only other bi-directional exchange study in a semi-natural, non-fertilized grassland. A Lagrangian dispersion model (Hybrid Single-Particle Lagrangian Integrated Trajectory – HYSPLIT) was used to calculate air parcel back-trajectories throughout the campaign and revealed that NH$_3$ mixing ratios had no directional bias throughout the campaign, unlike the other atmospheric constituents measured. This implies that soil–atmosphere exchange over a non-fertilized grassland can significantly moderate near-surface NH$_3$ concentrations. In addition, we provide indirect evidence that dew and fog evaporation can cause a morning increase of [NH$_3$]$_g$. Implications of our findings on current NH$_3$ bi-directional exchange modelling efforts are also discussed.

1 Introduction

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

NH$_3(g)$ exists in equilibrium with aqueous ammonia (NH$_3(aq)$) in surface reservoirs (i.e. apoplastic tissues of plants or soil pore water) that, at least in theory, can be described by the Henry’s law constant ($K_H$). NH$_3(aq)$ is also in equilibrium with aqueous-phase ammonium (NH$_4^+(aq)$), governed by the acid dissociation constant ($K_a$) of NH$_4^+$ and the pH of the solution. The gas-phase concentration above this aqueous phase at thermodynamic equilibrium is known as the compensation point ($\chi$) and can, to a first approximation, be predicted according to

$$\chi = \frac{K_a \cdot [\text{NH}_4^+]_{aq}}{K_H \cdot [\text{H}^+]},$$

where [H$^+$] is the concentration of the hydronium ion in solution. If the atmospheric mixing ratio of NH$_3$ over a surface...
is below this value, net emission from the surface pool will be expected until the equilibrium NH$_3$ value (i.e. $\chi$) is reached and vice versa. In order to account for the temperature dependence of the equilibrium constants, the van ‘t Hoff equation must be applied so Eq. (1) can be updated to

$$\chi = 13.587 \cdot \Gamma \cdot e^{\frac{-10.39K}{T}} \times 10^9,$$

(2)

where $T$ is the temperature of the surface reservoir in K, $\Gamma$ is the emission potential equal to the ratio between [NH$_3^+$] and [H$^+$] in the surface reservoir ($\Gamma = [\text{NH}_3^+] / [\text{H}^+]$), and $\chi$ is given in ppb or nmol mol$^{-1}$ (Nemitz et al., 2001, 2004). A large $\Gamma$ indicates the surface has a high propensity to emit NH$_3$ since it is directly proportional to $\chi$. Values for $K_H$ ($10^{-1.76}$ atm M$^{-1}$) and enthalpy of vaporization (34.18 kJ mol$^{-1}$) at 25 °C were obtained from Dasgupta and Dong (1986). The $K_a$ and enthalpy of dissociation of NH$_3^+$ at 25 °C are $10^{-9.26}$ M and 52.21 kJ mol$^{-1}$, respectively (Bates and Pinching, 1950).

This conceptual model of a compensation point for NH$_3$ was first suggested by Farquhar et al. (1980). Over the subsequent decades, numerous laboratory and field studies over a wide range of land types have been undertaken to validate and improve this framework. Single-layer exchange models were developed in the 1990s to account for bi-directional exchange with plant stomata and deposition to the cuticle (e.g. Sutton et al., 1993, 1995, 1998). A two-layer model was developed by Nemitz et al. (2001) that also included exchange with the soil. Nemitz et al. (2000) were able to create a multi-layer model that allowed for exchange with different layers within the canopy (i.e. inflorescences, bottom leaves) of oilseed rape. The flux of NH$_3$ (F$_{NH_3}$) above a surface reservoir can be calculated from $\chi$ with an exchange velocity ($v_{ex}$) using the following:

$$F_{NH_3} = v_{ex} \cdot (\chi - [\text{NH}_3(g)])$$

(3)

The $v_{ex}$ (units of m s$^{-1}$) can be parameterized by applying resistances in either a series and/or parallel schematic. These resistances represent physical barriers to mass transfer and are analogous to electrical resistances. The number of resistances applied is dependent on how many surface reservoirs are incorporated into the field-scale model. In all cases, aerodynamic ($R_a$) and quasi-laminar ($R_b$) resistances must be considered to account for the turbulence between the surface reservoir and NH$_3$ mixing height.

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

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

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

Agricultural fields and fertilized croplands have traditionally been the focus of NH$_3$ bi-directional exchange studies due to their high propensity to emit NH$_3$ (Massad et al., 2010; Zhang et al., 2010 and references therein). Semi-natural and non-fertilized ecosystems have been examined less often. Although these areas are much less likely to be large sources...
of NH$_3$, they account for a large land fraction and have the potential to impact the quality of atmospheric ammonia predictions from these updated regional-scale models. In particular, there have been fewer studies measuring NH$_3$ fluxes over grasslands (e.g. Mosquera et al., 2001; Spindler et al., 2001). Several studies (David et al., 2009; Herrmann et al., 2009; Milford et al., 2001; Sutton et al., 2001, 2009) have explored how different grassland management practices (cutting and fertilization) affect NH$_3$ fluxes; however, all of these studies were performed in fields that had received some degree of fertilization within the last 10 years. To our knowledge, only Wichink Kruit et al. (2007) have investigated NH$_3$ bi-directional exchange over a non-fertilized grassland. The authors used several denuders and the aerodynamic gradient method to measure fluxes above the canopy and then infer both a canopy $\chi$ and $\Gamma$.

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

2 Methods and materials

2.1 Field site

Measurements were taken from 12 August to 2 October 2012 at a rural site near Egbert, ON, located approximately 70 km north of Toronto. The long-term sampling site, Centre for Atmospheric Research Experiments (CARE, 44°13'51"N, 79°46'58"W, 251 m a.s.l.), is operated by Environment Canada and situated in an agricultural area. Figure 1 shows the location of CARE in relation to major Canadian cities and is coloured according to annual NH$_3$ emissions from 2008 (NPRI, 2008). Canada’s National Pollutant Release Inventory (NPRI) does not include soil or vegetative emissions from non-managed ecosystems. The site is located on a sharp transition with high NH$_3$ emissions to the south and negligible emissions to the north. Air masses originating from the south are typically polluted since they pass over urban, industrial, and agricultural areas of southern Ontario and the north-eastern United States, whereas cleaner air usually arrives from the north (e.g. Rupakheti et al., 2005). As a result, soil–atmosphere exchange of NH$_3$ can be examined under a wide range of atmospheric pollution regimes.

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

2.2 Bi-directional exchange framework

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

$$\nu_{\text{ex}} = \frac{1}{R_a + R_b + R_{\text{inc}} + R_{\text{soil}}}$$ (4)
The aerodynamic ($R_a$) and quasi-laminar ($R_b$) resistances reflect the macro- and molecular-scale turbulence, respectively, between the soil and measurement height of NH$_3$(g). The impenetrable (R$_{inc}$) and soil (R$_{soil}$) resistances account for processes within the canopy and at the soil interface that hinder the exchange of gases. According to the theory outlined in Hicks et al. (1987), $R_a$ and $R_b$ can be calculated as such:

$$R_a = \frac{\ln(z_{ref}) - \ln(z_0)}{\kappa \cdot u_\alpha},$$

$$R_b = \frac{2}{\kappa \cdot u_\alpha} \cdot \left(\frac{Sc}{Pr}\right)^{2/3},$$

where $z_{ref}$ is the height of the NH$_3$ measurement (2.7 m), $z_0$ the roughness length, equal to 0.05 m for uncultivated grass (Seinfeld and Pandis, 2006), and the von Karman constant $\kappa = 0.4$. The Schmidt number ($Sc = 0.58$) and Prandtl number ($Pr = 0.72$) are taken from Hicks et al. (1987) and account for the diffusivity of NH$_3$ and heat transfer, respectively. The friction velocity, $u_\alpha$, can be calculated by

$$u_\alpha = \sqrt{\frac{\nu' \cdot w'^2 + v' \cdot w'^2}{\nu}},$$

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

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

It should be reiterated that using Eqs. (3) to (7) to estimate soil–atmosphere NH$_3$ fluxes neglects any vegetative effects (e.g. recapture of NH$_3$, stomatal emission) and that this serves only as an approximation of NH$_3$ fluxes between the soil and the atmosphere.

### 2.3 Soil measurements

Measurements of soil [NH$_4^+$], pH, and temperature were necessary for calculating the $\chi$. Soil cores were collected in triplicate on 6 days during the campaign, all within 30 feet of the atmospheric measurement inlet. The sampling methodology outlined below is based on work done by Li et al. (2012) and van Miegroet (1995). Samples were collected six times throughout the campaign on the days listed in Table 1. Sites 1, 2, and 3 correspond to small ($\sim 1$ m$^2$) areas 10 m west, directly below, and 10 m east of the sonic anemometer, respectively. The soil was sampled more frequently towards the end of the campaign since meteorology (i.e. precipitation, air temperature) was more variable and was expected to perturb the $\Gamma_{soil}$ to a greater extent than in August when meteorological conditions were more consistent. Specifically, the ranges in air and soil temperature were larger in September than in August. After removing grass and any residual litter (of which there was very little), a PVC tube (5.1 cm inner diameter) was inserted into the ground to a depth of 10 cm and a soil core was removed by pulling out the tube with a soil core intact. Each core was thoroughly mixed and an $\sim 8$ g subsample was immediately placed into a pre-weighted extract solution (50 mL of 0.25 % KCl w/w) and transported on ice back to the lab for analysis. After shaking for 30 min, extracts were gravity filtered (ashless filter #40, Whatman Ltd., Maidstone, UK) then sent through a 0.2 µm PES membrane syringe filter ( Pall Ion Chromatography Acrodisc®, VWR International, Mississauga, ON). Ammonium, nitrate, and nitrite were then quantified using two ion chromatograph (IC) ICS-2000 systems (Dionex Inc., Sunnyvale, CA) operated with suppressed conductivity detection and reagent-free eluent (potassium hydroxide for anions, methanesulfonic acid for cations). Gradient elution schemes were optimized so that analyte peaks were baseline resolved. CS12A analytical and CG12A guard columns were used for the cation IC, and AS19 analytical and AG19 guard columns for the anion IC. In both cases, 25 µL loops were used. ICs were calibrated by injection of commercially available ( Dionex Corp., Sunnyvale, CA) mixed standards of seven anions (F$^-$, Cl$^-$, NO$_2^-$, Br$^-$, NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$) and six cations (Li$^+$, Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$). Serial dilutions of the standards in matrix-matched 0.25 % KCl allowed for a five-point calibration which yielded reasonable calibration curves (slope of $R^2 > 0.99$) for all analytes. Extraction with a 0.25 % KCl solution proved sufficient to desorb all accessible ions in the soil matrix, yet dilute enough to allow for quantification of NH$_4^+$ and NO$_3^-$ in every sample. The inherent assumption is that the extract solution sufficiently mimics the ability of soil pore water to liberate NH$_4^+$ ions from the soil matrix to participate in soil–air exchange. An additional extraction into deionized water (DIW) was performed on one set of soil samples. The [NH$_4^+$] measured in the DIW extract was between 30–45% of that measured with the KCl extraction. Extraction into DIW is an absolute lower bound on soil [NH$_4^+$] since higher ionic strength solutions will desorb more NH$_4^+$, and soil pore water has a much higher ionic strength than DIW. Flechard et al. (2013) and Cooter et al. (2010) have suggested fundamental analytical research is required to assess the validity of this assumption, but this is outside the scope of this current study. A field blank was run with every triplicate to account for any contamination (always less than 1 % of the measured soil [NH$_4^+$]) from sample handling and extraction.

Soil pH was measured by mixing $\sim 10$ g of soil with an equal mass of deionized water (1:1 soil:DIW slurry). A standard pH electrode (SypmHony 14002-782, VWR
Table 1. Soil parameters measured in this study.

<table>
<thead>
<tr>
<th>Date</th>
<th>Site</th>
<th>[NH$_4^+$] (mg kg$^{-1}$ wet soil)</th>
<th>pH (1 : 1 slurry soil : deionized water)</th>
<th>Average $\Gamma_{\text{soil}}$ (=1$\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 August</td>
<td>1</td>
<td>1.4</td>
<td>6.9</td>
<td>978 ± 750</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.67</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.85</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>28 August</td>
<td>1</td>
<td>1.43</td>
<td>6.6</td>
<td>290 ± 110</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.31</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.87</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>13 September</td>
<td>1</td>
<td>1.31</td>
<td>5.8</td>
<td>51 ± 20</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.17</td>
<td>6.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.51</td>
<td>6.09</td>
<td></td>
</tr>
<tr>
<td>20 September</td>
<td>1</td>
<td>1.01</td>
<td>5.8</td>
<td>176 ± 140</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.89</td>
<td>6.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.94</td>
<td>6.53</td>
<td></td>
</tr>
<tr>
<td>25 September</td>
<td>1</td>
<td>2.1</td>
<td>6.22</td>
<td>172 ± 43</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.6</td>
<td>6.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.93</td>
<td>6.59</td>
<td></td>
</tr>
<tr>
<td>27 September</td>
<td>1</td>
<td>0.61</td>
<td>6.16</td>
<td>91 ± 40</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.46</td>
<td>6.59</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.25</td>
<td>6.95</td>
<td></td>
</tr>
</tbody>
</table>

International, Mississauga, ON) was immediately immersed in the slurry until a stable pH reading was obtained. This was done in triplicate for each soil core, and an average pH for each was calculated. Performing the pH measurements in a saline solution of 0.25 % KCl desorbs more H$^+$ and was found to lower the pH reading by up to 1 unit relative to extraction into deionized water, which has been reported previously (e.g. Walker et al., 2014). Soil temperature was logged hourly using five in situ sensors (iButtons, Maxim Integrated, San Jose, CA) placed 10 cm deep dispersed across the 30 foot radius of the soil sampling area. Moisture content was determined gravimetrically for a subsample (~3 g) of each core by drying in an oven at 105 °C for at least 24 h.

2.4 Atmospheric measurements

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

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.

Backgrounds were acquired by overflowing the inlet with high-purity zero air for 24 h 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 20 h 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 L min$^{-1}$, pressure of 760 mm Hg and temperature of 298 K.

Atmospheric species of primary interest for this study are NH$_4^+$, SO$_4^{2-}$, NO$_3^-$ in PM$_{2.5}$ and their precursor gases (NH$_3$,
suggested by Zhang et al. (2010). $\Gamma_g$ includes both soil and litter, but during this study there was a negligible amount of litter on the ground; therefore, $\Gamma_g$ and $\Gamma_{soil}$ should be analogous. The suggested range in $\Gamma_g$ (2000 to 200000) is based on 14 values from six studies, all of which were in fertilized grasslands. Of these studies, only two (David et al., 2009; Mattsson et al., 2009) directly measured $\Gamma_g$, whereas the other four either inferred it from measurements of dead or dying leaves (Herrmann et al., 2009; Mattsson and Schjoerring, 2003) or modelled it (Burkhardt et al., 2009; Personne et al., 2009). All the $\Gamma_{soil}$ values (35 to 1850) measured in this study are below the range from the Zhang et al. (2010) review, likely because the field at CARE is non-fertilized and so has a lower N content. Suggested ranges of $\Gamma_g$ from Zhang et al. (2010) for various land types were recently incorporated into a regional air quality model (STILT-Chem) by Wen et al. (2013) to allow for bi-directional exchange. The authors found the updated model, using $\Gamma_g = 2000$ over grasslands, overestimates NH$_3$(g) in sites with lower NH$_3$(g) concentrations (i.e. CARE). This could be a consequence of overestimating $\Gamma_g$ in these regions, as implied by the $\Gamma_{soil}$ measurements given here.

Massad et al. (2010) carried out a similar review and suggested that $\Gamma_g$ be parameterized as 500 in non-fertilized, semi-natural environments without vegetation. To our knowledge, the results presented here represent the first values of $\Gamma_{soil}$ directly measured in a non-fertilized grassland. These measurements underscore the importance of distinguishing between fields that receive fertilization and those that do not. The $\Gamma_g$ range from Zhang et al. (2010) is not applicable to the field at CARE, whereas the estimation ($\Gamma_g = 500$) from Massad et al. (2010) is more suitable.

It is worth comparing $\Gamma_{soil}$ to the range of stomatal emission potentials ($\Gamma_{stom}$) in grasslands proposed by Zhang et al. (2010) (Fig. 2, green line). $\Gamma_{stom}$ values (300 to 3000) are based on roughly 50 measurements from over two dozen studies which reflect the narrower range in $\Gamma_{stom}$ compared to $\Gamma_g$. Massad et al. (2010) also parameterized $\Gamma_{stom}$, but did so by empirically fitting measurements to total annual N input instead of using a constant value for each land use type. These suggested $\Gamma_{stom}$ values from each review are on the same order as the $\Gamma_{soil}$ measured in this study, suggesting that in a non-fertilized field, the soil and vegetation might have a very similar propensity to either emit or uptake NH$_3$ (i.e. they likely have similar $\chi$).

3.2 Inferred soil compensation point and fluxes

A linear interpolation of $\Gamma_{soil}$ between the six sampling dates in combination with hourly soil temperature measurements were used to generate a time series of soil compensation point $\chi_{soil}$ (black trace in Fig. 3a) according to Eq. (2). The shaded region around $\chi_{soil}$ was calculated from a linear interpolation of $\pm$ 1$\sigma$ in $\Gamma_{soil}$ measurements and therefore reflects the uncertainty in $\chi_{soil}$ attributed to variability in soil pH and
Hourly gas-phase \(\text{NH}_3\) measured by the AIM-IC (orange trace) is also shown. These two traces frequently cross indicating a net flux from the soil to the atmosphere. On the other hand, \(\chi_{\text{soil}}\) values were significantly lower in September as a result of lower soil temperatures. Accordingly, the diurnal profiles of the difference between \(\chi_{\text{soil}}\) and \([\text{NH}_3]\) are distinct. In August, the difference between \(\chi_{\text{soil}}\) and \([\text{NH}_3]\) is positive throughout the majority of the day (excluding 07:00–11:00 in the morning), indicating a net flux from the soil to the atmosphere. On the other hand, in September the difference is negative throughout the entire day, meaning the soil is a continuous sink for atmospheric \(\text{NH}_3\). This suggests a clear transition from the soil being a net source to a net sink for atmospheric \(\text{NH}_3\). It should be noted that grass senescence had not yet begun and that there was no appreciable accumulation of litter, which has been shown to act as a strong source of \(\text{NH}_3\) (e.g. David et al., 2009; Mattsson et al., 2009; Mattsson and Schjørring, 2003).

In order to determine the magnitude of this exchange, the \(v_{\text{ex}}\) was estimated using Eqs. (4) to (7) and the flux was calculated from Eq. (3). The diurnal profile of \(\text{NH}_3\) fluxes (in ng m\(^{-2}\) s\(^{-1}\)) for both months is shown in Fig. 4. Throughout August there is an average net \(\text{NH}_3\) emission from the soil of 2.6 ± 4.5 ng m\(^{-2}\) s\(^{-1}\). In September, there was an average net deposition of 5.8 ± 3.0 ng m\(^{-2}\) s\(^{-1}\) from the atmosphere to the surface. Average fluxes measured by Wichink Kruit et al. (2007) were 4 ng m\(^{-2}\) s\(^{-1}\) in summer and −24 ng m\(^{-2}\) s\(^{-1}\) in autumn, which are of the same order of the flux values estimated in this study. Wichink Kruit et al. (2007) used their measured fluxes to infer a canopy emission potential (\(\Gamma_{\text{canopy}}\)) using data points where cuticular deposition can be neglected (dry conditions) and stomatal exchange is dominant (daytime). Exchange with the soil is ignored in their study due to the low soil pH (about pH = 5); however, this would not be a valid assumption in this study as the soil pH at CARE is about 7, as shown in Table 1. Nonetheless, the inferred \(\Gamma_{\text{canopy}}\) was 2200 and is higher than the \(\Gamma_{\text{soil}}\) measured in this study. At least to a first
3.3 Evidence for bi-directional exchange

Since CARE lies on a sharp gradient between high NH\textsubscript{3} emissions to the south and low emissions to the north (Fig. 1), one might expect air masses from the north to be lower in NH\textsubscript{3} relative to air masses from the south. Similarly, the greater level of anthropogenic activity south of CARE suggests an enrichment of anthropogenic pollutants (i.e., SO\textsubscript{2}, SO\textsubscript{4}\textsuperscript{2-}, HNO\textsubscript{3} and NO\textsubscript{3}) in air masses from the south. In order to interrogate this hypothesis, 2-day back-trajectories were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model for every 6 h throughout the study. Each 6-hour time stamp was then classified as having had the air mass pass through Toronto (a box defined from 43.5–44.0\degree N by 79.0–80.0\degree N), or having originated from the north (spent more than half its time above 44.23\degree N) or the south (spent more than half its time below 44.23\degree N and not passing through Toronto). Results from this analysis are shown in Fig. 5 and yield a distinct directional bias for all species except NH\textsubscript{3}; air masses passing through Toronto are clearly enhanced in SO\textsubscript{2}, HNO\textsubscript{3}, NH\textsubscript{4}, SO\textsubscript{4}\textsuperscript{2-}, and NO\textsubscript{3} but not NH\textsubscript{3}. A lack of directional bias for NH\textsubscript{3} could be explained by proximity to a large NH\textsubscript{3} source, but as seen in Fig. 1, there is a sharp regional (tens of kilometres) gradient in the emissions inventory suggesting that no such local source exists. A more likely explanation is that bi-directional exchange of NH\textsubscript{3} between the surface and atmosphere modulates near-surface NH\textsubscript{3} mixing ratios sufficiently to eliminate any directional bias that would result from traditional emission sources.

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

Second, this exchange could only sufficiently impact NH\textsubscript{3} mixing ratios if it occurs quickly enough. To test this, fast (0.005 m s\textsuperscript{-1}, at 14:00) and slow (0.003 m s\textsuperscript{-1}, at 01:00) average exchange velocities from August were used to calculate the time it would take the system (soil and atmosphere) to arrive halfway to equilibrium with an atmospheric height of 1000 m, as well as with the height at which AIM-IC measurements were made (3 m). For 1000 m, the timescale approximation, it appears that NH\textsubscript{3} fluxes in both these non-fertilized fields are comparable. The larger deposition in the autumn in Wichink Kruit et al. (2007) is likely attributable to higher NH\textsubscript{3} mixing ratios (~9 ppb average versus ~2 ppb in August average in this study). It is noteworthy that both sites are considered the same land type but likely have very different canopy-level processes driving NH\textsubscript{3} fluxes. Specifically, the soil in Wichink Kruit et al. (2007) had a sufficiently low pH (~5) to suppress appreciable soil–atmosphere exchange, which is not the case at CARE. Furthermore, a review by Schlesinger and Hartley (1992) estimate volatilization rates of NH\textsubscript{3} from undisturbed grasslands are between 0.3 and 30 ng m\textsuperscript{-2} s\textsuperscript{-1}, which encompasses the values from this work and that of Wichink Kruit et al. (2007).

It is also important to consider wet deposition when assessing net exchange of NH\textsubscript{3} between the atmosphere and an ecosystem. The Canadian Air and Precipitation Monitoring Network (CAPMoN) collects daily precipitation samples at CARE and reports the results online (http://www.on.ec.gc.ca/capmon/login/login.aspx). The average NH\textsubscript{4} wet deposition rates from 2001–2011 for August and September are 12.4 ± 4.6 ng m\textsuperscript{-2} s\textsuperscript{-1} and 11.3 ± 5.4 ng m\textsuperscript{-2} s\textsuperscript{-1}, respectively. In the context of our results (fluxes of 2.6 ± 4.5 ng m\textsuperscript{-2} s\textsuperscript{-1} in August and -5.8 ± 3.0 ng m\textsuperscript{-2} s\textsuperscript{-1} in September), the site at CARE has net NH\textsubscript{3} deposition in both months when one considers both wet deposition and bi-directional exchange. In other words, the magnitude of wet deposition fluxes is roughly 2–5 times larger than the magnitude of bi-directional exchange. However, it is important to note that wet deposition occurs in discrete events, whereas dry exchange is continuous.
is calculated to be between 40 and 62 h for the fast and slow $v_{ex}$, respectively. However, for a height of 3 m, only 7 and 11 min are required to get halfway to equilibrium. Although this calculation neglects vertical mixing beyond 3 m (which will occur), these short timescales suggest soil–atmosphere exchange is an important component of observed negative [NH$_4^{+}$] gradients with height. In other words, soil–atmosphere exchange over non-fertilized grasslands has the ability to strongly influence near-surface NH$_3$ despite the low $\Gamma_{soil}$ (relative to fertilized fields) whereas the impact on NH$_3$ levels throughout the boundary layer is dampened due to slower exchange.

### 3.4 Morning increase of NH$_3$

A morning increase in NH$_3(g)$ between 08:00–10:00 is clearly evident in Fig. 3b and c and has been observed elsewhere (e.g. Bash et al., 2010; Ellis et al., 2011; Flechard et al., 2013; Nowak et al., 2006; Wichink Kruit et al., 2007). The factors contributing to this phenomenon at CARE are not entirely clear but may include one or more of the following: dew evaporation, volatilization of particulate NH$_4$NO$_3$, emission from plants/soil, and/or mixing down of NH$_3$ rich air entrained above the nocturnal boundary layer. Wichink Kruit et al. (2007) observed a similarly timed increase that coincided with a decrease in leaf wetness. Furthermore, Flechard et al. (1999) and Bussink et al. (1996) found that water layers sorbed on leaves can store significant quantities of NH$_3$ even at an RH below 100%. Although no leaf wetness sensor was employed during this study, we use nighttime RH as a surrogate for dew and fog formation. Figure 7 shows the difference between the morning NH$_x$ ($\equiv$ NH$_3(g)$ + NH$_4^{+}$(particle)) and the average overnight NH$_x$ concentration.
the spike to coincide, but given that sunrise at CARE was
between 06:00 and 07:15 throughout the campaign, stomatal
emission is not likely the driving factor behind this trend at
CARE. It is also possible this morning increase is linked to
the break-up of the nocturnal boundary layer, as observed by
Walker et al. (2006), who measured surface NH$_3$ fluxes over
a fertilized soybean field. Observations from this study rule
out soil emissions and suggest that dew/fog evaporation plays
a key role in enhancing morning NH$_3$ mixing ratios.

4 Conclusions

Measurements of $\Gamma_{\text{soil}}$ and $T_{\text{soil}}$ in a non-fertilized grassland
were used to construct a time series of $x_{\text{soil}}$ over a 50-day
period. $\Gamma_{\text{soil}}$ ranged from 35 to 1850 with an average value
of 290, which is well below the 2000 $< \Gamma_g < 200,000$ suggestion
recommended this range based on field studies exclusively in
fertilized grasslands, which is likely the reason $\Gamma_g$ values in
this study are lower. Indeed the distinction between fertilization
and non-fertilization is critical in accurately assessing bi-
directional exchange. Our findings are more in line with the
parameterizations of Massad et al. (2010), who suggested a
$\Gamma_g$ of 500 for semi-natural, non-fertilized areas without veget-
ation. Seasonal and diurnal trends in $x_{\text{soil}}$ were observed
with lower values at night and in September due to decreases
in $T_{\text{soil}}$.

Fluxes of NH$_3$ between the soil and atmosphere were esti-
imated using [NH$_3$(g)] measurements and a simple resistance
scheme that neglects the influence of vegetation. August
fluxes were primarily upwards, except between 07:00–11:00,
and resulted in an average emission of 2.6 ± 4.5 ng m$^{-2}$ s$^{-1}$
from the soil. September was characterized by exclusive
deposition from the atmosphere at a rate of 5.8 ± 3.0 ng
m$^{-2}$ s$^{-1}$. These values are fairly similar to fluxes measured
by Wichink Kruit et al. (2007), who reported fluxes of 4 and
–24 ng m$^{-2}$ s$^{-1}$ in the summer and autumn, respectively.

HYSLIP analysis revealed that air masses passing
through Toronto were enriched in atmospheric pollutants ex-
cept NH$_3$. Since CARE lies on a sharp gradient of high emis-
sions to the south and low emission to the north, this lack of
directional bias implies that bi-directional exchange effi-
ciently modulates NH$_3$ mixing ratios. Back-of-the-envelope
calculations confirm that: (1) the reservoir of NH$_3^+$ in soil
of non-fertilized grasslands is large enough to sustain fluxes
to the atmosphere and (2) fluxes are rapid enough to impact
surface concentrations on a relevant timescale.

Figure 7 suggests that dew and fog evaporation can en-
chant the frequently observed morning increase in NH$_3$. It
is unlikely that soil emissions contribute to this increase as
deposition to the soil is predicted during the morning.

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

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