



Summertime Soil-Atmosphere Ammonia Exchange in the Colorado Rocky Mountain Front Range Pine Forest

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Abstract: Understanding the NH₃ exchange between forest ecosystems and the atmosphere is important due to its role in the nitrogen cycle. However, NH₃ exchange is dynamic and difficult to measure. The goal of this study was to characterize this exchange by measuring the atmosphere, soil, and vegetation. Compensation point modeling was used to evaluate the direction and magnitude of surface-atmosphere exchange. Measurements were performed at the Manitou Experimental Forest Observatory (MEFO) site in the Colorado Front Range by continuous online monitoring of gas and particle phase NH₃-NH₄⁺ with an ambient ion monitoring system coupled with ion chromatographs (AIM-IC), direct measurements of [NH₄⁺] and pH in soil extracts to determine ground emission potential (Γ_g), and measurements of [NH₄⁺] bulk in pine needles to derive leaf emission potential (Γ_s t). Two different soil types were measured multiple times throughout the study, in which Γ_g ranged from 5 to 2122. Γ_{st} values ranged from 29 to 54. Inferred fluxes (F_g) from each soil type predicted intervals of emission and deposition. By accounting for the total [NH₄⁺] pool in each compartment, the lifetime of NH₃ with respect to the surface-atmosphere exchange in the soil is on the order of years compared to much faster naturally occurring processes, i.e., mineralization and nitrification.

Keywords: ammonia; soil flux; soil-atmosphere interactions; ammonia lifetime

1. Introduction

Atmospheric ammonia (NH₃) plays an important role in the global nitrogen cycle [1–3]. A large portion of NH₃ sources are directly linked to human activities, such as agriculture [4], transportation [5–7], and industry [8]. NH₃ is also the main neutralizing agent for atmospheric trace acidic gases, such as HCl, HNO₃, or H₂SO₄, so it can also be found in particulate form (NH₄⁺), allowing it to travel long distances. As a result, the lifetime of NH_x, the sum of gas phase NH₃ and particle phase NH₄⁺, can range from several hours to several days before being removed from the atmosphere by dry or wet deposition [9]. In contrast, the fate and mobility of NH_x (dissolved NH₃ + NH₄⁺) found in soils is dictated by soil type, moisture content, and local microbiota. NH₄⁺ can be chemically fixed to clay minerals and organic matter, physically sorbed to colloids, or dissolved in soil pore water [10]. Soil NH_x can also undergo nitrification as part of the natural N cycling occurring within the soil leading to the production of NO₂⁻ and NO₃⁻, as shown in Scheme 1.

The local soil biota also dictates the mineralization and immobilization processes that control the fate of NH_x . The coupling of these two contrasting systems, the soil and the atmosphere, results in a dynamic exchange of NH_3 involving many different drivers.





Scheme 1. Simplified scheme of NH_x exchange between an ecosystem, composed of soil and vegetation, and the atmosphere. The solid orange boxes highlight the NH_x measured in this study, with the grey dashed boxes showing processes and pools that were not measured.

Due to their N sensitivity, forest ecosystems are generally believed to be a sink for NH₃, which has led to a large body of research focusing on what are the critical loads for these systems [11–13]. However, the exchange of NH_3 in forested regions has been shown to be dependent on the atmospheric concentrations. There are many factors controlling the movement of NH₃ through the forest ecosystem making it difficult to assess to what degree is the forest a source or sink of NH₃. Langford and Fehsenfeld found the direction of atmosphere-ecosystem exchange of NH₃ in Roosevelt National Forest in Northern Colorado could be positive (emission) or negative (deposition) depending on the direction of the prevailing wind. The study location was on the boundary between a natural forest ecosystem that is NH₃-poor and regions with heavy anthropogenic activities, namely urban and agricultural centers. They observed the NH₃-rich air masses from anthropogenic activity centers were being depleted and NH₃-poor air from the nearby forest were gaining NH₃ as the air passed through the forested site [14]. The NH₃ concentration of the air mass entering the forest seemed to dictate the forest ecosystem exchange. The correlation they observed with air temperature led to the assumption the plant canopy was solely responsible for increased NH₃ concentrations in the NH₃-poor air. More than two decades later, a study examined the soil contribution of NH₃ emissions to the atmosphere within the Colorado Front Range [15]. Based on chamber measurements of extracted soil cores, Stratton et al. reported an average emission flux of 0.21 \pm 0.03 mg NH₃–N m⁻² d⁻¹. However, this was derived from temperature-dependent NH₃ flux modeling, not direct forest measurements.

Understanding the magnitude and direction of NH₃ exchange is critical in assessing its environmental impact. Subalpine mountain ecosystems in particular, such as the Colorado Front Range, are vulnerable to slight increases in additional N input, 3–5 kg N ha⁻¹ y⁻¹ [11,16]. A critical review of the effect of N input into the Colorado Rocky Mountains and southern Wyoming reported eutrophication and acidification of surface water, soil, and lake with only an additional input of 1.5–3 kg N ha⁻¹ y⁻¹, causing a measured decrease in diatom population and biodiversity of the surrounding forest [17].

Exchange of NH₃ between the soil and the atmosphere is still subject to large uncertainties due to difficulty in direct flux measurements and an incomplete understanding of the biological processes occurring in the soil. As a result, the magnitude, and even sign, of net NH₃ exchange are challenging to predict. Many reports, including Stratton et al., use compensation point (χ) modeling to predict the magnitude and direction of NH₃ exchange (i.e., flux) [15,18–23]. Due to the technical and instrumental demands of measuring fluxes directly (i.e., through eddy covariance), compensation point modeling offers an affordable alternative to infer fluxes.

NH₃ fluxes between the soil (F_g) and atmosphere can be inferred based on the concentration difference in compensation point of the ground surface (χ_g) and atmospheric NH₃ and accounting for

the physical limitation to exchange between the surface and the air within the canopy, represented by a transfer velocity (v_{tr}) , shown by Equation (1):

$$F_g = v_{tr} \cdot (\chi - [NH_3]). \tag{1}$$

The transfer velocity characterizes the transport between the ground surface and height of the atmospheric NH₃ measurement. Its parameterization is described in detailed in Section 2.1 in the Supplementary Materials, where NH₃ in Equation (1) is denoted as the NH₃ concentration at the canopy top (χ_{z0+d}), representing the transport of NH₃ over the vertical extent of the pine forest canopy.

Compensation point modeling provides a framework for estimating NH_3 exchange between a surface reservoir and the atmosphere. The compensation point χ represents the atmospheric NH_3 concentration in equilibrium with the ammonium content of the surface reservoir at the surface-atmosphere interface. The relationship between the compensation point is governed by the Henry's law constant of neutral NH_3 (K_H), and the acid dissociation constant of NH_4^+ (K_a). This relationship at the interface between a surface pool and the atmosphere can be described as

$$\chi = \frac{K_a \cdot [NH_4^+]}{K_H \cdot [H^+]},$$
(2)

where χ is the surface compensation point as a function of soil NH₄⁺ and H⁺ concentrations, and the equilibrium constants K_H and K_a. Both equilibrium constants (K_H and K_a) are strongly temperature dependent, making temperature an important driver for scaling χ . When accounting for the temperature dependence of the equilibrium constants, Equation (2) can be rewritten using the van 't Hoff equation:

$$\chi = 13587 \cdot \Gamma \cdot \exp(-10396/T), \tag{3}$$

where T is surface temperature in Kelvin, the emission potential (Γ) is a unitless value equal to $[NH_4^+_{(aq)}]$ (mol kg⁻¹) divided by the pH-derived $[H^+]$ (mol kg⁻¹), and χ is in units of atm [21,24]. Using the local temperature and pressure conditions, and the molecular mass of NH₃, the compensation point can be converted from a partial pressure to an air concentration in units of μ g m⁻³. Assuming the atmosphere tends toward equilibrium with the surface reservoir, the deviation of ambient concentrations of NH₃ from χ above a surface determines the direction of the net exchange, flux, that would occur to restore equilibrium. For example, mixing ratios in the ambient atmosphere larger than the calculated compensation point lead to net deposition.

In most current bi-directional exchange models, Γ is treated as a static value [25–27]. The Γ is independent of meteorological conditions and represents the potential of a surface to emit NH₃ based on what proportion of NH_x is not protonated, which is governed by the surface acidity, i.e., [H⁺]. The ground layer emission potential is typically determined by the soil, but in some cases can also be influenced by the litter layer, particularly during periods of heavy leaf fall [26]. An extensive model review by Zhang et al. has shown that values of Γ_g (ground emission potential) of unfertilized areas generally fall within 20–1000, with the majority of the data reported for grasslands where the soils are largely homogeneous across the landscape [20]. This review reported only a single emission potential measurement for forest soil and the value of $\Gamma_g = 20$ was interpreted as having been impacted by a nearby swine facility [28]. However, based on data reported in Stratton et al., the Γ_g for their extracted forest soil is an order of magnitude larger, 117 ± 49 (n = 7). This presents a wide range of possible Γ_g in the few reported ground layer emission potentials from forest soils. In addition, current studies have not distinguished between the variety of soil environments that exist within a forested region.

In representing ecosystem-atmosphere exchange of NH₃ in forests, interactions with the forest canopy should also be considered. Bi-directional exchange with vegetation can also be expressed in terms of a compensation point [29–32]. Measuring the available NH₃ for exchange with the atmosphere from plants is far more challenging compared to soil analysis. It is assumed NH₃ deposition occurs

onto the leaf surfaces (cuticles) and NH₃ bi-directional exchange occurs through the stomata depending on the stomatal compensation point [29]. For the stomatal exchange pathway, the relevant emission potential (Γ_{st}) is determined by the [NH₄⁺] content found in the apoplastic fluid within the leaf membrane. A direct measurement of this emission potential requires selective extraction of the apoplastic fluid from inside the vegetation. As a result of this technical challenge, other methods have been developed to characterize the emission potential of vegetation, such as the bulk method proposed by Massad et al., which relates the Γ_{st} to the [NH₄⁺] measured in bulk leaf samples [18]:

$$\Gamma_{\rm st} = 19.3 \exp(0.0506 \cdot [\rm NH_4^+]_{\rm bulk}), \tag{4}$$

where the $[NH_4^+]_{bulk}$ is the ammonium concentration in full leaf extracts in $\mu g g^{-1}$ of leaf tissue.

The goal of this study was to characterize the ammonia content of the atmosphere, soil and dominant vegetation, Ponderosa pine, to evaluate the direction and magnitude of atmosphere-ecosystem exchange. Measurements were performed at the Manitou Experimental Forest Observatory (MEFO) site in the Colorado Front Range by continuous online monitoring of gas and particle phase NH₃-NH₄⁺ with an ambient ion monitoring system coupled with ion chromatographs (AIM-IC), direct measurements of $[NH_4^+]$ and pH in soil extracts to determine Γ_g , and measurements of $[NH_4^+]_{bulk}$ in pine needles to derive Γ_{st} . We measured the soil multiple times during the study to evaluate whether the assumption of static values of Γ_g are reasonable. The values reported in this study can better inform inferential models in predicting atmosphere-ecosystem exchange of montane forests in summer conditions.

2. Materials and Methods

2.1. Site Description

The Manitou Experimental Forest Observatory (MEFO) lies in the Front Range of the Colorado Rocky Mountains in the South Platte River drainage (39.1006° N, 105.0942° W), representative of a mid-elevation (~2000–2500 m a.s.l.), semi-arid, Ponderosa pine ecosystem common in the Rocky Mountain West. The temperature ranged from 6 to 28 °C with 70% of its annual precipitation (396 mm) occurring between April and August. The site has been managed as a research facility under the USDA Forest Services Rocky Mountain Research Station since 1938, therefore, the site has been well protected and changes in the landscape have occurred naturally. It spans roughly 6760 ha of semi-arid montane forest ecosystems sitting ~80 km south of Denver and ~40 km northwest of Colorado Springs. The site straddles the watershed of Trout Creek, a tributary of the South Platte River.

The forest surrounding the field site is an open canopy filled with uneven aged trees ranging from 27 to 201 years old, dominated by Ponderosa pine and containing some Douglas fir, oak, spruce and aspen. The average canopy height is 16 m with reported leaf area index (LAI) of 3.0 [33]. During the campaign period (26 July to 19 August 2015), areas with no tree coverage and direct sunlight showed understory development of sage brush, wild grass and thistle, particularly in August. The cryptogrammic soil is exposed in places with no vegetation and classified as deep, well-drained sandy loams and sandy gravelly loams originating from alluvial deposits weathered from the arkosic sandstone and granite formations [34]. Previous soil studies measured a soil pH range between 5.4 to 7.8, organic matter content of 1-4%, and a 50 to 150 mm h^{-1} permeability with an average 1.3 m root depth [33].

The MEFO field site consists of a combination of two distinct soil environments. The open canopy is characterized as an area where significant sunlight reaches the forest floor resulting in a well-developed understory. In contrast, the dense canopy area contains mature pines and a thick plant litter layer mainly composed of fallen pine needles.

The site was also equipped with a chemistry/flux tower, maintained by National Center for Atmospheric Research (NCAR), measuring temperature, relative humidity and wind speed at various heights within (1.8 m, 7.0 m, and 14.1 m) and above the canopy (27.8 m), above canopy global radiation,

in-canopy particle size distribution, and soil moisture and temperature at 5, 20, 35, and 120 cm depths. Precipitation composition data was retrieved from the National Trends Network, in part of the National Atmospheric Deposition Program, site CO21, Manitou. The site has been collecting deposition data since 1978.

2.2. In-Canopy Trace Gas and Particle Composition Measurements

Water-soluble PM_{2.5} and trace gases were measured using an Ambient Ion Monitoring system (AIM 9000D, URG Corp, Chapel Hill, NC, USA) coupled with two Ion Chromatographs (Dionex ICS-2000, Thermo Fisher Scientific, Mississauga, ON, Canada). The AIM-IC inlet was positioned at ~5 m above the forest floor. A detailed description of the AIM-IC sampling system can be found in Markovic et al., 2012 [35]. In brief, ambient air was drawn at 3.0 L/min through a $PM_{2.5}$ impactor allowing the bulk flow containing particles less than 2.5 μ m to pass through a parallel plate denuder equipped with nylon membranes. A continuous flow of 2 mM H_2O_2 solution was fed into the parallel plate denuders to capture all water-soluble gases. Particles that pass through the denuder were then hygroscopically grown and collected in a particle condensation chamber. Flows containing the dissolved forms of the gas and particle analytes were collected over an hour in separate sample reservoirs. Concentrator columns were used to improve the detection limit of the overall system by trapping all analyte molecules prior to injection on the ion chromatographs. Samples were analyzed with suppressed conductivity detection and reagent-free eluent (methylsulfonic acid for cation separation and potassium hydroxide for anion separation). The ICs were calibrated using high-purity mixed standards (Thermo Fisher Scientific). Systematic background runs were conducted by overflowing the inlet using ultra-pure zero air (Praxair, Loveland, CO, USA). Using the measurements from background runs, the 3σ detection limits were determined to be 0.1, 0.002, 0.001, and 0.001 μ g m⁻³ of NH₃, HCl, HNO₃, and SO₂, respectively. The higher detection limit for NH₃ is mainly the result of more variability in the signal during systematic background experiments.

Due to technical difficulties, anionic particulate components (pCl, pNO₃, pSO₄, and organics) were measured during the first half of the campaign, and acidic gases (HCl, SO₂, and HNO₃) measured during the latter half. Measurements of these compounds are presented in the Supplementary Materials.

2.3. Soil Measurements

In order to fully characterize the soil-atmosphere exchange of NH₃, it is necessary to investigate the dominating soil types. The field site consists of a combination of two distinct soil environments, open and dense canopy areas, in which both elements cover roughly 50% of the MEFO site. The open canopy is characterized as an area where significant sunlight reaches the forest floor resulting in a well-developed understory. In contrast, the dense canopy area contains mature pines and a thick plant litter layer mainly composed of fallen pine needles. Within a 70-m radius of the AIM-IC inlet, 5 m by 5 m sampling sites were demarcated, depicted in Figure 1, including the two predominant types of soil surfaces in contact with the atmosphere.



Figure 1. Bird's-eye view of the research site, with AIM-IC and soil sampling locations (\sites 1 and 2) marked.

Site 1 (dense canopy) was in a small clearing between several mature pines with roughly a ~5 cm thick needle bed and no forest floor flora. Site 2 (open canopy) contained a mix of bare soil and understory, including sagebrush, wheatgrass, bluegrass, thistles, fleabane, and wild flowers. Beneath the surface, the soil profile characteristics between the two sampling sites showed marked differences. The open canopy plot, with its mature understory, supported a relatively shallow root system that dominated the top 5 cm, and patches of bare soil with no organic matter including needle litter. In contrast, the dense canopy contained root network of the surrounding pine reaching >1 m in depth.

Soil samples were collected on four dates between 31 July 2015 and 17 August 2015. Within each sampling site, vegetation was removed, and five randomly spaced soil cores were taken using a 5 cm diameter by 12 cm deep beveled soil corer in a 0.3 by 0.3 m plot. These plots were sampled once. Each sampling day involved a new plot within the sampling site. Only the top 5 cm of the soil core, excluding the litter layer, was taken for processing and analysis. Samples in the dense canopy plot had a consistent appearance over the top 5 cm, whereas in the open canopy plot, the surface soil was dark brown only 2–3 cm deep before reaching dry, brittle, densely-packed soil underneath.

The five soil cores from the same plot were immediately mixed and sieved with 2 mm coarse mesh to create a single batch sample. Three ~8 g subsamples were dispersed in 50 mL 0.25% KCl w/w solution and agitated for 30 min [24,36]. The suspensions were then filtered by gravity using ashless filters (Whatman Ltd., Maidstone, UK). Filtrates were filtered again using 0.2-µm PES membrane syringe filters (Pall Ion Chromatography Acrodisc®, VWR International, Mississauga, ON, Canada) to remove any fine particulates before analysis by IC. Water content was determined by comparing weight before and after drying 10 g of subsample overnight in a preheated oven set to 105 °C. Soil pH was measured by creating a 1:1 w/w slurry of soil and deionized water (DIW) and using a standard pH probe (SympHony 14002-782, VWR International).

Soil temperature measurements are necessary to calculate χ_g , as expressed in Equation (2). Soil temperature profiles (Campbell Scientific, Logan, UT, USA, model T107 thermistors) from 5, 20, 35, and 120 cm depths and soil moisture (Decagon Devices, Pullman, WA, USA, model EC-5) in the top 5 cm were provided from National Center for Atmospheric Research Atmospheric Chemistry Observations and Modeling (NCAR-ACOM): Manitou Experimental Forest Observatory Field Site. The temperature measured at 5 cm was used to calculate the χ_g of each plot, so any temperature difference related to the amount of direct sunlight and litter was not measured. Pine needles were collected from the same mature Ponderosa pine tree (8.5 m tall) to avoid any variability found between different aged trees. To account for the different levels of sunlight exposure to different sections of the tree, needle samples were taken at three sampling heights (1, 3.6, and 7 m) and analyzed for bulk NH_4^+ content. Pine needle samples were collected in early morning, midday, and evening periods on 16 to 18 August. Collected pine needles were immediately frozen using liquid nitrogen, mixed with sand, and homogenized with mortar and pestle. Both the pine needle sample mass (~0.2 g) and the sand mass (~0.5 g) were determined before the homogenization step. The total mass after the homogenization was determined to account for any loss of pine needle material during the process. The sample mixture was dispersed in 1 mL of DIW in a 1.5-mL Eppendorf tube and centrifuged at 12,000 g for 15 min. Five hundred microliters of the supernatant were transferred to a 2-mL 0.45 µm polysulphone centrifuge filter tube (Micro VectraSpin, Whatman, VWR International), stabilized with 1 mL of citric acid solution and spun at 2000 g for 5 min. The filtrate was then directly analyzed by IC. The pine needle water content was determined gravimetrically by drying pine needle subsamples for 24 h at 105 °C.

2.5. Flux Calculations

The flux of NH₃ between the soil and the atmosphere (F_g) is governed by the soil compensation point (χ_g), calculated using Equation (2), and the ambient NH₃ concentration at the canopy top (χ_{z0+d}), coupled by the transfer velocity (v_{tr}):

$$F_g = -v_{tr} \cdot \left(\chi_{z0+d} - \chi_g\right). \tag{5}$$

The top of the canopy is defined as the sum of the roughness length (z_0) and the zero-plane displacement height (d), which is applied for tall canopies such as forests. For z_0 a typical value of 2 m for forests was used, while d equals $2/3 \cdot h_c = 10.67$ m with an average canopy height (h_c) of 16 m. Due to the sparse forest canopy structure, we assumed that χ_{z0+d} is equal to the concentration measured by the AIM-IC taken at ~5 m a.g.l.

In accordance with the two-layer compensation point model described by Nemitz et al. (2001), the stomatal flux (F_s) is driven by the difference between the canopy compensation point (χ_c) and the stomatal compensation point (χ_s) (see Equation (2)) and calculated as follows:

$$F_s = -\frac{\chi_c - \chi_s}{R_s},\tag{6}$$

where R_s is the stomatal resistance.

The deposition of NH₃ to the pine needles' cuticles (F_{cut}) was determined by the ratio of χ_c and the cuticular resistance R_{cut} :

$$F_{cut} = -\frac{\chi_c}{R_{cut}}.$$
(7)

The derivations of v_{tr} , χ_c , R_s , and R_{cut} are found in the detailed description of the compensation point resistance model in the Supplementary Materials.

3. Results

3.1. Atmospheric Trace Gas and PM_{2.5} Composition

Atmospheric measurements made by the AIM-IC, depicted in Figure 2, show a consistent diurnal cycle of ambient NH₃ concentrations reaching highs of ~0.5 to 1.5 μ g m⁻³ during midday while dropping to below detection limit at night. Particulate NH₄⁺ mass loadings were typically close to the detection limit, with a maximum at 0.08 μ g m⁻³. The diurnal pattern of ambient NH₃

concentrations observed by the AIM-IC shows no drastic increase in concentration associated with large emission events.



Figure 2. Ambient concentrations particulate NH_4^+ (top) and ambient NH_3 (bottom) observed in MEFO by the AIM-IC from 27 July to 13 August 2015, in which date and time are presented in Mountain Standard Time (MST).

Overall low particle concentrations were confirmed with particle sizing data, provided by NCAR measuring a few meters away from the AIM-IC inlet. Average particle number concentrations were less than 2×10^3 cm⁻³, which is typical for rural continental environments. Acidic trace gas concentrations (Figure S1) are comparable to background concentrations seen in a summer montane forest [26,37]. Ambient concentrations of HCl and HNO₃ were on average well below 0.4 µg m⁻³, and their concentrations appeared correlated. In contrast, SO₂ was typically close to the detection limit with a few exceptions where events occurred causing spikes of 0.4 to 1 µg m⁻³ over a period of three hours. In general, the concentrations of acidic gases that react readily with NH₃ were all less than 20% of the observed NH₃ concentrations. The low concentrations of acidic gases and fine particulate NH₄⁺ simplifies our interpretation of the behavior of gas phase NH₃ because it indicates that gas-to-particle partitioning is not dominating its behavior.

The average diurnal cycles of temperature and relative humidity shown in panels (a) and (b) in Figure 3, were typical of previous summers. However, precipitation occurred in the form of moderate showers, ranging from 2 to 6 mm per event. In typical years, precipitation more commonly occurs during heavy rain storms in the late afternoon. The difference in rainfall patterns may influence the removal rate of trace gases and particles from the atmosphere and input into the forest ecosystem.



Figure 3. Cont.



Figure 3. Meteorological conditions observed during the campaign period from 24 July to 12 August 2018. Ensembled averages of (**a**) RH and (**b**) T. (**c**) Time series of daily precipitation amounts and accumulation in mm from NTN.

With only a few periods of heavy thunderstorms, occurring later in August, the majority of the measurement period captured atmospheric concentrations and soil emission potentials during warm and dry conditions.

3.2. Physiochemical Soil Properties

The soil physical structure, pH, moisture content and temperature gradient directly impact the processes that govern NH_x loss to assimilation, nitrification and exchange with the atmosphere. Soil temperature and moisture data, collected by NCAR, shown in Figure 4 depict a consistent water content within the top 5 cm of the soil bed.



Figure 4. Soil temperature and water content in the top 5 cm of the soil from 26 July to 13 August 2015.

Soil temperatures in the top 5 cm of the profile showed a typical diurnal cycle of retaining heat from incoming radiation peaking at on average 25 °C and slowly dissipating heat during late night and early mornings. The amplitude of the soil temperature daily cycle ranged between 5 and 10 °C. Following a rainy period that preceded the campaign, the soil moisture slowly decreased during our study period with small and large increases following periods of precipitation on 4 and 10 August, respectively.

3.3. Measured Soil Emission Potentials

The average and standard deviations of the soil composition measurements are shown in Table 1. For each sampling date and plot, the standard deviation of the soil $[NH_4^+]$ is derived from the variability among the triplicate extracts. In contrast, the variability in pH among replicate extracts was

always less than 0.1 pH units. Each measurement of soil $[NH_4^+]$ is combined with the measurement of soil $[H^+]$ to calculate the average and standard deviation of the soil emission potential. Comparison of Γ_g in open and dense canopy areas of the forest shows the inherent heterogeneity in the forest ecosystem. In general, the soil supporting the dense canopy is more acidic, leading to lower emission potentials for comparable soil $[NH_4^+]$.

Sampling Date	Dense Canopy Soil			Open Canopy Soil			
	$[NH_4^+]$ µg g ⁻¹ wet soil	pН	$\Gamma_{ m g}$	$[NH_4^+]$ µg g ⁻¹ wet soil	pН	$\Gamma_{ m g}$	
July 31	44.8 ± 13.5	6.0	2122 ± 642	0.72 ± 0.36	6.2	61 ± 22	
Aug 2	51.5 ± 14.6	5.4	708 ± 200	1.44 ± 1.08	5.9	62 ± 46	
Aug 10	1.08 ± 1.44	5.4	5 ± 4	2.7 ± 0.54	6.2	220 ± 39	
Aug 17 ¹	0.72	5.4	8	3.6	6.4	466	

Table 1. Extracted [NH₄⁺], soil pH and resulting Γ_g in open and dense canopy areas of MEFO.

¹ Values from 17 August are based on a single sample extract.

Over the course of the campaign period, the open canopy areas displayed active brush and understory development. In contrast, the dense canopy areas maintained a thick layer of decomposing litterfall primarily composed of pine needles. It is well known that decomposing pine needles acidify soil, and with high acidity, a larger proportion of NH_3 is trapped in its protonated form (NH_4^+) unable to volatilize. Soil from the dense canopy plot had much higher NH_4^+ on the first two sampling dates leading to the largest emission potentials observed during the campaign. The NH_4^+ content of the soil in the dense canopy plot decreased dramatically for the last two samples, leading to emission potentials that were orders of magnitude smaller. In contrast, the open canopy soil exhibited moderate increases in its NH_4^+ content with decreasing soil acidity, leading to comparable relative increases in the emission potential. Overall, our soil measurements from the MEFO site in summer of 2015 produced Γ_g values with a wide range in variability from 5 to 2122 for the dense canopy soil alone.

3.4. Measured Stomatal Emission Potentials

A single mature Ponderosa pine tree was used to characterize stomatal emission potential variability and to determine the direction of NH_3 exchange with the forest canopy. Extracted NH_4^+ concentrations were all within a factor of two as seen in Table 2.

Sampling Time of Day	ng Time of Day Tree Base (1 m)		Middle (3.6 m)		Near Top (7 m)	
	$[NH_4^+]$ µg g ⁻¹ needle	Γ_{st}	$[NH_4^+]$ µg g ⁻¹ needle	Γ_{st}	$[NH_4^+]$ µg g ⁻¹ needle	Γ_{st}
Morning (5:00–7:00)	12.9 ± 0.2 (2)	37	11.3 ± 1.4 (2)	54	8.3 ± 0.7 (2)	30
Midday (10:00–16:00)	7.9 ± 1.3 (2)	29	$12.6 \pm 5.6 \ (11)$	38	13.7 ± 7.6 (2)	40
Evening (17:00-19:00)	12.8 ¹	37	12.1 ¹	35	10.8 1	33

Table 2. Averaged [NH₄⁺]_{bulk} from a single mature Ponderosa pine on 16-18 August 2018.

Sample number is denoted in parentheses. ¹ Values based on single sample extract.

The Γ_{st} was calculated for each sample, or group of samples, using the bulk leaf relationship described by Equation (3). In the exponential fit used by Massad et al. [18], the bulk NH_4^+ values measured in MEFO fall within the linear section leading to a factor of two range in the stomatal emission potential.

4. Discussion

4.1. Challenges of Measuring NH₃ in Ecosystem Compartments

Predicting the direction and magnitude of surface-atmosphere NH_3 exchange is difficult in natural ecosystems, where the legacy of land use and nutrient inputs is often not known. The bi-directional flux

framework was developed to represent the flux of NH₃ between different environmental compartments (e.g., soil, vegetation, atmosphere) driven by thermodynamics [21,29]. Ground and stomatal emission potentials (Γ) can provide insight about the net exchange of NH_x in these ecosystems. Decoupling each compartment can be challenging, particularly when all compartments come together to comprise an ecosystem. Isolating the soil Γ_g parameter, for example, requires removing other closely linked influences, such as litter and root systems that can also have an impact on the amount of N in the soil system [26]. There have been extensive studies on developing proper soil extraction methods [36]. By virtue of all aqueous extraction methods, all removable NH_x is extracted in the form of NH₄⁺. This assumes all extracted $[NH_4^+]$ represents the amount found in soil pore water that can volatilize into the atmosphere. Recent chamber studies of soil, either of core samples [15] or overtop the intact soil [38,39], overcome this limitation by measuring the NH₃ emission directly. However, enclosure experiments, such as chambers, have difficulty in recreating the turbulent mixing that regulates the transfer velocity between the soil and atmosphere under ambient conditions, which is critical for fluxes that are driven by a compensation point, such as for NH₃. Both approaches are limited but are an important step in providing necessary data to determine the extent of available NH_x in the soil. The soil extraction method used in this study is a commonly used technique that was further refined by Wentworth et al. to improve the NH₄⁺ detection using IC. The method uses a lower concentration of salt in the extraction solution and therefore may slightly underestimate the total amount of NH_4^+ in the soil. However, given that the proportion of total soil NH_x that is exchangeable with the atmosphere is unknown, it is not clear if this introduces a bias in the soil emission potentials we report.

Direct NH_x measurements of vegetation are equally challenging. In bi-directional exchange models, the vegetation-atmosphere exchange is the sum of NH_3 exchange with plant stomata and deposition to the thin liquid layer that forms on the cuticles of the plant. In principle, calculating the stomatal emission potential requires measurements of $[NH_4^+]$ and $[H^+]$ in the apoplastic fluid. For practical reasons, Γ_{st} is often inferred from $[NH_4^+]$ concentration found in the bulk leaf material.

The data used to produce the fit described in Equation (3) were assembled from measured data and inferred $[NH_4^+]_{bulk}$ values [19]. Only two studies by Hill et al. and Mattsson and Schojoerring involved apoplast extraction, bulk measurements, and plant chamber measurements to calculate χ_{st} , and by inversion of Equation (2), Γ_{st} [40]. In the remaining studies $[NH_4^+]_{bulk}$ concentrations from unmanaged grassland and forest ecosystem types were not measured but were derived based on a relationship with total nitrogen deposition (N_{dep}) estimates [41]. The relationship in Equation (3) was derived for a range of bulk $[NH_4^+]$ between 0 to 120 µg per g of leaf tissue, with forest ecosystems spanning the entire concentration range. The measurements of bulk $[NH_4^+]$ concentrations observed at MEFO remained within a range from 7.9 to 13.7 µg g of needle⁻¹. Therefore, the small variability in $[NH_4^+]_{bulk}$ was reflected in the small variability calculated in Γ_{st} .

4.2. Implications of Γg Variability on NH₃ Flux

Emission potential (Γ) and temperature collectively regulate the NH₃ compensation point (χ) of a compartment. When compared to the ambient concentrations, χ in turn defines the direction and influences the magnitude of the NH₃ exchange. Compensation points that are greater than ambient concentrations suggest emission to the atmosphere will occur in order to re-establish equilibrium. The reverse is also true, in which compensation points smaller than concentrations observed in the atmosphere are predicted to tend towards deposition from the atmosphere. To account for changes in the measured soil [NH₄⁺] content and pH, mean Γ_g values were linearly interpolated between measurement periods for both soil types to generate hourly Γ_g values over the course of the campaign period. This approach assumes that the change between the measured values of Γ_g is linear. The soil temperature of the top 5 cm was then used to compute the hourly values of χ_g for each soil type, using Equation (2). The large variability in Γ_g of both soil types, especially for the dense canopy, translates into large variability in χ_g , in which values range from 0.02 to 14.2 µg m⁻³, as seen in Figure 5. The χ_{st} was calculated using mean Γ_{st} (35) in Equation (3) and hourly air temperatures. Given that Γ_{st} had much smaller variability compared to Γ_g , using the average value of Γ_{st} measured following the atmospheric measurement period should not introduce too much uncertainty.



Figure 5. Change in soil and stomatal compensation points with respect to atmospheric NH₃ concentrations measured by the AIM-IC from 31 July to 13 August 2015.

The calculated values of χ_g show substantial variability in the gas phase NH₃ that would be in equilibrium with the soil compartment. The range of χ_g values for both the dense and open canopy soils span the range of the atmospheric concentrations of NH₃ observed by the AIM-IC (0.1 to 1.5 µg m⁻³). As a result, there are periods in which the soil is predicted to emit NH₃, and other periods where the soil is more likely to receive NH₃ through deposition.

The two soil types display significantly different trends in χ_g over the course of the measurement campaign. The χ_g of the dense canopy soil type exhibits a decline in compensation point from 14.2 to 0.83 µg m⁻³ between 31 July and 9 August. After 10 August, the sudden decrease in χ_g to 0.15 µg m⁻³ implies that atmospheric exchange with the dense canopy soil area changes sign. The decreasing trend observed in dense canopy soil χ_g is predominately caused by a sharp decrease in [NH₄⁺] content, while the soil pH and diel pattern of soil temperature remained consistent throughout the measurement period. The opposite trend was observed in open canopy soil χ_g values. There is a gradual increase in open canopy soil χ_g that initially lies below atmospheric concentrations and eventually is slightly above. Therefore, the predicted open canopy soil-atmosphere exchange of NH₃ begins as deposition and evolves into emission over the measurement period. This gradual increase is related back to the increase in [NH₄⁺] content paired with a decrease in soil acidity and consistent soil temperature pattern. On the other hand, extrapolated time series for χ_{st} , ranges from 0.04 to 0.31 µg m⁻³, suggesting that the direction of exchange is consistently from the atmosphere into the vegetation via the stomata.

The dynamic trends in χ_g translate into variable NH₃ fluxes for both soil types during the measurement period. The resulting inferred fluxes shown in Figure 6, highlight the influence of varying χ_g over time for both soil types, leading to both NH₃ emission (positive) and deposition (negative) fluxes. From the dense canopy soil, inferred NH₃ fluxes range from 370 to $-14 \,\mu g \,m^{-2} \,h^{-1}$. Open canopy NH₃ fluxes showed a smaller range of 39 to $-10 \,\mu g \,m^{-2} \,h^{-1}$. The drastic changes in the soil [NH₄⁺] content and inferred F_g can, therefore, have a large impact on the composition of the atmosphere.

The stomatal NH₃ fluxes using the χ_{st} values presented in Figure 5. In addition, the deposition of NH₃ to the pine needle cuticles was inferred as a function of relative humidity and the acid ratio in ambient air. Details on the calculation of the pine needle flux pathways are presented in Section 2.2 in the Supplementary Materials. The fluxes from the Ponderosa pine shown in Figure 6 represent the sum of both stomatal and cuticular fluxes. In contrast to the fluxes from soil, the Ponderosa pine NH₃ fluxes also change sign, but to a much smaller degree ranging from 0.14 to $-21.5 \,\mu g \,m^{-2} \,h^{-1}$.

Therefore, the inferred pine-atmosphere exchange in the MEFO ecosystem shows a predominate negative flux, or deposition, portraying the surrounding Ponderosa pine as constant sink for NH_3 during the measurement period. This is consistent with the small χ_{st} calculated.



Figure 6. Inferred soil NH₃ fluxes based on χ_g of both soil types and the Ponderosa pine flux (sum of stomatal and cuticular pathways) from 31 July to 12 August 2015 in $\mu g m^{-2} s^{-1}$ and $\mu g m^{-2} h^{-1}$. Both $\pm 0.0025 \mu g m^{-2} s^{-1}$ or 9 $\mu g m^{-2} h^{-1}$ are marked with grey dotted line for reference.

Inferential modeling of NH₃ fluxes typically holds the emission potential of an ecosystem or land cover type constant; however, we found through repeated measurements of soil characteristics under open and dense canopies that the soil χ_g changed dramatically over just a three-week measurement campaign. As a consequence, the magnitude and even direction of the NH₃ flux between the soil and atmosphere inferred by our measurements is very different than had the χ_g of the soil compartment only been driven by temperature changes. Beyond the variability in time, there is the additional challenge in correctly representing the spatial distribution of the two distinct soil types observed at MEFO. Addressing both types of variability would be necessary for larger scale modeling.

Precipitation volume and composition data reported by the National Trends Network can be used to calculate the wet deposition of NH_x during the measurement period. As a result of the rainfall events between 4 and 11August, a total of 17 mg m⁻² of NH_3 was scavenged from the atmosphere and delivered to the ecosystem. Despite the infrequency of rain events that occurred during the campaign period, wet deposition is still a more significant process in delivering NH_3 into the forest soil. Focusing on the periods of dry deposition depicted in Figure 6 can provide an estimate of total dry deposition NH_3 input from the atmosphere to the soil when periods of negative fluxes are calculated. From 31 July to 3 August, dry deposition totaling 202 µg m⁻² of NH_3 occurred over the open canopy soil type. The estimated amount of dry deposition NH_3 input to the dense canopy soil between 10 and 13 August is ~360 µg m⁻². Thus, wet deposition is roughly two orders of magnitude more important than dry deposition as a source of NH_3 to the soil during this period. When compared to the size of the NH_x pools in both soil types, the total NH_4^+ input from wet deposition over one week still falls in the lower end of the total NH_x observed in the estimated range of soil NH_4^+ content (10,000 to 850,000 µg m⁻²).

4.3. Distribution of NH₃ Pools in Forest Ecosystem

The measurements from our study can be used to provide a sense of the relative amounts of NH_x in the atmosphere, Ponderosa pine, and soil, by calculating the moles of NH_x present in each

compartment for a given ground surface area. The total NH_x pools of each measured compartment in the MEFO site is displayed in Figure 7 in μ g m⁻².



Figure 7. Comparison of measured NH_x pools on a logarithmic scale in two distinct soil sampling areas (dense and open canopy soils), the Ponderosa pine (assuming specific leaf area = 43.8 cm² g⁻¹, [42]) and LAI = 3 [33], and the atmosphere (assuming 1000 m boundary layer depth). Whiskers represent 10 and 90 quartiles, with the box within the 25 to 75 quartiles and the mean marked with a solid line.

The range of NH_x shown in each compartment covers all the measurement data collected for the campaign period. Both dense and open canopy soil NH₄⁺ pools were calculated using the total sampling area (0.98 m²), based on the area of the soil corer, the total mass of soil collected from the top 5 cm, and the extracted [NH₄⁺] μ g per kg of soil. The range of the Ponderosa pine NH₄⁺ pool was estimated assuming a specific leaf area index (43.8 cm² g⁻¹), associating leaf surface area with pine needle mass, to express [NH₄⁺]_{bulk} ug g⁻¹ in terms of needle surface area [38]. Then by using the leaf area index characterized for the MEFO canopy (LAI = 3) reported by Ortega et al. [33], the [NH₄⁺]_{bulk} μ g cm² was converted from leaf surface area to ground surface area. The atmospheric NH₃ pool was approximated based on NH₃ mixing ratios measured during the campaign and an assumed 1000-m boundary layer height that provided the total NH₃ μ g m⁻².

Examining all the major NH_x pools characterized in the study shows the wide range of NH_x content between the different compartments that undergo surface-atmosphere exchange of NH_3 . It is evident the pool of NH_4^+ found in both soil types, despite their differences, is far greater than what was estimated in the pine needles and in the atmosphere combined. The calculated ranges of NH_4^+ of dense canopy soil and open canopy soil were 10,000 to 850,000 and 20,000 to 110,000 $\mu g m^{-2}$, respectively. This is 2–3 orders of magnitude larger than the NH_4^+ amount estimated in the Ponderosa pine needles, with a range of 3000 to 15,000 $\mu g m^{-2}$.

The implications of dynamic χ values from different environmental compartments make it difficult to predict the direction of the net NH_x exchange between the atmosphere and remote forest ecosystems. The relevance of atmospheric input into the soil system and surrounding canopy is, therefore, examined in terms of lifetime of soil NH_x with respect to surface-atmosphere exchange. The lifetime of NH₃ is defined by the size of the chemical pool and the net flux, the combination of loss and gain rate of NH₃ between the compartment and the atmosphere. The ranges of calculated NH_x pools and fluxes, are shown in Figure 8, highlighting the areas of the forest compartments measured in MEFO. The open black triangle represents the previously reported soil NH_x content of unmanaged forest soils from Stratton et al., for comparison. Soil density is needed to calculate the size of the [NH₄⁺] pool, which is rarely reported. Therefore, the average soil density observed at MEFO (0.2 kg of soil per m²) was used to estimate the extent of the $[NH_4^+]$ pool from Stratton et al. study. The forest site studied in Stratton et al. falls within the $[NH_4^+]$ pool observed at MEFO. The emissions average they reported from their chamber studies is also on the same order of magnitude, as was calculated by compensation point modeling in this study.



Figure 8. Lifetime of NH_x in h with respect to soil-atmosphere exchange as a function of NH_x concentration and flux in $\mu g m^{-2} h^{-1}$ on logarithmic scales. The ranges of measured $[NH_x]$ content and inferred fluxes for the atmosphere, Ponderosa pine, dense and open canopy soils are highlighted.

From the perspective of the atmosphere, the lifetime of NH_3 with respect to the most extreme emission case calculated is on the order of minutes to hours. From the perspective of the soil, the lifetime of NH_x against exchange with the atmosphere can range from weeks to years depending on the strength of the flux. Thus, the process of soil-atmosphere NH_3 exchange has a big influence on the composition of the atmosphere, and a much smaller relative effect on the composition of the soil system. The overall lifetime of NH_x within the soil must be much shorter, given the extreme variability we observed in soil [NH₄⁺]. This implies that other processes like mineralization and denitrification must be important for regulating soil $[NH_4^+]$, and consequently these processes also impact soil-atmosphere NH₃ exchange. Some studies have shown the gross rates of nitrification in mature forests containing Ponderosa pine to be as high as 25 and 79 mg N m⁻² d⁻¹ in New Mexico and Oregon field sites, respectively [43]. Such rates are orders of magnitude larger than the largest computed fluxes based on χ_g and χ_{st} . Using the median value of the Ponderosa pine-atmosphere exchange we inferred $(-3.61 \,\mu\text{g m}^{-2} \,\text{h}^{-1})$, corresponds to a lifetime against exchange of 12 weeks for the needles and five days for the atmosphere. Our framework does not investigate the rate of exchange of NH₄⁺ between the pine and the soil, which may be much greater than the rates of exchange of either of these compartments with the atmosphere.

One of the challenges to these approaches is the lack of information on the biological processes, namely local biota that govern mineralization, immobilization, and nitrification. More research into genomics, paired with flux chamber experiments, for other atmospherically relevant gases are currently being explored and show promise in converging our understanding of the physical processes that govern trace gas exchange and the microbiology that contributes to this exchange [44]. This also highlights the need for ecological data on the soil, such as microbiological processing and litter decay rates that can be another source of NH₃ input. This could potentially lead to the advent of more available N-rich nutrients through the mineralization of organic nitrogen. Many studies have

broadened the number of N-fixation bacteria investigated in order to improve our understanding of

5. Conclusions

The resulting study offers the extent of NH_x pools observed in MEFO during summertime conditions and the impact of atmospheric input into the forest ecosystem. The changes and variability in NH_4^+ we observed in the soil system suggest there are processes, namely mineralization, immobilization and nitrification, occurring on a much shorter timescale compared to a year and that during these summertime conditions, the ecosystem-atmosphere exchange of NH_3 is negligible from the perspective of the soil NH_x budget.

the total N budget found in forest regions [45-47]. Ultimately, more research on the soil pools of NH₃

Supplementary Materials: The following are available online at http://www.mdpi.com/2571-8789/3/1/15/s1. Figure S1. Ambient concentrations of trace gases (HCl, SO₂, HNO₃, and NH₃) and average PM_{2.5} composition (pCl, pNO₃, pSO₄, pNH₄, and *organics) observed in MEFO by the AIM-IC from 27 July to 13 August 2015.

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input could help explain the high [NH₄⁺] seen in MEFO soils.

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