

On the efficiency of biosphere–Atmosphere ammonia exchange processes over a Scots pine forests and its link to ecosystem activity

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ABSTRACT

Ecosystem productivity and availability of reactive nitrogen (N_r) are inevitably linked. Here, we study the link between ecosystem productivity and biosphere–atmosphere exchange of ammonia (NH₃) and the influence of seasonal variability. We collected a year-round dataset of high temporal resolution measurements of NH₃-fluxes (F_{NH_3}) between forest and atmosphere obtained with the eddy covariance method above a Dutch temperate Scots pine forest (Loobos). We observed a pronounced difference in NH₃-exchange between the winter and summer season. During summer, we found a strong correlation between monthly gross primary productivity (GPP) and monthly F_{NH_3} , while during winter such a relation was absent. We hypothesized that this relation is a result of N-remobilization and N-assimilation, which scales with ecosystem activity. The high data-coverage, extensive meteorological observations, and deployment of additional leaf wetness sensors, also allowed us to study NH₃-exchange in more detail. To that end, we divided the dataset into six categories to compare the efficiency of different exchange processes. We found exchange with wet leaf surfaces to be most efficient, even though limited by prevalent turbulent conditions. Finally, we compared the results of this study to measurements of F_{NH_3} at the nearby forest site Speulderbos (Melman et al., 2025). Despite apparent similarities between the two sites, such as location, exposure to NH₃ and forest type, they behave very differently in terms of their NH₃ fluxes. We related these differences to the N-behavior of the different tree species, and N-availability in the ecosystem and GPP, which results in a low emission potential (hence large fluxes; Loobos) or a high emission potential, creating ‘push-back’ of NH₃ (hence smaller fluxes; Speulderbos).

1. Introduction

Ecosystems productivity is determined by availability of reactive nitrogen (N_r), including ammonia (NH₃), and therefore fluxes of NH₃ and carbon dioxide (CO₂) are inevitably linked. On short timescales, both fluxes are tied by physiological activity such as plant photosynthesis (Schrader et al., 2020; Schulte et al., 2024), while on longer timescales, such as seasonal and inter-annual scales, NH₃ and CO₂ fluxes are linked by the ecosystems demand for N_r (Du et al., 2020; LeBauer and Treseder, 2008). Forests are among the most important ecosystems of the world and are impacted by (dry) deposition of NH₃ through various ways, affecting, among others, their role in biodiversity provision (Bleeker et al., 2011; Bobbink et al., 2010) and climate regulation (Du et al., 2024). Previous studies into NH₃ biosphere–atmosphere

exchange focused on short timescale processes and identified several controlling mechanisms over NH₃-exchange (F_{NH_3}), which vary throughout the day and year (in no particular order): (i) turbulence, (ii) atmospheric NH₃ concentration (hereafter [NH₃]), (iii) temperature and relative humidity (including leaf wetness), (iv) stomatal activity and (v) soil microbial activity (Schulte et al., 2021; Hansen et al., 2015; Flechard et al., 2013; Andersen and Hovmand, 1999). In general, we consider three exchange processes: (i) Exchange with stomata, (ii) exchange with the external leaf and (iii) exchange with the soil (e.g. Wichink Kruit et al., 2010). In this study, we investigate the processes that determine NH₃ exchange between forest and atmosphere and investigate whether these processes are affected by the ecosystem’s productivity.

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As NH_3 is a very soluble gas (Dasgupta and Dong, 1986), it has a compensation point which also has an effect on the total flux (e.g. Flechard et al., 2013; Wichink Kruit et al., 2010). The compensation point is ultimately controlled by the emission potential (Γ), which is given by the ratio of $[\text{NH}_4^+]$ and $[\text{H}^+]$. Generally, in NH_3 -polluted areas the vegetation is more exposed to atmospheric NH_3 and has a higher emission potential. Simultaneously, the vegetation characteristics such as plant age also determine a plant's internal N-cycling (Sun et al., 2016), and this may impact their emission potential. For beech forests, Wang et al. (2013) also found a clear seasonality in the emission potential (Γ) of leaf tissue, analogous to the foliation/defoliation phases and speculated on the pH as a regulation mechanism for Γ . They also analyzed two coniferous forest, where a to NH_3 exposed Douglas fir stand (NL, Speulderbos) showed a peak in Γ during summer and a remote Scots pine forest (FI, Hyytiälä) showed a peak during spring, highlighting that ecosystem activity, Γ and F_{NH_3} are linked. On half hourly scales, Schulte et al. (2024) investigated similarities between NH_3 fluxes and the gross primary production (GPP) flux of CO_2 . They were limited to a short dataset (17 days), for which they found a weak correlation between the two fluxes. A longer dataset, spanning multiple seasons, obtained with high temporal resolution instruments, could provide insights into what extent the two fluxes are related and focus on the ecosystems internal N-fluxes, which appear on timescales of weeks to months (Millard and Grelet, 2010).

Until recently, no open-path fast analyzer suitable for eddy covariance (EC) was available for ammonia (NH_3) (Swart et al., 2023; Wang et al., 2021) and flux process studies were often reliant on the use of the aerodynamic gradient method (AGM; e.g. Abdulwahab et al., 2025; Vendel et al., 2023). Over forests, the use of AGM can be complicated due to the presence of the roughness sublayer (RSL), which enhances turbulence efficiency (Brunet, 2020; Högström, 1996) and increases uncertainty in flux calculations (Melman et al., 2025). Moreover, the use of AGM to calculate NH_3 fluxes relies on the assumption that NH_3 is transported in a similar way as heat, while this is in fact under discussion (Vilà-Guerau de Arellano et al., 1995). Instead, EC is a more direct method to measure fluxes and overcomes most of these issues (Burba, 2013; Aubinet et al., 2012; Foken and Mauder, 2008), decreasing uncertainty and facilitating interpretation. Previous studies were done using closed path EC (Zöll et al., 2016). This method, however, also has drawbacks; e.g. power consumption and NH_3 sticking to the inlet lines and/or filters, diluting the signal (Parrish and Fehsenfeld, 2000). These issues are overcome with an open-path EC instrument. A dataset with open-path EC measurements allows the capture of short-lived processes (e.g. emission pulses), which is necessary to further investigate the biosphere-atmosphere exchange of NH_3 (Jongeneelen et al., 2024; Melman et al., 2025).

In this study, we present a year-round dataset of NH_3 fluxes (F_{NH_3}) over a temperate Scots pine forest in the Netherlands obtained with the EC method. With that, we would like to answer the following questions: (i) *How do different meteorological conditions affect F_{NH_3} , and how effective are the various F_{NH_3} exchange processes?*, and (ii) *is there a seasonal variability in F_{NH_3} related to ecosystem productivity?* To that end, we will first analyze the dataset by investigating commonly known mechanisms that affect the NH_3 flux, such as meteorological conditions and ambient $[\text{NH}_3]$, ranging from diurnal to seasonal scales. Secondly, we will analyze the contribution of different exchange processes to the total NH_3 -flux. Thirdly, we will compare the ecosystem productivity (expressed in GPP) to the F_{NH_3} to establish whether there is a link between the two fluxes that could explain a seasonal variability in F_{NH_3} . Subsequently, we will compare the results of this study with NH_3 -exchange measurements from a nearby site (Speulderbos), to evaluate whether ecosystem activity could also explain spatial variability. Finally, we will evaluate whether a 1D inferential model (DEposition of Acidifying Compounds (DEPAC); van Zanten et al., 2010) which is used to calculate NH_3 fluxes is able to capture the observed variability on diurnal and seasonal scale.

2. Methodology

2.1. Observation site

Measurements were collected at the Loobos ICOS (Integrated Carbon Observation System) class 2 ecosystem station (NL-Loobos) (van der Molen et al., 2026b; Zhao et al., 2026). The Loobos forest is located in the Netherlands near Kootwijk ($52^\circ 09' \text{N}$, $5^\circ 44' \text{E}$), and is characterized by Scots pine trees (*Pinus sylvestris*) with deciduous undergrowth (black cherry, *Prunus serotina*). The mature forest was planted in 1911 on sandy dunes and the canopy currently reaches 20–22 m ($h_c = 21$ m). Local topography is characterized by small dunes on a flat plane (see also Fig. 1b for an elevation map of the measurement area, depicting both individual tree heights as well as local topography). This also causes a spatially variable ground water table depth, which ranges between 3.5 and 6.5 m deep. At the site, an observation mast has been operative since 1994 and in 2021 a new mast (T2) was constructed just south of the old mast (T1), which could no longer extend high enough above the canopy after substantial forest growth (see Fig. 2b for their respective orientation). The site is enclosed by a main road 1.9 km to the west, small roads with little traffic 0.6 km and 1.9 km to the north and south, respectively, and sand dunes/heather 1 km to the east. The forest is located right next to the Foodvalley (1.9 km west from observation mast; www.regiofoodvalley.nl; last access date 2025-07-09), which is a region with intensive livestock farming and a major source for atmospheric NH_3 . Fig. 1a shows agricultural areas near the observation mast which can be NH_3 sources.

Throughout the measurement period (2023-08-24 to 2024-09-05), the leaf area index (LAI) was, following ICOS protocol, measured with up to 13 digital hemispherical photos of multiple continuous plots (see also www.icos-etc.eu; last access date 2025-07-09). The LAI varied between $2.2 \text{ m}^2 \text{ m}^{-2}$ and $2.8 \text{ m}^2 \text{ m}^{-2}$ with a mean standard deviation of $0.05 \text{ m}^2 \text{ m}^{-2}$ (Fig. 3a) over the different plots. To further support the LAI -measurement and to determine when new leaf growth started, we used phenocam data to analyze the green chromatic coordinate (GCC) of the canopy (see also Fig. 3a). The GCC is an indicator of the 'greenness' of the canopy and can be used to determine when leaf growth starts or ends. For this, we used the R implementation of Hufkens et al. (2018) and determined the start of the leaf growth at 24-05-2024 (indicated with a dotted line in Fig. 3). Note that Fig. 3a shows a high variability in the GCC during winter time, which is likely due to noise rather than due to process based variability. Because we have only limited availability of LAI measurements, we kept LAI constant between 04-02-2024 and 24-05-2024 to better capture the actual increase in LAI . Based on the GCC, it is possible that we missed the peak LAI in August; however, we are unable to further refine the LAI estimates at this time. Finally, we split the dataset into two seasons based on the sign of the daily net ecosystem exchange (NEE; net carbon uptake), which we refer to as (i) the winter season (from 2023-10-01 to 2024-03-01) and (ii) the summer season. More information on all available data can be found on www.icos-cp.eu (last access date 2025-07-09) or on www.maq-observations.nl (last access date 2025-07-09), where data can also be downloaded. An overview of all measurements used in this study is given in Fig. 2. These measurements will be used to quantify the ecosystem productivity (GPP, see also Section 2.5) and to assess the impact of meteorological drivers on NH_3 -exchange.

2.2. Meteorological observations

The observation mast is 36 m tall and at the top of the tower a pole is attached (reaching to 38.2 m) on which a 3D sonic anemometer (HS-50, Gill Instruments Ltd., UK), a high frequency CO_2 and H_2O closed-path gas sensor (LI-7200, LI-COR inc., US), a relative humidity sensor (RH; HMP155A, Vaisala, FI) and a pressure sensor (BMP390, Bosch Sensortec GmbH, GE) are mounted. At a second pole at 36 m, the four radiation components (shortwave incoming (R_g) and outgoing

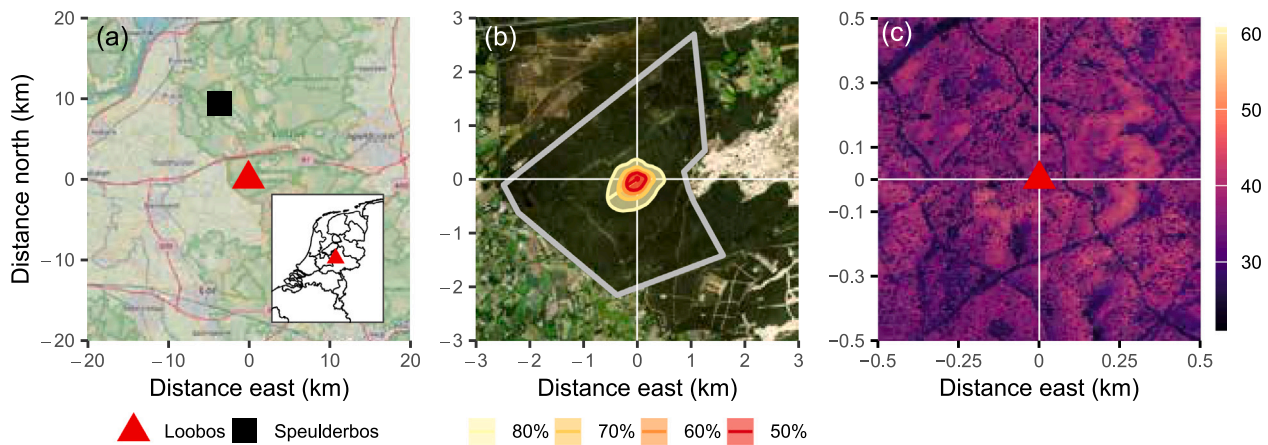


Fig. 1. (a) Location of observation site, where light green areas indicate agricultural fields (source: OpenStreetMap) which may be NH_3 source areas. (b) Satellite picture of direct surroundings of observations mast (source: Esri world imagery) and flux footprint climate for the measurement campaign according to Kljun et al. (2015). The grey polygon defines the target area. (c) Elevation map (in m relative to Amsterdam Ordnance Datum) of direct surroundings of Loobos observation mast, obtained from AHN4 (www.ahn4.nl).

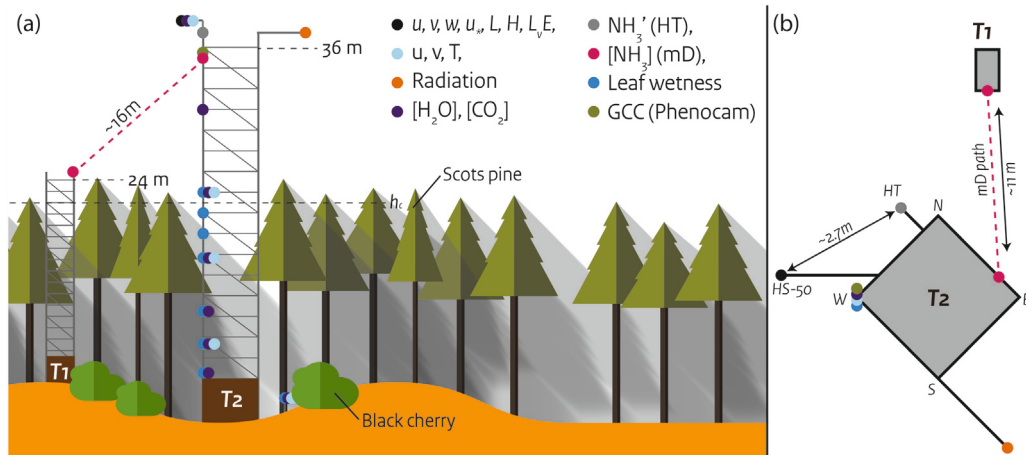


Fig. 2. (a) Side view and (b) top view of experimental set-up.

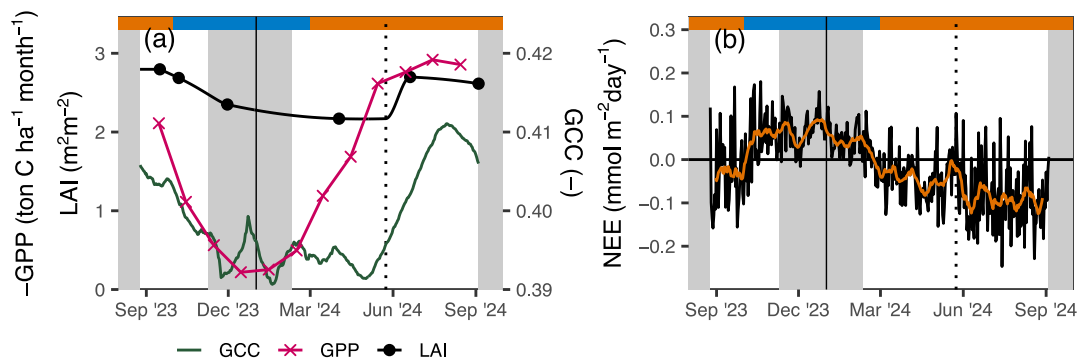


Fig. 3. (a) Interpolated LAI throughout measurement period, where points denote measurements; monthly summed GPP and GCC. (b) Daily summed NEE (black) and its 14-day centered rolling mean (orange), positive values indicates net CO_2 -emission. The dotted vertical line shows the start date of leaf growth based on the GCC. The gray shaded areas indicate days on which the NH_3 flux analyzer (HT) was not deployed and the orange/blue strip indicates summer and winter months respectively.

radiation, and longwave incoming and outgoing radiation) are measured (CNR4, Kipp & Zonen, NL). Along a profile along the tower, measurements of air temperature (T_{air} ; PT100 1/3DN) and wind speed and direction (u, v ; Gill Windsonic) are conducted at 5 levels and measurements of CO_2 mixing ratio [CO_2] and water vapor mixing ratio [H_2O] are conducted at 11 levels (LI-850, LI-COR inc., US). A

precipitation sensor (TRWS 4E25, MicroStep-MIS, AT) was installed at a third tower, approximately 60 m north of the main tower. Soil water content (SWC) and soil temperature measurements were collected (CS655, Campbell Sci. Inc., USA) at four locations at a depths of 0.05 m and at two locations at additional depths of 0.10 m, 0.20 m, 0.50 m and 1.00 m.

In addition, we installed leaf wetness sensors (LW; PHYTOS 31, MeterGroup, US) at 8 levels in and below the canopy (2.4 m, 4.5 m, 7.4 m, 11.2 m, 15.7 m, 18.0 m, 20.0 m, and 22.1 m, see also Fig. 2a). In this study we use the three levels inside/at the top of the canopy (i.e. 18.0 m, 20.0 m and 22.1 m; hereafter also referred to as LW_{canopy}) to assess whether the canopy is wet or not and to study how leaf wetness affects the F_{NH_3} .

2.3. NH_3 observations

Measurements of $[NH_3]$ were collected from 2023-08-25 to 2024-09-04, using a combined set-up of an HT8700E (Healthy Photon Co. Ltd, CN; hereafter HT) and a miniDOAS (miniDOAS 2.2, RIVM, NL; hereafter mD). The HT is a recently introduced instrument designed to measure $[NH_3]$ at high frequency such that it can be used for EC flux calculation (Wang et al., 2021). Previous deployment demonstrated that additional measurements of accurate $[NH_3]$ were necessary to calibrate the instrument in the field, as the HT showed sensitivity to ambient temperature (Swart et al., 2023). Hence, an uncalibrated HT could introduce a bias into the fluxes. To address this, we also installed the mD, a standard reference instrument in the Netherlands, to provide reliable $[NH_3]$ measurements that could be used to field-calibrate the HT.

2.3.1. $[NH_3]$ measurements (mD)

The mD uses the differential optical absorption spectroscopy technique with an active light source to measure the atmospheric $[NH_3]$ over an open line-path between the detector unit and a retro-reflector. The miniDOAS 2.2 is an upgraded version of the miniDOAS 1.x (Berkhout et al., 2017; Volten et al., 2012). The standard single path length of the mD is 22.1 m (i.e. total path length is 44.2 m), but logistical issues prevented use in a standard way. To achieve an as close to optimal set-up possible, we placed the main detector unit on T1 at 35 m. The retro-reflector was mounted at the top of T2 at 24 m, resulting in a single path length of 16 m under an angle of $\sim 45^\circ$ (see Fig. 2). Finally, we installed an air conditioning system to keep the temperature of the instrument stable. Following the instrumental set-up, we assumed the measured concentrations are representative for a measurement height of 29 m (geometric mean of 24 and 35 m).

The mD was deployed from 2023-08-25 to 2024-09-04 and operated 94.9% of the time. The measurement interval was set to 2 min, with concentration data subsequently averaged to 30 min concentrations. Over time, spectrally inhomogeneous degradation of the lamp caused the shape of the spectrum to shift, which negatively affected the quality of the fit of the (high-concentration) gas calibration spectra to the field measurements (as described in Berkhout et al. (2017)). This caused the precision (1σ) in the concentration to increase from $0.05 \mu g m^{-3}$ to $0.12 \mu g m^{-3}$ over the measurement period. To account for this, we performed a post-deployment zero-calibration in the lab (in addition to a standard pre-deployment zero-calibration). The pre- and post-deployment calibration spectral curves are used to simulate the lamp spectrum for intermediate period, with timesteps of approximately 3 days. This improved the average precision in the last 3 months from $0.12 \mu g m^{-3}$ to $0.10 \mu g m^{-3}$. More information on the zero-calibrations in the lab can be found in Swart et al. (2023).

2.3.2. F_{NH_3} measurements (HT)

The HT was installed at 37 m and was deployed from 2023-08-25 to 2023-11-09 and again from 2024-02-09 to 2024-09-04 and thus operated 76% of the measurement campaign. The HT is an open-path QCL-based instrument and measures $[NH_3]$ at 10 Hz with the wavelength modulation spectroscopy technique. A full technical description of an earlier version of the instrument is given in Wang et al. (2021). Recent advancements have been made on the mirror coating, resulting in less degradation of the signal over time. Secondly, a heating system was installed, which warms the lower mirror up to $5^\circ C$ above

ambient temperature. This was done to ensure that water remaining on the lower mirror after a rain or dew event evaporates more quickly, allowing measurements to resume sooner and improving overall data coverage. Unfortunately, the heating system sustained damage during transport and was non-functional at the onset of the 2024 deployment. Finally, an automatic cleaning system was installed to maintain high optical signal strength (OSS) and ensure data quality. It uses a two-step process: demi-water spray to remove dust, followed by a dry-air pulse to clear residual moisture. However, the dry-air cleaning was largely non-functional due to the long pipe distance (37 m) from the ground to the top of the tower, limiting air pressure delivery and regular manual cleaning of the mirrors was necessary. Installing the HT directly next to the sonic anemometer was not possible, and as such the instrument is located 2.2 m eastward, 1.6 m northward (total horizontal separation equals 2.7 m) and 1.3 m downward (see also Fig. 2b). We expect the sensor separation to have a negligible effect on the flux, as: (i) at this height above the canopy large eddies dominate over smaller eddies (see also Fig. 12 in van der Molen et al., 2026b), (ii) we use an empirical damping function which is more representative for in-situ conditions (similar to Wintjen et al., 2020) and (iii) a larger separation also causes less flow distortion. The instrument was removed between 2023-11-09 and 2024-02-09 to prevent freezing and for redeployment elsewhere. Because instruments of this type are sensitive to transport, a separate field calibration was conducted for each deployment.

An HT that is not field-calibrated would overestimate (or underestimate) the flux, if $[NH_3]$ -fluctuations are reported larger (smaller) than in reality. In our case this would lead to an overestimation of 22% (see Appendix A). For the field-calibration, we averaged $[NH_3]$ of both HT and mD instruments to 30 min periods. To ensure that we use only high-quality data, we filtered out half hours where the OSS dropped below 20%, as below this threshold the disagreement between HT and mD becomes substantially larger, indicating low data quality. Additionally, we need to account for the different instrumental set-ups of the HT and mD. The mD measures at a different height, along a diagonal path and it measures at a 2 min interval. In contrast, the HT measures at a single point at 10 Hz, which may result in the HT measuring plumes which are not captured by the mD. To address this, we filtered for well-mixed ($u_* > 0.3 m s^{-1}$, where u_* denotes friction velocity) and relatively stationary conditions during the 30-min averaging interval ($\sigma_{HT}/[NH_3]_{HT} < 0.25$, where σ_{HT} denotes the standard deviation of the $[NH_3]$ measured by HT). While a small vertical gradient may still be present, it is expected to fall within the measurement uncertainty. Finally, we excluded 75 half-hour periods in October 2023 during which the concentration patterns of the HT and mD deviated strongly for unknown reasons, because these observations were strongly affecting the linear fit between the concentrations of the mD and HT. During the 2023 deployment, we found a linear relation between the HT and the mD. During the 2024 deployment, the offset between the HT and mD correlated with both the HT's internal temperature and $[NH_3]_{mD}$. The temperature effect likely resulted from the non-functional heating system on the HT's lower mirror. We corrected for this using multiple regression: a third-order polynomial for temperature and a linear fit for $[NH_3]_{mD}$. More details on the concentration correction for both deployments can be found in Appendix A and a discussion on the induced error on the flux is given in Section 2.7.

2.4. Flux calculation

After the concentration correction, the 10 Hz data was processed using EddyPro version 7.0.4 (Biosciences, 2019; Fratini and Mauder, 2014) to calculate the flux at 30 min intervals. We set the maximum missing sample allowance to 40% to ensure representative fluxes. An overview of all used data processing steps in EddyPro is given in Tab. S1. To account for high-frequency spectral losses, we used an empirical approach based on Wintjen et al. (2020). Finally, to account for atmospheric density fluctuations, we applied a modified

Table 1

Filter criteria for NH_3 concentration (mD) and flux measurements (HT). Half hourly measurements were collected between 2023-08-25 and 2024-09-04. Acceptance rate shown applies to filter criteria applied in sequence and values in brackets denote acceptance rate relative to deployment period.

Filter #	Condition	Acceptance	
		mD	HT
	Measurement period	100%	75.5% (100%)
0	Instrument operating	95.7%	58.6% (77.6%)
1	Instrumental quality check	94.9%	51.3% (67.9%)
2	Quality flag < 2		48.3% (64.0%)
3	Representative footprint (SW)		46.2% (61.2%)
4	Reliable turbulence	$u_* > 0.1 \text{ m s}^{-1}$	43.1% (57.2%)
5	Coupled forest-atmosphere	$u_* > 0.3 \text{ m s}^{-1}$	32.5% (43.1%)

form of the Webb, Pearman and Leuning (WPL) (Webb et al., 1980), because H_2O fluctuations also affect the absorption line used for NH_3 (i.e. spectroscopic effect, see also Burba et al. (2019)). We used the modified WPL-term following Swart et al. (2023) for the NH_3 flux. These processing steps resulted in an average flux increase of 20% compared to ‘plain’ covariance. For more information see also Swart et al. (2023).

2.5. Data treatment

All data were analyzed using R (R Core Team, 2024). We calculated CO_2 and H_2O storage fluxes following Nicolini et al. (2018), and used the ICOS L2 product (van der Molen et al., 2025) for processed and gap-filled ecosystem carbon fluxes, including net ecosystem exchange (NEE), gross primary production (GPP) and ecosystem respiration (RE). We used the R implementation of Wutzler et al. (2024) to determine the u_* -threshold at 0.3 m s^{-1} with the method of Papale et al. (2006).

To guarantee high quality data, suitable for process investigation, we applied filter criteria as listed in Table 1. Filter 1 assures reliable instrumental conditions. For the mD, we filtered out measurements where the peak intensity of the two-minute interval suddenly dropped (e.g. due to rainfall). For the HT, we filtered out measurements where OSS dropped below 20%, and the measurements that showed strongly deviating patterns from $[\text{NH}_3]_{\text{mD}}$ (as described in Section 2.3). Furthermore, only fluxes with quality flag of 0 or 1 are selected (Mauder and Foken, 2006).

Although the forest extends much further than the footprint climate (Fig. 1b), under (very) stable conditions the 80% contribution level can extend over the agricultural fields in the southwest. Comparison under similar turbulent conditions with fluxes that originate fully from within the target area showed that fluxes originating for more than 20% outside the target area deviate, hence we removed these measurements from further analysis. Although the target area is also exceeded with easterly winds, analysis did not show substantial differences when comparing to fluxes that are from within the target area. Hence, we include these measurements in the analysis, but care must be taken when focusing on easterly observations.

From here on, we consider two scenarios: (i) with a low u_* -threshold ($u_* > 0.1 \text{ m s}^{-1}$; Filter 3) and (ii) with a high u_* -threshold ($u_* > 0.3 \text{ m s}^{-1}$; Filter 4). The u_* -threshold is a commonly used method to select for conditions with reliable turbulent conditions (i.e. a coupled forest-atmosphere). With a decoupled atmosphere, the measured flux will give an inaccurate estimate of the real flux, unless storage and advection are taken into account (Peltola et al., 2021), for which a complex measurement set-up is required. Fluxes with $0.1 \text{ m s}^{-1} < u_* < 0.3 \text{ m s}^{-1}$, however are typically smaller than when $u_* > 0.3 \text{ m s}^{-1}$, and hence ignoring these values will lead to an overestimation of the annual flux. Moreover, over forests transport is intermittent (e.g. Finnigan et al., 2009) and turbulent ejections are regularly able to transport (fractions of) air from near-soil to above-canopy (Moonen et al., 2025). Therefore, we will use the low u_* -threshold when determining the annual deposition load. For process studies, such as investigation of

diurnal cycles and model evaluation, we will only consider fluxes that pass the high u_* -threshold.

After field-calibration and data quality filtering, the error on $[\text{NH}_3]_{\text{HT}}$ has become sufficiently small and thus can be used for process studies. $[\text{NH}_3]_{\text{HT}}$ is a more suitable choice than $[\text{NH}_3]_{\text{mD}}$, as during more stable atmospheric conditions there will be a gradient between the two sensors, leading to a skewed comparison. Therefore, we will use, unless otherwise noted, $[\text{NH}_3]_{\text{HT}}$ for process studies throughout the rest of the manuscript.

2.6. Gap-filling

2.6.1. Concentration

We gap-filled the $[\text{NH}_3]_{\text{mD}}$ with $[\text{NH}_3]_{\text{HT}}$ were available. This decreased the missing data from 5.1% to 3.0%. Most remaining gaps are less than 2 h, but there are three gaps of more than 1 day. We filled these gaps with linear interpolation.

2.6.2. Fluxes

To fill gaps in the NH_3 -flux data, we used eXtreme Gradient Boosting (XGB). We selected XGB because it generally performs well for gap-filling of trace gas fluxes, and it is less prone to overfitting (Mahabati et al., 2021). Additionally, XGB allows us to assess the contribution of each variable, and it requires less computational power compared to models like artificial neural networks. For the input variables, we focused on those with a known direct or indirect effect on F_{NH_3} (such as factors influencing stomatal activity) including: $[\text{NH}_3]_{\text{mD}}$, RH , vapor pressure deficit (VPD), LAI , Surface temperature (T_{surf} , estimated from outgoing long-wave radiation), u_* , U , WD , NEE , $SWC_{5\text{cm}}$, the level with the highest contribution. We use $[\text{NH}_3]_{\text{mD}}$ instead of $[\text{NH}_3]_{\text{HT}}$ because it has a better data coverage and thus instrumental artifacts are less likely to appear in the XGB model. Finally, to mimic a (stomatal) compensation point we added a rolling average of the $[\text{NH}_3]_{\text{mD}}$, and optimizing the window from 31 days (as default setting in DEPAC) down to 6 days for best model performance.

For model development, we used the xgboost implementation in R (Chen et al., 2025). To enable independent testing, two months from different seasons (March and July) were set aside. For model training, we applied time-separated three-fold cross validation by dividing our training data into three equally sized groups based on their timestamps and the optimal hyper-parameters (learning rate = 0.16, max depth = 10, nrounds = 100, min child weight = 1, subsample = 1, colsample by tree = 1, gamma = 0.05) were selected through grid search. Finally, the model was trained for two scenarios: (i) with the low u_* -threshold and (ii) with the high u_* -threshold, as described in Section 2.5, which also enabled estimation of uncertainty in the gap-filling process.

2.7. Flux error analysis

We identified three sources of errors with our flux calculation and annual deposition load calculation that are either random or systematic and will discuss each below:

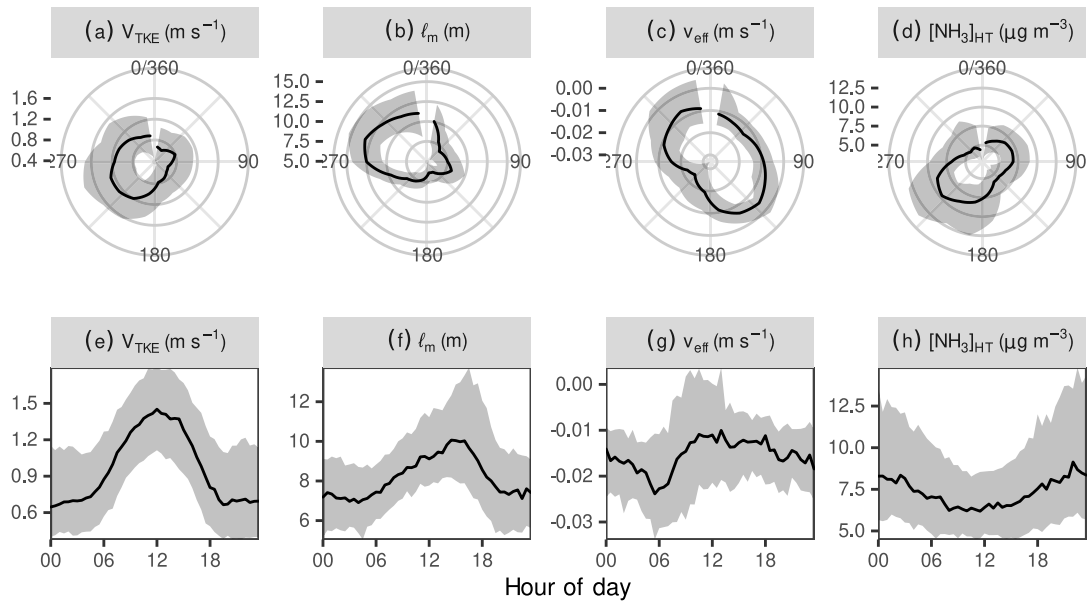


Fig. 4. (a–d) Directional variability of median V_{TKE} , l_m , effective exchange velocity (v_{eff}) and $[NH_3]$. (e–h) Diurnal variability of median V_{TKE} , l_m , v_{eff} and $[NH_3]$. Shaded areas indicate 25th–75th percentile.

Error due to field calibration of the HT based on mD measurements: The concentration correction induces two errors. Firstly, a random error; After correction the RMSE between mD and HT is 1.15 μg m⁻³ in 2023 and 1.08 μg m⁻³ in 2024, introducing a random error (2σ) of 17% and 13%, respectively. Note that differences between mD and HT may partially be explained by physical processes (see also Section 2.3), and hence the random error estimates given here are at the upper limit. Secondly, a possible systematic error: The concentration correction is sensitive to filtering choices. We set the u^* threshold at 0.3 m s⁻¹, which means that the correction used may not be representative for period with $u^* < 0.3$ m s⁻¹. To test the effect of the u^* -threshold on the concentration correction, we applied both a high ($u^* > 0.3$ m s⁻¹) and a low ($u^* > 0.1$ m s⁻¹) threshold. Appendix A shows that the slope between mD and HT decreased with a higher u^* threshold. This translates to an on average 6.6% smaller flux in 2023 and a 5.7% smaller flux in 2024 and for both years a 5.9% smaller flux (1σ).

Random error due to sampling error: With EC flux calculations a random uncertainty arises because only a small amount of large eddies is captured during the 30 min sampling period. This so-called sampling error was calculated in EddyPro using the method of Finkelstein and Sims (2001). This resulted in an average error of 26% (1σ).

Error due to gap-filling: We determined the error due to gap-filling by taking the standard error of the two different gap-filling models used (see also Section 2.6.2). This gave an average error of 10.5% (1σ).

Total error: The total error on half-hourly fluxes is calculated using quadratic summation of both the random and systematic errors due to the concentration correction and the random error due to flux corrections. This results in an average error of 30.6% (1σ). For yearly aggregated fluxes, the random errors reduce with a factor $\sqrt{N}$, and hence become irrelevant. However, the systematic error due to the concentration correction and the error due to gap-filling remain relevant. Quadratic summation gives a total error of 14.0% (1σ) on the yearly aggregated flux.

3. Results & discussion

3.1. Characterization of the site and dataset

3.1.1. Meteorology and leaf wetness

Overall, in the Netherlands, the period 2023-09 to 2024-09 was wet and warm compared to average climatological conditions (www.knmi.nl/over-het-knmi/jaarverslagen; last access 2025-07-09). At Loobos, the average temperature was 12.0 °C, which is considerable warmer than the long-term mean annual temperature at Loobos of 10.2 °C. The total precipitation sum was 1380 mm, which is around 50% higher than the long-term mean annual sum of 900 mm at Loobos. An overview of the meteorological conditions throughout the measurement period is given in Fig. S1. In short, relative humidity is generally higher in autumn and winter and monthly precipitation shows a variable pattern.

In total, we measured 367 wetness events (where we defined a wetness event as consecutive half hours with wetness) during the entire measurement campaign (mostly due to precipitation events) and in total the canopy (LW_{canopy}) was wet during 38% of the measurement period. The distribution of the amount of observations with canopy wetness throughout the measurement period and their average diurnal cycle is shown in Fig. S1e. In general, winter months experienced the most moments with leaf wetness. On a diurnal scale, we observed most wetness in the early morning and least wetness in the afternoon.

3.1.2. Turbulence

Although the fetch is more or less homogeneous, there are some differences in total elevation (surface height + tree height). Fig. 1b shows the elevation of the direct surroundings of the tower. Both towards the west and east are some elevated areas, and there are also some clearings. Towards the southwest and southeast there are small areas where a storm caused tree fall, resulting in a more open canopy (wind throw area). To evaluate the effect of these roughness transitions, we examined both the turbulent velocity scale V_{TKE} (turbulent kinetic energy velocity scale Stull, 1988) and the vertical mixing length for momentum l_m (Harman and Finnigan, 2007), which are calculated as:

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$$V_{TKE} = \sqrt{0.5 (\overline{u'^2} + \overline{v'^2} + \overline{w'^2})} \quad (1)$$

$$l_m = 2\beta^3 L_c = 2 \frac{\beta h_c}{LAI} = 2 \frac{u_* / u(h_c) \cdot h_c}{LAI} \quad (2)$$

V_{TKE} (defined as the square root of TKE) is a measure for the turbulent efficiency, while l_m represents a depth through which eddies can penetrate the canopy. For more reflections on V_{TKE} over forest canopies see Lee et al. (2025) and for l_m Harman and Finnigan (2007). Fig. 4a and b show the variability of V_{TKE} and l_m with respect to different wind directions and Fig. 4e and f show their diurnal variation and Fig. 5c shows V_{TKE} throughout the year. The variability of V_{TKE} is

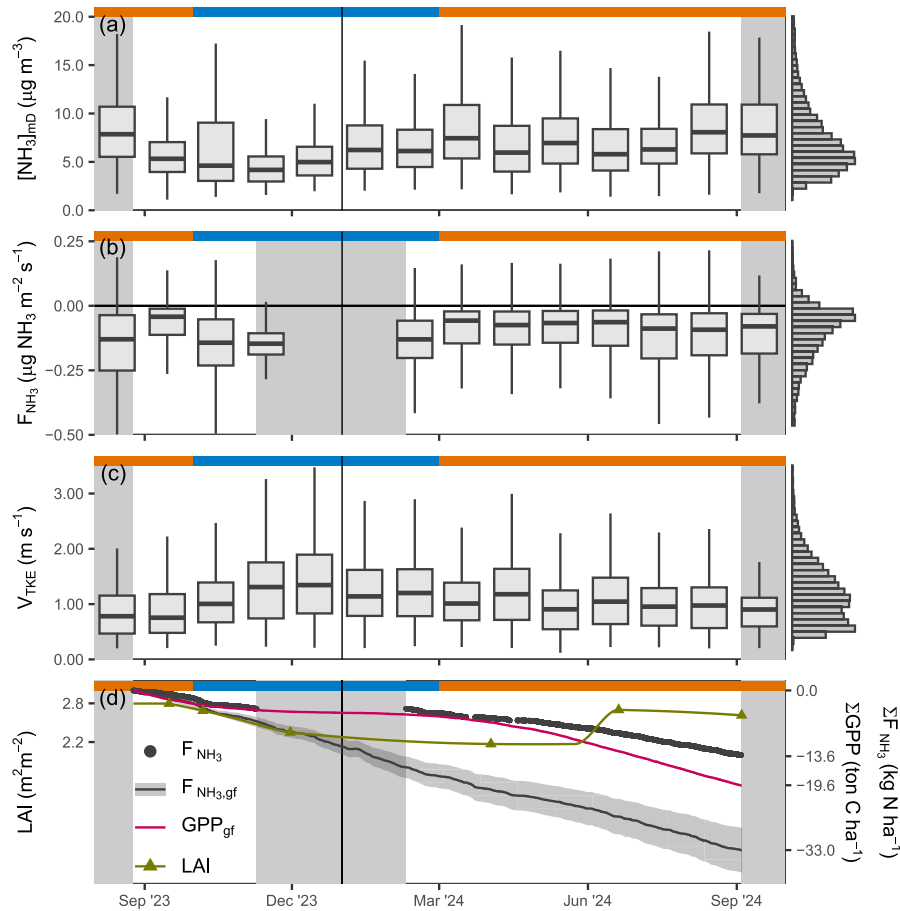


Fig. 5. (a) Timeseries of boxplots (with median and interquartile range) and histogram of $[\text{NH}_3]_{\text{mD}}$, with y-axis capped at $20 \mu\text{g m}^{-3}$ (omitting 733 observations, 4%). (b) Timeseries of boxplots and histogram of F_{NH_3} measured by the HT, with y-axis capped at -0.50 and $0.25 \mu\text{g m}^{-2}\text{s}^{-1}$ (omitting 17 emission and 171 deposition observations; 0.1% and 0.9%, respectively). (c) Timeseries of boxplots and histogram of V_{TKE} . In panels (a–c) the outliers are omitted for convenience. (d) Cumulative sum of (dots) observed and gap-filled F_{NH_3} (black line; $\pm\sigma$ in gray shaded band) and GPP (red line), and interpolated LAI throughout the measurement period. ticks denote the minimum (2.2) and maximum (2.8) LAI and on the right-side the sum of respective variable. The gray shaded areas indicate days on which the respective instrument was not deployed (some months contain only a few days of data); the orange/blue strip indicates summer and winter months respectively.

highest with wind direction and on diurnal scale, indicating that they are most influenced by stability and by local roughness characteristics. The variability of ℓ_m is strongest with wind direction and thus mostly determined by local site characteristics. Here, we will focus on variability with wind direction, as these are locally determined. At Loobos, V_{TKE} is largest with southwesterly winds. In this direction there is a (small) wind throw area (see also Fig. 1b), indicating that this transition increases turbulent mixing. Similar results have been shown before (e.g. Wuyts et al., 2008). ℓ_m has also two peaks, with a slight offset from the peaks of V_{TKE} (i.e. more (south)east and more north respectively). Towards these directions, the forest seems (slightly) less dense compared to other directions, enabling eddies to further penetrate into the forest canopy.

3.1.3. NH_3 observations

Fig. 5 shows the (a) $[\text{NH}_3]_{\text{mD}}$, (b) F_{NH_3} and (d) cumulative F_{NH_3} during the measurement period. The median and mean $[\text{NH}_3]$ were $6.1 \mu\text{g m}^{-3}$ and $7.9 \mu\text{g m}^{-3}$ respectively and monthly medians peaked in March and in August. The maximum half hourly measured $[\text{NH}_3]$ was $171.2 \mu\text{g m}^{-3}$ during nighttime in August 2024. The F_{NH_3} varied throughout the measurement period between -1.84 and $0.34 \mu\text{g m}^{-2}\text{s}^{-1}$ with mean flux $-0.13 \mu\text{g m}^{-2}\text{s}^{-1}$ and median flux $-0.11 \mu\text{g m}^{-2}\text{s}^{-1}$. We observed emission of NH_3 during all months (13% of total measurement period), but most frequently in the early summer months (Mar–June, 16%–19%) and least frequently in autumn/winter (Oct, Nov, Feb,

5%–7%). Figs. 5b and d show that (cumulative) deposition is strongest in summer, but in general shows little variation throughout the year.

Turbulent properties determined by local meteorological and site conditions are a major factor in controlling F_{NH_3} (Andersen and Hovmand, 1999). Fig. 4c and h show the effective exchange velocity ($v_{\text{eff}} = F_{\text{NH}_3} / [\text{NH}_3]_{\text{HT}}$) for wind direction, and their diurnal variation, and their variability throughout the year is given in Fig. 5c. In Section 3.1.2, we determined that directional dependency of the flow is the most dominant in explaining the turbulent distortion (expressed in V_{TKE} and ℓ_m), and hence we will focus on the directional dependency of v_{eff} . By plotting v_{eff} rather than the absolute flux, we eliminate the first order effect of $[\text{NH}_3]$ on the flux and can focus on the turbulent effects. Note that with this method, the temporal dependence in the compensation point is projected on v_{eff} . For completeness, we also added the median directional pattern of $[\text{NH}_3]_{\text{HT}}$ in Fig. 4d and h. The peak in V_{TKE} coincides well with the peak in maximum $|v_{\text{eff}}|$, which is expected due to the dominant role of turbulent mixing in NH_3 -exchange. The origin of the minimum in $|v_{\text{eff}}|$ around 120 degrees is less obvious from Fig. 4. Overall, ℓ_m seems less dominant in determining v_{eff} than V_{TKE} . Interestingly, peaks in V_{TKE} , $|v_{\text{eff}}|$ and $[\text{NH}_3]$ roughly coincide, causing largest NH_3 -fluxes with southwesterly winds.

3.2. Gap-filling & annual deposition load

An annual deposition load can be used to quantify the impact of NH_3 pollution on the ecosystem (Bleeker et al., 2011; Bobbink

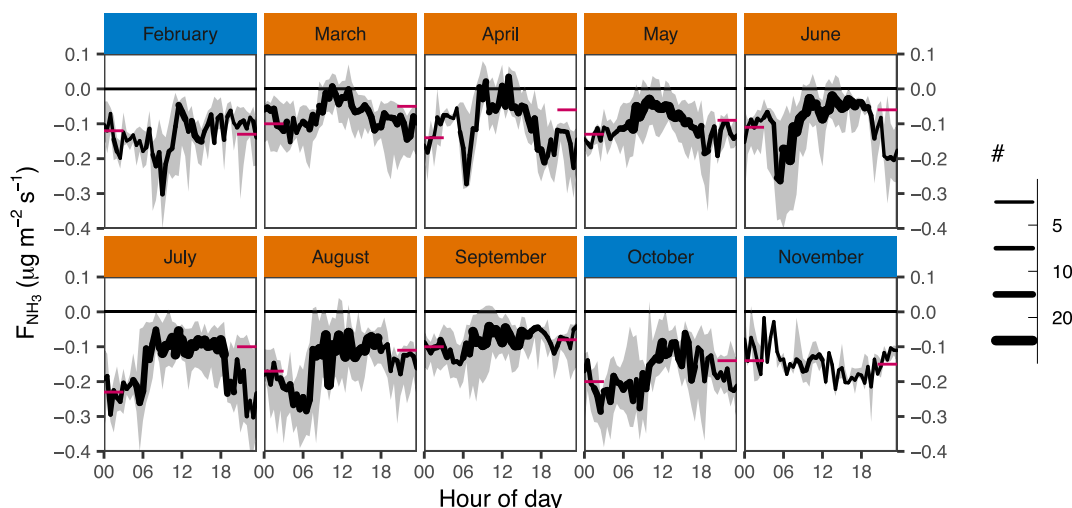


Fig. 6. Observed median and 25th-75th percentiles of F_{NH_3} for each month. The linewidth shows the number of observations for each respective value and the line segments show for each month the median (left-axis) nighttime and (right-axis) daytime of the diurnal F_{NH_3} . The color of the title shows (blue) winter months or (orange) summer months.

et al., 2010). For the estimation of the annual deposition load, we will consider the period from 2023-09-01 to 2024-08-31. The results of the XGB model are discussed in detail in Appendix B, including the importance of each input variable of both XGB-models (for the low and high u_* -threshold; Fig. B.2). A cumulative sum for the full year is also given in Fig. 5d.

We used the low u_* -threshold when filling these gaps for both models (i.e. 43.1% measurements and 56.9% gap-filled fluxes, see also Table 1). We calculated the annual dry-deposition load as the mean of the two XGB models, which gave $32.0 \pm 4.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (with mean $[\text{NH}_3]$ $7.9 \mu\text{g m}^{-3}$), of which the observed NH_3 -fluxes accounted for $12.9 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. Such a load is very high compared to recent estimates in the Netherlands, especially given the fact that there was also an exceptional amount of rain during our measurement campaign (see also Section 3.1.1). In general, with a higher annual precipitation sum one would expect a lower dry deposition load, as a larger fraction of the ambient $[\text{NH}_3]$ is removed from the atmosphere by wet deposition. In Melman et al. (2025) we reported for a nearby forest site (Speulderbos; see also Fig. 1a for their respective locations) an annual NH_3 -load of $8.5\text{--}11.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for 2009–2010 with a mean $[\text{NH}_3]$ of $6.0 \mu\text{g m}^{-3}$, which is a factor 3–4 lower than the results of this study. We will make a more elaborate comparison between Speulderbos and Loobos in Section 3.6.

3.3. NH_3 concentrations

The $[\text{NH}_3]$ was generally highest with wind directions originating from source area's, which in our case is with southwesterly winds. During some months we also found elevated $[\text{NH}_3]$ with (north)easterly winds (see also Fig. S5). In both directions there are locations with agricultural fields (Fig. 1a), which could explain these higher $[\text{NH}_3]$. From these directions, $[\text{NH}_3]$ peaked in March and August (see also Fig. 5b), which are common months for manure application and therefore result in elevated $[\text{NH}_3]$ (van Zanten et al., 2017).

During late autumn and winter months, the median $[\text{NH}_3]$ shows little variation during the day, while during summer we observed more variability (see Fig. S3). In general, the spread (and median) in $[\text{NH}_3]$ is largest during nighttime, which can be explained by ABL-dynamics. The ABL is generally stable and shallow during nighttime, resulting in high $[\text{NH}_3]$. During daytime, on the other hand, the ABL grows, entraining $[\text{NH}_3]$ depleted air from the residual layer above the stable boundary layer into the mixed layer (Schulte et al., 2021) and diluting the present $[\text{NH}_3]$ to lower values (this is well pronounced in e.g. June). Similar behavior in the diurnal cycle of $[\text{NH}_3]$ has been observed before (e.g. Hansen et al., 2015, 2013).

3.4. NH_3 fluxes

3.4.1. Diurnal variability

Fig. 6 shows the diurnal cycle of the median F_{NH_3} for each month. In general, median fluxes were largest and negative (deposition) during nighttime, and minimal during daytime, when we also observed positive median fluxes (emission) during some of the months. These patterns are caused by prevalent patterns in meteorological conditions and in ambient $[\text{NH}_3]$. RH is generally higher during nighttime conditions, while T_{air} is higher during daytime conditions. Moreover, we observed more canopy wetness during nighttime than in daytime (see also Fig. S1e). Together, they explain a large part of the NH_3 -solubility, which gets higher with humid conditions and lower temperatures, such that deposition fluxes onto the external leaf surface are stronger during nighttime. Moreover, Fig. S3 shows that, for most months (especially summer months), $[\text{NH}_3]$ was higher at night than during the day, resulting causing stronger fluxes. Finally, in polluted areas stomatal opening can cause NH_3 -emission (Melman et al., 2025; Wichink Kruit et al., 2007), which reduces the fluxes during daytime. Similar diurnal cycles in F_{NH_3} over forests have been observed before (Melman et al., 2025; Xu et al., 2023; Hansen et al., 2015; Neiryck and Ceulemans, 2008). However, Guo et al. (2022) reported an opposite pattern with strongest deposition during daytime, which they attributed to possible recapture of soil and litter emissions and a low vegetative compensation point. A large difference between their study site (Duke forest, US) and this study site is the median $[\text{NH}_3]$ during the measurement period ($0.48 \mu\text{g m}^{-3}$ at Duke forest vs $6.1 \mu\text{g m}^{-3}$ at our study site), which could explain the low vegetative compensation point and consequently the different diurnal patterns.

3.4.2. Seasonal variability

Next to the variation on a diurnal scale, Figs. 5 and 6 also show that there is variation on a seasonal scale, with more deposition during winter and summer months and minimal fluxes in the early summer months. Results from a two-way ANOVA indicate that both the overall level and the diurnal pattern of F_{NH_3} vary significantly between months (see Tab. S2). In most summer months (April, June–August), $[\text{NH}_3]$ was higher during nighttime (see Fig. S3), which contributes to higher nighttime fluxes. Moreover, LAI increased from end of May till August, which provided additional deposition surface and thus may have contributed to stronger deposition fluxes. Differences in meteorological conditions offer also an explanation. Fig. 5c shows that V_{TKE} was stronger during winter months and Fig. S1c shows that the canopy was

Table 2

Filter criteria corresponding to Fig. 7 and acceptance rate compared to the total measurement period in each panel. Filters are in addition to the filters listed in Table 1. The efficiency is calculated as $F_{\text{NH}_3}/F_{\text{max}} \cdot 100\%$, where F_{max} denotes the maximum possible flux allowed by turbulence. Rows are sorted for largest efficiency.

Fig.	Exchange process	Day/Night	Filter criteria	Acceptance	Efficiency (avg $\pm$ std)
7e	Ext. leaf (wet)	Night	$LW_{\text{canopy}} > 273 \text{ mV}$ & $R_g < 10 \text{ W m}^{-2}$	0.9%	$68 \pm 39\%$
7b	Stomata and Ext. leaf (wet)	Day	$LW_{\text{canopy}} > 273 \text{ mV}$ & $R_g > 10 \text{ W m}^{-2}$	1.4%	$57 \pm 41\%$
7d	Ext. leaf (humid)	Night	$LW_{\text{canopy}} \leq 273 \text{ mV}$ & $R_g < 10 \text{ W m}^{-2}$ & $RH > 60\%$	7.3%	$36 \pm 22\%$
7f	Mixture			13.4%	$30 \pm 31\%$
7c	Ext. leaf (dry)	Night	$LW_{\text{canopy}} \leq 273 \text{ mV}$ & $R_g < 10 \text{ W m}^{-2}$ & $RH < 60\%$	0.5%	$18 \pm 11\%$
7a	Stomata	Day	$LW_{\text{canopy}} \leq 273 \text{ mV}$ & $R_g > 10 \text{ W m}^{-2}$ & $RH < 60\%$	9.1%	$13 \pm 24\%$

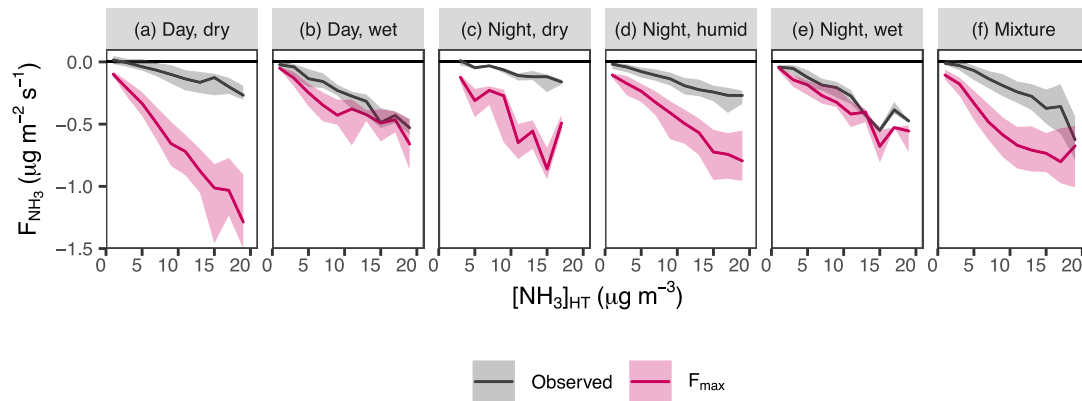


Fig. 7. Median and 25th-75th percentiles of the F_{NH_3} for bins of $2 \mu\text{g m}^{-3}$. Each panel represents different filtering conditions; see Table 2 for filter criteria and number of observations in each panel. F_{max} represents the maximum NH_3 flux allowed by turbulence.

more often wet during winter months than during summer months, increasing the deposition velocity in winter compared to summer (see also Section 3.4.3 and Fig. 7). Moreover, frequent rain events may also wash-off NH_4^+ that remain at the leaf surface, and thereby lower the emission potential. Together this explains (part of) the seasonal variability. There is, however, also a trend visible over the course of the summer months. From Fig. 5b and c it is clear that this is not related to turbulent conditions, and instead may be related to (i) new leaf growth or (ii) photosynthetic activity. We will discuss this in more detail in Section 3.5.

3.4.3. Contribution of different exchange processes

Fig. 7 shows the median F_{NH_3} for bins of $[\text{NH}_3]_{\text{HT}}$. The different panels represent different filtering conditions, with which we aim to isolate the different exchange processes that contribute to the total NH_3 flux. The used filter criteria and number of observations in each panel are listed in Table 2. Overall, it can be seen that for all different conditions deposition increases with increasing $[\text{NH}_3]$, indicating that, on average, all exchange processes are a sink for NH_3 . We also included the maximum NH_3 flux (F_{max}), calculated by considering only aerodynamic resistance (r_a) and quasi-laminar boundary layer resistance (r_b) in Eq. (C.1). This approach assumes an infinitely small canopy resistance and the absence of a compensation point. By comparing the observed NH_3 flux (F_{NH_3}) to F_{max} , we can assess the efficiency of the exchange process under varying meteorological conditions. Table 2 also shows the mean efficiency of each exchange process, which is calculated as $F_{\text{NH}_3}/F_{\text{max}}$. The response of F_{max} to increasing ambient $[\text{NH}_3]$ is largest during dry daytime conditions (Fig. 7a) and mixed conditions (Fig. 7f), followed by humid (Fig. 7d) and dry nighttime (Fig. 7c) conditions, and wet daytime conditions (Fig. 7b), and is smallest during wet nighttime conditions (Fig. 7e). During the daytime, V_{TKE} typically reaches its maximum value (see also Fig. 4), resulting in the largest F_{max} . In contrast, wet nighttime conditions, especially those accompanied by dew formation, are generally associated with a stable

boundary layer, which suppresses turbulence and leads to lower F_{max} values. Humid and dry nighttime conditions lead to F_{max} values that are in between these two extremes.

The comparison among the different conditions changes when we consider the observed F_{NH_3} . The response of F_{NH_3} to increasing $[\text{NH}_3]$ is strongest during wet conditions and during nighttime it is virtually equal to F_{max} , even for higher values of $[\text{NH}_3]$, indicating that there is no saturation. Note that at higher concentrations we have only a limited number of observations, and thus the fact that F_{NH_3} is larger than F_{max} is probably due to uncertainty in the measurements. Exchange is slightly less efficient during wet daytime conditions (57%) than during wet nighttime conditions (68%). This is likely due to the fact that part of the exchange still is with the stomata, which is much less efficient than with liquid water on leaves. Interestingly, the response to increasing $[\text{NH}_3]$ in Fig. 7a and d are approximately equal, indicating that exchange with stomata and with the external leaf under humid (but not wet) conditions are approximately equally contributing, though exchange with the stomata is a less efficient process (which is compensated by the stronger turbulent conditions). We find the lowest response to increasing $[\text{NH}_3]$ during dry nighttime conditions (Fig. 7c). The fact that a water layer on leaf surfaces provides the most efficient sink for NH_3 aligns well with the fact that NH_3 is a highly soluble gas (Dasgupta and Dong, 1986), and earlier comparisons of observed F_{NH_3} to F_{max} (Neiryck et al., 2005; Wyers and Erisman, 1998).

Since the canopy (i.e., levels 18–22 m) was wet during 38% of the complete measurement period (see also Section 3.1.1), this contributed to an overall efficient deposition process during our measurement campaign and may (partly) explain the large annual deposition load found in Section 3.2. For dry daytime conditions and a mixture of the conditions we find at low concentrations also emission of NH_3 (in the 25th-50th quantile range in Fig. 7, see also Fig. C.2 for a zoomed-in version), representing emission by the stomata.

3.4.4. Model evaluation

We evaluated the one-dimensional NH_3 exchange model DEPAC, which is used in the Netherlands as a module in air quality models

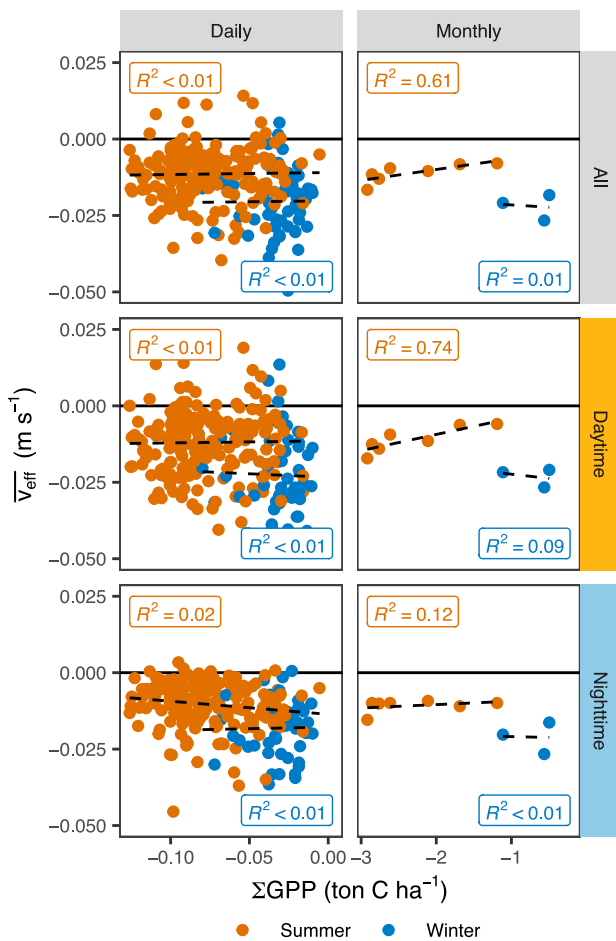


Fig. 8. Mean observed v_{eff} plotted against gap-filled summed carbon flux GPP, where negative values show net deposition. We used v_{eff} instead of F_{NH_3} to account for seasonality in $[NH_3]$ (see also Section 3.3), and we used the mean v_{eff} such that increased day length does not affect the results. A separate linear fit was made for summer months and winter months, and for all fluxes, or only daytime ($R_g > 10 \text{ W m}^{-2}$) or nighttime NH_3 -fluxes (as proxies for exchange with the external leaf or with the stomata). Note that all plots show the sum of the total GPP (i.e. no subselection for day or night on the x-axis), as we are interested in effects on longer timescales related to ecosystem activity.

(Sauter et al., 2023; Manders et al., 2017). A model description and more detailed summary of the results are provided in Appendix C. Overall, the model captures the diurnal variability well; however, it tends to underestimate fluxes. The derived stomatal emission potential (Γ_s) is significantly smaller than the predicted Γ_s (Fig. C.3), and the increasing deposition throughout the summer season, as found in Section 3.4.2, is not captured due to its complex nature which is further investigated in Section 3.5. Comparing the annual sums of observed and DEPAC-predicted fluxes for half hours where both have available data, the observed sum gives 12.9 ± 3.6 (2σ) $\text{kg N ha}^{-1} \text{ yr}^{-1}$ and the DEPAC predicted value is 7.1 ± 4.3 (2σ) $\text{kg N ha}^{-1} \text{ yr}^{-1}$ (assuming an error of 60% in DEPAC for locally predicted fluxes according to Hoogerbrugge et al. (2024)). This means that the best estimate of DEPAC is 45% lower than the observed flux, but both loads are within each-others uncertainty margin.

3.5. Linking ecosystem activity and F_{NH_3}

In Section 3.4.2, we found a variation in NH_3 -exchange throughout the summer season, with less deposition or even emission in early

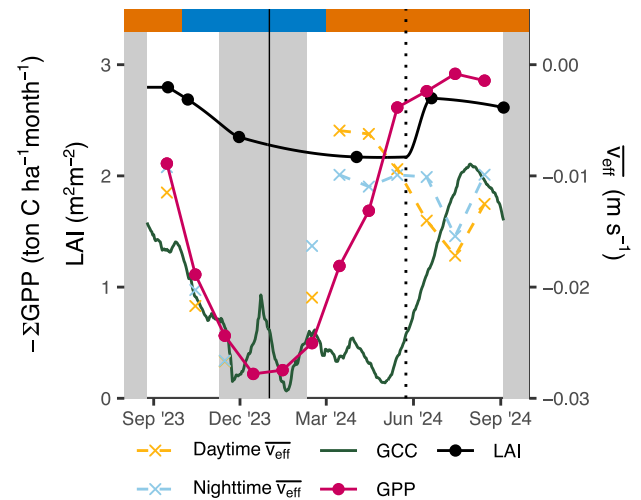


Fig. 9. Interpolated LAI throughout measurement period, where the black dots denote measurements. Note that we reversed the sign of the GPP for easier graphical representation, and that the GCC does not have an y-axis, but is merely showed for its seasonal dynamics (see also Fig. 3a). The orange and blue crosses denote the monthly mean effective exchange velocity (v_{eff}) for only daytime or only nighttime values (analogous to Fig. 8), where negative values show net deposition. Finally, the dotted vertical line shows the start date of leaf growth based on the GCC, the gray shaded areas indicate days on which the HT was not deployed, and the orange/blue strip indicates summer and winter months respectively.

summer months and increasing deposition towards peak summer. Fig. 5d shows the cumulative sum of the gap-filled F_{NH_3} and gap-filled GPP. Overall, there seems to be a similarity between the two different fluxes, with stronger deposition with a higher GPP. In the early summer months, however, there seems to be a delay between increasing GPP and increasing F_{NH_3} , hinting towards a coupled hysteresis between F_{NH_3} and GPP, potentially driven by seasonality in the emission potentials Γ_s and/or Γ_w .

To further investigate such a hysteresis, we compared v_{eff} to GPP on different timescales, as v_{eff} implicitly contains information on the emission potential Γ which may be the cause for a coupled hysteresis between F_{NH_3} and GPP. Fig. 8 depicts the daily and monthly mean v_{eff} as a function of the summed carbon uptake (ΣGPP) and shows no clear relations on daily basis, both during the summer and winter seasons. On monthly basis, however, we found a moderately strong relation ($R^2=0.61$) between v_{eff} and GPP during the summer season, where $|v_{eff}|$ increases with more photosynthetic activity. This relationship is stronger when considering only daytime values ($R^2 = 0.74$). In contrast, during nighttime, the relationship is substantially weaker ($R^2 = 0.12$), suggesting a lack of correlation between ecosystem activity and NH_3 exchange with the external leaf surface. Furthermore, these results indicate that the increasing LAI during the summer season is not the dominant factor to explain the trend during the summer season (expressed as a link between GPP and v_{eff}), as this would lead to similar relationships during day and nighttime (by enhancing the deposition surface area). Therefore, it is more likely that Γ changes throughout the summer season. We formulated two hypotheses that could explain this: (i) Before leaf growth starts, N is mobilized and translocated from storage (a.o. mature leaves) to leaf buds to be used for leaf tissue formation and (ii) with an increasingly active ecosystem (higher GPP), more NH_3 is assimilated (i.e. converted into organic nitrogenous compounds for enzyme production and plant growth, or stored for use during the next year's leaf expansion phase), and consequently Γ decreases as GPP increases. Both mechanisms are schematically shown in Fig. 10.

The initial growth during the early summer months is mainly supported by N from storage locations (a.o. in shoots), before it is supported by uptake of N from the soil (Millard and Grelet, 2010; Millard

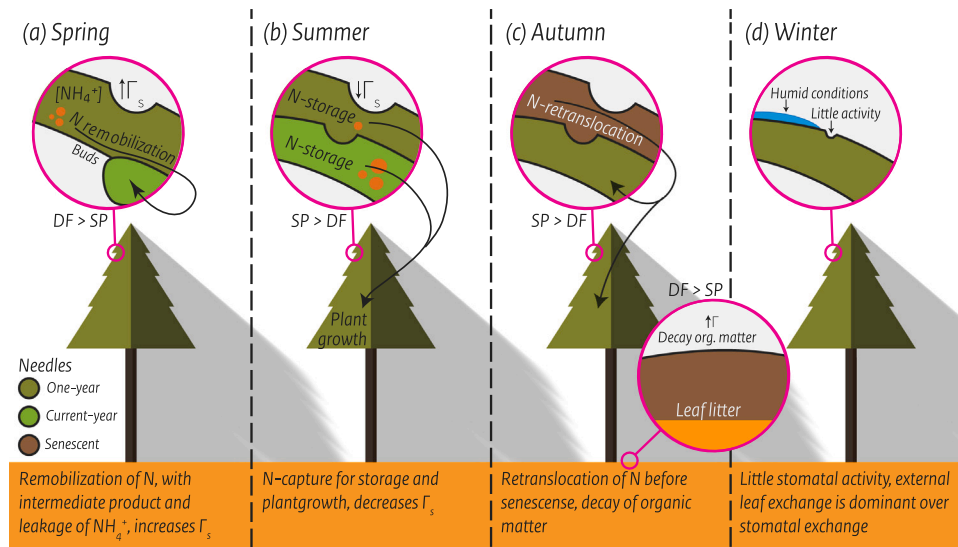


Fig. 10. Overview of plant physiological processes that affect biosphere–atmosphere NH_3 exchange. Emphasis is on processes involving needles and N-transport from soil is not shown. With each process it is indicated for which tree type the resulting effect on Γ is stronger, where SP indicates Scots pine trees and DF indicate Douglas fir trees.

et al., 2001; Millard and Proe, 1992). To mobilize N from storage, it is ‘repackaged’ to a more suitable (organic) form for transport, with NH_4^+ as an intermediate product (Pearson et al., 2002). During this repackaging, the recapture of NH_4^+ may not be instantaneous or result in some leakage, resulting in increased Γ values. Remobilization of N then causes Γ_s to temporarily increase during the early summer months (mainly in the one-year needles), thus suppressing NH_3 deposition. N mobilization typically begins well before leaf growth (Millard and Grelet, 2010), and for Scots pine trees it can start 2 to 4 weeks before visual needle expansion (Näsholm, 1994). Extrapolating this to the Loobos site, we would expect N mobilization to begin earliest in April. Fig. 9, however, shows that $|v_{eff}|$ is at its minimum in March, indicating that Γ_s is already elevated. It is not unlikely that interannual variability and climatic factors modulate the timing of N -mobilization, and thus it could well be that during our measurement campaign this process started already in March. Unfortunately, we lack the (plant physiological) measurements, such as apoplastic $[\text{NH}_4^+]$ or pH, required to consolidate these hypotheses. Measurements of bulk leaf tissue pH and $[\text{NH}_4^+]$ (Γ_{bulk}) have been performed before for a boreal Scots pine forest (Hyytiälä, FI; Wang et al., 2013), and showed a peak in February–June (depending on canopy base or canopy top). These observations fit our hypothesis, though it is unclear how representative Γ_{bulk} is for Γ_s . Moreover, Γ_s derived from fluxes over an exposed Scots pine forest also showed elevated values during spring compared to summer (Neiryck and Ceulemans, 2008), which also fits our hypothesis. After leaf expansion is completed, Γ_s restores to normal values and $|v_{eff}|$ increases (as in Fig. 9).

When leaf expansion is finished, the N -assimilation metabolism becomes more active and N is stored in organic form for later use (next spring) (Millard and Grelet, 2010). Previous studies showed that the foliar uptake of N_r is an important process (Hu and Fernandez, 2014; Sparks, 2009; Geßler et al., 2002; Pérez-Soba et al., 1994), and it could be as important as uptake by the roots (Ferraretto et al., 2022; Harrison et al., 2000), mostly through the stomata (Krupa, 2003). Moreover, Pérez-Soba et al. (1994) showed an increase in Glutamine Synthetase (GS) activity in Scots pine needles with higher exposure to NH_3 , indicating that the additional N is assimilated for plant growth or storage. For N -assimilation, a carbon (C) skeleton is also required (Pearson et al., 2002). Thus, during times of plenty in atmospheric NH_3 (as in Loobos) and low photosynthetic activity, N -assimilation could potentially be constrained by carbon availability. Altogether, this

supports the hypothesis that the NH_3 uptake by the forest scales with GPP (hypothesis ii). During winter months daytime v_{eff} is high, despite the low stomatal activity, which is probably due to increased exchange with the external leaves due to the humid conditions (see also Fig. S1 and Section 3.4.3).

Schulte et al. (2024) performed a study to the similarities between CO_2 uptake (GPP) and NH_3 exchange during daytime conditions on a half hourly basis. They report a low positive relation ($R = 0.48$) between GPP and F_{NH_3} and attribute part of the noise to different atmospheric conditions (stability and relative humidity). In contrast, they found a much stronger relation between the latent heat flux ($L_v E$) and F_{NH_3} ($R = 0.70$), indicating a strong link between stomatal activity and NH_3 exchange. Here, we studied longer timescales to focus on ecosystem activity rather than on instantaneous stomatal activity. The fact that we did not find relations between GPP and v_{eff} on daily and weekly basis (not shown), but found a strong relation on monthly basis indicates that it takes some time for the nitrogen status of the forest to adjust, and thus during the growing season we need to consider larger timescales when comparing carbon assimilation and NH_3 exchange. Altogether, we found indications that the ecosystem activity and NH_3 -exchange are inherently linked through multiple processes which are dominant in different seasons.

3.6. Comparison to the nearby site Speulderbos

Between 1990 and 2010 various NH_3 -deposition measurements took place at Speulderbos, a forest site approximately 10 km north of Loobos. The latest campaign with high temporal-resolution measurements took place in 2009 and 2010, of which the results, as well as an overview of all NH_3 -deposition measurements at Speulderbos, are presented in Melman et al. (2025). As this forest is relatively close, it makes an interesting comparison. The Speulderbos site is characterized as a patchy forest, and it is directly surrounded with Douglas Fir trees ($h_c = 32$ m) with a dense canopy ($LAI = 6.1 \text{ m}^2 \text{ m}^{-2}$). See Melman et al. (2025) for a more complete site description. The Speulderbos is located a bit further away from the high emission area than Loobos, which is reflected in a lower annual median $[\text{NH}_3]$ ($4.8 \mu\text{g m}^{-3}$ at Speulderbos vs $6.1 \mu\text{g m}^{-3}$ at Loobos). Table 3 shows a comparison of the two sites.

Despite their proximity, the two locations have a very different annual deposition load. At Speulderbos, the best estimate for (gap-filled) annual deposition load was between 8.5 and $11.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$

Table 3

Comparison of site properties of Speulderbos and Loobos during their respective campaigns (unless otherwise noted). Both NH_3 and GPP fluxes are gap-filled.

	Speulderbos	Loobos	
Campaign	2009+2010	2023–2024	
Planting yr.	1962	1911	
Dominant veg.	Douglas fir	Scots pine	
h_c	32	21	(m)
LAI	6.1	2.3–2.8	(m^2m^{-2})
z_0	1.3	1.0	(m)
ℓ	2.5 ± 1.2	8.8 ± 4.4	(m)
V_{TKE}	1.4 ± 0.7	1.1 ± 0.6	(m s^{-1})
$[\text{NH}_3]$	4.8	6.1	($\mu\text{g m}^{-3}$)
Annual F_{NH_3}	8.5–11.8	32.0 ± 4.5	(kg N ha^{-1})
Annual NEE	3.5–4.5	1.2	(ton C ha^{-1})
Annual GPP	14.0–15.1	18.8	(ton C ha^{-1})
Soil C/N	24.5 ^a	23.1–28.4 ^b	(–)
Foliar C/N	25.0 ^a	30.0 ^c	(–)
Campaign precip.	735 and 768	1380	(mm)
Canopy wetness ^d	34.8% and 35.2%	38.6%	(–)
Campaign $\overline{T}_{air}$	10.0 and 11.6	12.0	($^{\circ}\text{C}$)

^a Wang et al. (2013).

^b van der Molen et al. (2026a), C/N > 25 for 8 out of 12 observations.

^c van der Molen et al. (2026b).

^d Fraction of observations with canopy wetness.

for the most recent campaign, which is a factor 3–4 lower than the best estimate of $32.0 \pm 4.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for Loobos (gap-filled). Part of the difference may be due to a higher annual $[\text{NH}_3]$ at Loobos ($6.1 \mu\text{g m}^{-3}$) compared to Speulderbos ($4.8 \mu\text{g m}^{-3}$), but it cannot explain the entire difference. It also cannot be explained by greater co-deposition with SO_2 , since concentrations were lower during the Loobos campaign ($0.54 \mu\text{g m}^{-3}$) compared to the Speulderbos campaign ($1.36 \mu\text{g m}^{-3}$). The difference is equally unlikely due to a different ratio between wet and dry deposited NH_3 as a result of different precipitation amounts, given that substantially more precipitation was measured at Loobos (1380 mm) than at Speulderbos (735 and 768 mm). A more plausible explanation is that different local factors control the flux at each site, which can either be (i) turbulence-related or (ii) biochemically related.

In Table 3 some turbulent parameters and statistics are summarized and Fig. S5 shows the directional variability of ℓ and V_{TKE} , together with the direction variability of $[\text{NH}_3]$ for both sites. Speulderbos has a larger roughness length, which also results in more intense turbulence (as expressed by a larger V_{TKE}) and thus this cannot explain the difference between the two sites. Simultaneously, at Loobos ℓ is much larger due to a more open canopy compared to the very dense canopy in Speulderbos. This may result in efficient exchange occurring only at the upper canopy at Speulderbos, and thus the effective exchange surface decreases. Fig. 11 shows the probability density distribution of v_{eff} , $[\text{NH}_3]$ and F_{NH_3} for both sites. $|v_{eff}|$ at Speulderbos peaks at lower values than Loobos, in spite of the higher V_{TKE} (Table 3). Simultaneously, $[\text{NH}_3]$ peaks at higher values at Loobos, which altogether leads to larger F_{NH_3} at Loobos compared to Speulderbos. Here, it must be noted that the two measurements sites had a different instrumental set-up, where at Speulderbos measurements were collected with the AGM at heights of 32 ($h_c + 0\text{m}$) and 44 m ($h_c + 12\text{m}$) and at Loobos measurements were collected with the EC method at 36 m ($h_c + 14\text{m}$), which means that flux divergence could bias this comparison (see e.g. Gao et al., 2025).

A pronounced difference in Fig. 11 is that the F_{NH_3} at Speulderbos is approximately centered around 0 and has a high peak (indicating a lot of emission events), while at Loobos the observations are more spread out (Fig. 11). This behavior is also evident from Fig. S4, which shows the median F_{NH_3} for bins of $[\text{NH}_3]$ for both Speulderbos and Loobos for different filtering conditions (similar to Fig. 7), where during all different conditions the F_{NH_3} at Speulderbos is less responsive to increasing $[\text{NH}_3]$ compared to Loobos. This is especially well pronounced for the

dry daytime conditions, where Speulderbos is virtually irresponsive to increasing $[\text{NH}_3]$. Altogether, this indicates that the two different sites have different compensation points (biochemical difference). The derived Γ_s (as described in Appendix C) for Loobos is much lower than for Speulderbos, and in fact much lower than expected based on literature (see also Fig. C.3), which is also the case for Γ_w (not shown here).

A difference in compensation point between the two sites may be related to the different tree species. Scots pine trees are abundant at all latitudes (e.g. Brichta et al., 2023), while Douglas fir trees thrive best in temperate climates (e.g. Nicolescu et al., 2023). The climate and nutrient conditions in which a tree has to cope may well be reflected in their N-mechanisms (e.g. for Scots pine trees; Oleksyn et al., 2003), in which case Scots pine trees have to be more efficient with N than Douglas fir trees (Since Scots pine trees have to be able to face ‘harsher’ conditions). Wang et al. (2013) performed a study to the N-retranslocation efficiency for three different sites in Europe, one of which was Speulderbos. They found that Douglas fir trees (Speulderbos) had a lower efficiency compared to the other two forests (Beech, Soroe (DK) and Scots Pine, Hyytiälä (FI)), resulting in a higher N-content of senescent leaves. Secondly, if NH_4^+ recapture processes during N-mobilization are less efficient in Douglas fir trees, this will result in a higher emission potential and hence smaller deposition or emission fluxes. The fact that older trees are generally more efficient with nitrogen resorption (Sun et al., 2016) may also contribute to the difference in emission potential between Loobos and Speulderbos, because Loobos was planted some 50 years before Speulderbos. Finally, Douglas fir trees grow much more rapidly than Scots pine trees and have a much higher biomass, leading to much larger internal N-fluxes. This, together with the much larger LAI at Speulderbos, makes the difference in N-metabolism for the two different trees even more important when analyzing NH_3 fluxes. Fig. 12 shows the diurnal cycle in v_{eff} for both forests, grouped for months with similar behavior. At Loobos, the magnitude of v_{eff} decreases already in March/April, while at Speulderbos this only starts in May/June. Secondly, it stays high for the remaining summer. This may indicate that the N remobilization starts later at Speulderbos, probably due to the lower temperatures at the time (see Table 3). More research is required to further support this hypothesis.

A second potential explanation for the difference in compensation point between the two sites may be related to soil properties and/or ecosystem activity. At Loobos, the most recent measurements of C/N (Carbon/Nitrogen) ratios are higher for both soil and foliage compared to Speulderbos, although spatial heterogeneity is high and locally values were found to be lower (van der Molen et al., 2026a). In general the C/N ratios should decrease with a higher N-load, unless the magnitude of NEE increases at a similar or higher rate (Vanguelova et al., 2024; Villada, 2013). A C/N ratio below 25 means that there is a potential risk of nitrate-leaching (Du et al., 2024), indicating nitrogen saturation of the ecosystem. Table 3 shows that the majority of C/N ratios measured at Loobos are higher than those at Speulderbos, and thus we can assume that Loobos is more N-limited than Speulderbos, despite the much higher annual deposition load. Moreover, the GPP is higher at Loobos compared to Speulderbos (despite the lower magnitude of NEE at Loobos), indicating that Loobos is photosynthetically more active and might have a higher demand for N. Krupa (2003) and Ferraretto et al. (2022) showed that for a N-limited forest the N uptake by the canopy was an important process, and Sun et al. (2016) found that forests which have a lower soil N-content, are more efficient with N retranslocation. Together, this may explain the low compensation points at Loobos. The fact that Loobos is more N-limited than Speulderbos might then be related to soil properties.

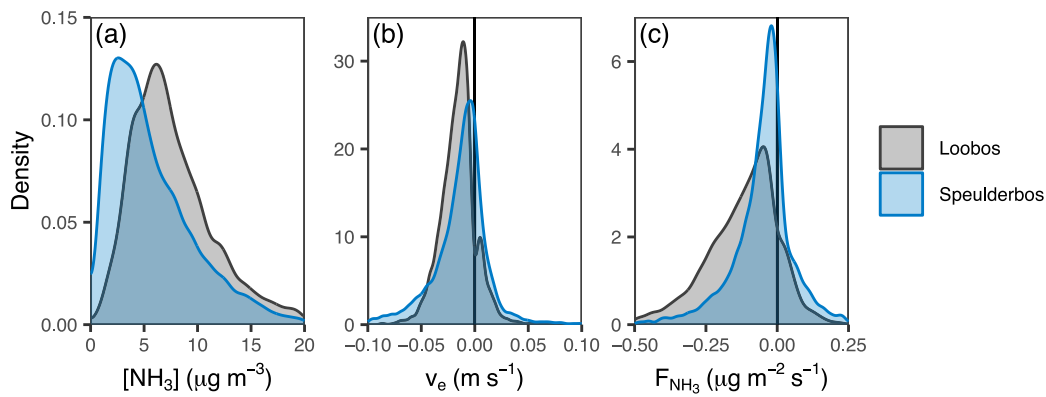


Fig. 11. Probability density functions for (a) $[\text{NH}_3]$, (b) v_{eff} , and (c) F_{NH_3} for both Loobos and Speulderbos. Values outside the x -axis ranges shown were excluded.

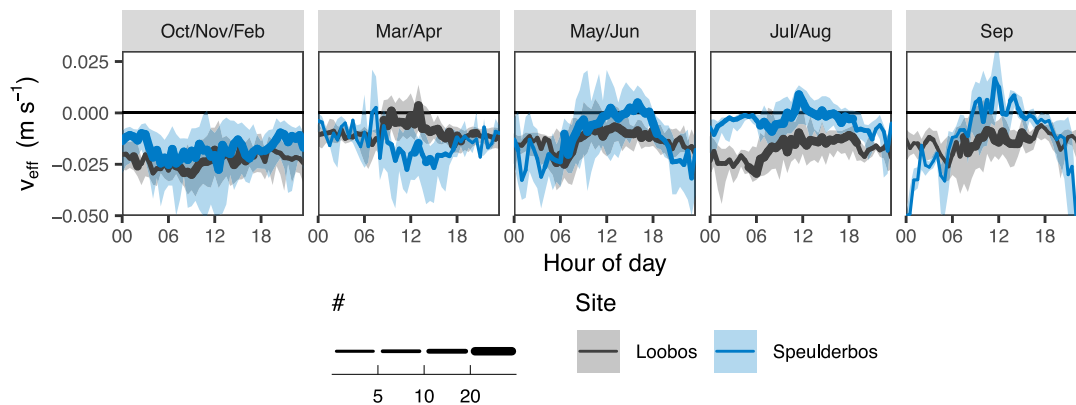


Fig. 12. Median and 25th-75th percentiles of the v_{eff} for both Loobos and Speulderbos. Each panel represents different grouped months and linewidth denotes the number of observations (#).

4. Conclusions & outlook

In this study, we presented a year-round dataset of NH_3 -flux measurements over a temperate Scots pine forest. The combined set-up of an open-path fast NH_3 analyzer (HT) to explicitly observe the NH_3 -flux (F_{NH_3}) and an open-path instrument (mD) to measure the absolute atmospheric NH_3 concentration ($[\text{NH}_3]$) resulted in a calibrated high-resolution dataset with high data coverage (33% after filtering) which allows for a detailed process study. During a majority of the time (87%) we measured deposition, while we observed emission fluxes during the rest of the time. The mean and median $[\text{NH}_3]$ were 7.9 and 6.1 $\mu\text{g m}^{-3}$ and after gap-filling we found an annual deposition load of $32.0 \pm 4.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, representing a potentially high load (compared to other estimates in the Netherlands).

We divided the dataset into six categories using appropriate filtering conditions for different exchange processes. We compared the observed flux to the maximum possible flux to investigate the efficiency and response to increasing $[\text{NH}_3]$. In general, the response to increasing $[\text{NH}_3]$ was strongest during wet conditions and minimal during dry nighttime periods. The turbulent mixing was strongest during daytime (which would allow for the largest F_{NH_3}), but the stomatal compensation point and resistance reduced exchange significantly. We found that the most efficient process is exchange between atmosphere and wet leaf surfaces, but exchange is limited due to less favorable atmospheric turbulent conditions.

Observed diurnal patterns in F_{NH_3} showed for most months maximum deposition during nighttime and minimum deposition or emission during daytime. We were able to explain these patterns with prevalent meteorological conditions and $[\text{NH}_3]$. Most emission fluxes occurred

in early summer and resulted from exchange with the stomata. On a seasonal scale, diurnal fluxes showed a pattern of increased deposition during the summer months. We found a moderately strong relationship between monthly GPP and monthly F_{NH_3} (through the exchange velocity) during the ecosystem's growing season, but observed no such relationship in the winter season. We formulated two hypotheses, relating this pattern to plant physiological processes. Future research should investigate how the observed relationships between internal nitrogen cycling and atmospheric NH_3 fluxes vary among different vegetation types, with particular attention to differences in nitrogen availability and uptake strategies. Though the evaluated inferential model (DEPAC) was able to reproduce the observed diurnal cycle, it did not predict the increasing deposition throughout the summer season, resulting in an underestimation of 45%. We suggest future research on implementing parameterizations using the GPP as proxy.

In addition, we compared the results of this campaign to NH_3 flux measurements at a nearby site (Speulderbos) in 2009–2010. Despite the apparent similarities between the two sites (close proximity, coniferous species, high exposure to atmospheric NH_3), the magnitude of the fluxes are very different. At Loobos, we estimated the annual deposition load of NH_3 to be $32.0 \pm 4.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (with median $[\text{NH}_3]$ of 6.1 $\mu\text{g m}^{-3}$), while at Speulderbos the best estimates are between 8.5 and 11.8 $\text{kg N ha}^{-1} \text{ yr}^{-1}$ (with median $[\text{NH}_3]$ of 4.8 $\mu\text{g m}^{-3}$) for the most recent campaign (2009–2010). We attributed this strong difference due to differences in compensation points, which may be related to different tree species (Scots pine at Loobos and Douglas fir at Speulderbos) and to the lower N-availability (higher C/N ratios) and simultaneous larger ecosystem activity at Loobos compared to Speulderbos. The low(er) N-efficiency of Douglas fir trees and the high N-availability at Speulderbos

creates a 'push-back' of the ecosystem by a higher compensation point, leading to a lower annual deposition load. This illustrates that the "forest vegetation's perspective" should be considered when analyzing NH_3 exchange fluxes. This also highlights the link between atmospheric NH_3 deposition and C/N ratios. Therefore, we strongly recommend future campaigns to also make measurements of C and N-contents in soil and plant material, such that we can better explain the strong spatial variability between different sites. Moreover, if such measurements are performed regularly throughout the year (or measurement campaign), they might also be useful to explain seasonal differences in NH_3 fluxes.

CRediT authorship contribution statement

E.A. Melman: Writing – original draft, Visualization, Software, Project administration, Investigation, Formal analysis, Data curation, Conceptualization. **P. Wintjen:** Writing – review & editing, Software, Investigation, Data curation. **J. Zhang:** Writing – review & editing, Software, Investigation, Data curation. **S. Rutledge-Jonker:** Writing – review & editing, Supervision, Investigation, Conceptualization. **A. Hensen:** Writing – review & editing, Investigation, Conceptualization. **K. Felter:** Resources, Project administration. **M.K. van der Molen:** Writing – review & editing, Data curation. **H. Snellen:** Resources. **J. de Boer:** Writing – review & editing, Software. **M. Eijkelboom:** Resources. **M. Haaima:** Writing – review & editing, Software, Resources. **R. van der Hoff:** Resources. **H. van Mansom:** Resources. **M. Voorneveld:** Software. **J. Vilà-Guerau de Arellano:** Writing – review & editing. **R.J. Wichink Kruit:** Writing – review & editing. **M.C. van Zanten:** Writing – review & editing, Supervision, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Concentration correction of HT

Fig. A.1a shows the concentration difference ($\Delta[\text{NH}_3]$; HT - mD) plotted against the HT internal temperature (T_{HT} , °C), for the two years and for the two u^* thresholds. In 2023 there is no pronounced effect of the temperature, while in 2024 $\Delta[\text{NH}_3]$ decreases towards lower temperatures. We fitted a 3rd order polynomial equation to account for this for the 2024 deployment only. After filtering for well-mixed conditions and correction for the temperature effect, there is still a slope and an offset between the $[\text{NH}_3]$ as measured by the HT and the mD, both in 2023 and 2024, which we accounted for with a linear regression. See below our final correction method.

Fig. A.1b shows the agreement between HT and mD after the complete concentration correction. After all other corrections necessary for flux calculations were applied as listed in Section 2.5, the flux calculated based on field calibrated data gives a cumulative sum of 22% lower than uncalibrated HT data (Fig. A.2c). Fig. A.2a shows the median diurnal variability of fluxes calculated based on uncalibrated or field-calibrated HT data and a direct comparison is also shown in Fig.

A.2b. In general uncalibrated fluxes are larger compared to the field-calibrated flux. For some months (e.g. July), the difference is larger during nighttime compared to daytime, which is probably due to the temperature effect as shown in Fig. A.1a. Additionally, the spread for uncalibrated fluxes is larger compared to the spread for field-calibrated fluxes.

Appendix B. Gap-filling using XGB

Fig. B.1a shows the performance of the XGB model applied on the test dataset (March and July) and in Fig. B.1b the median diurnal cycle of observed and XGB predicted fluxes are compared. In general, XGB is able to reproduce the observed F_{NH_3} reasonably well. On the testing dataset, we found for the low u^* -threshold $\text{NSE} = 0.64$ and $\text{RMSE} = 0.081 \mu\text{g m}^{-2}\text{s}^{-1}$, and for the high u^* -threshold $\text{NSE} = 0.56$ and $\text{RMSE} = 0.090 \mu\text{g m}^{-2}\text{s}^{-1}$, which are comparable to the results from the statistics from the three-fold cross validations, which gave $\text{NSE} = 0.64$ and $\text{RMSE} = 0.088 \mu\text{g m}^{-2}\text{s}^{-1}$ for the low u^* -threshold and $\text{NSE} = 0.61$ and $\text{RMSE} = 0.093 \mu\text{g m}^{-2}\text{s}^{-1}$ for the high u^* -threshold. Note that from Fig. B.1a it seems that the model is less good in predicting emission fluxes, especially with the low u^* -threshold. This is likely due to the small amount of observations with emissions on which we could train the model. This is, however, expected to introduce only a limited error, since emissions typically occur during the daytime when data coverage is generally good.

During winter months, where we find the largest period with missing flux data, the XGB model predicts quite large fluxes. Here, turbulence was relatively intense (see also Fig. 5), relative humidity was high and temperature was low (see Fig. S1), and the canopy was wet for a large fraction of the time (see Fig. S1e). Note that we have limited training data during winter, but we expect this to not substantially affect the gap-filling procedure as: (i) the XGB feature importance (Fig. B2 in the revised manuscript) shows that the $[\text{NH}_3]$ concentration is the most important variable for gap-filling (with a contribution of >50%), of which we have year-round measurements. (ii) Secondly, winter in the Netherlands is typically characterized by more humid and cooler conditions, and low productivity in forests (see also Fig. 9 in Zhao et al. (2026)). These conditions are similar to nighttime conditions (which are, although in a lower quantity, present in our training dataset), and thus the model is expected to perform reasonably well in winter under such similar conditions. Therefore, it is not unlikely that there was relatively high deposition during the winter months. Finally, if we compare the sum of F_{NH_3} for the half hours that pass the low u^* -threshold for both the xgb-modeled fluxes and observations, we find that the XGB model overestimates the flux with 0.7%, which is only a minor overestimation.

Fig. B.2 shows the importance of the selected features (expressed as 'Gain'). The $[\text{NH}_3]$ is the most dominant variable and explains more than half of total variability in the flux. There are several other interesting features in the explaining variables: (i) The LAI has relatively large gain, indicating that there is a seasonal cycle in F_{NH_3} . (ii) The 6-day rolling average $[\text{NH}_3]$ to determine Γ_s is relatively short, indicating that at Loobos the physiological response is relatively fast and strong. (iii) The $SWC_{5\text{cm}}$ showed to be a relevant parameter. This may either be a result of its control on stomatal activity (though that is usually at deeper levels, which showed less relevancy compared to the 5 cm level; not shown here) or indicate that exchange with the soil is also relevant in explaining the total F_{NH_3} at Loobos. Furthermore, there are some differences in feature importance when using the low or high u^* -threshold. Mainly, the WD, u^* , and NEE gain importance when using the low u^* threshold, while $[\text{NH}_3]$, VPD and $[\text{NH}_3]_{6 \text{ days}}$ loose importance. The strong increase in importance of WD and u^* may reflect the fact that they have a large control on turbulent exchange, which is especially important when the canopy-atmosphere interface is not fully coupled. This has been previously shown for NEE (Papale et al., 2006), hence also the increased importance of NEE.

$$2023 : \begin{cases} \text{if } u^* > 0.1, & HT = 3.802 + 1.355 \cdot mD \\ \text{if } u^* > 0.3, & HT = 4.099 + 1.269 \cdot mD \end{cases} \quad (\text{A.1})$$

$$2024 : \begin{cases} \text{if } u^* > 0.1, & HT = -7.816 + 1.870 \cdot T_{HT} - 0.070 \cdot T_{HT}^2 + 0.001 \cdot T_{HT}^3 + 1.262 \cdot mD \\ \text{if } u^* > 0.3, & HT = -7.017 + 1.728 \cdot T_{HT} - 0.062 \cdot T_{HT}^2 + 0.001 \cdot T_{HT}^3 + 1.206 \cdot mD \end{cases} \quad (\text{A.2})$$

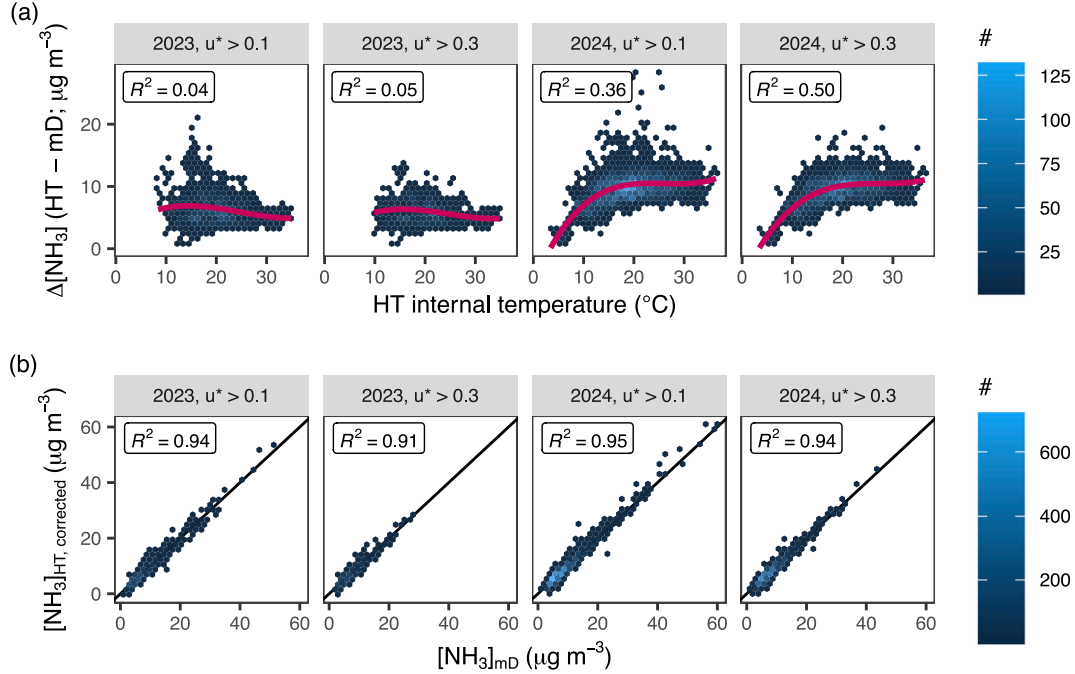


Fig. A.1. (a) $\Delta[NH_3]$ (HT - mD), for the two separate years and thresholds for u_* . (b) Comparison of mD and corrected HT $[NH_3]$, for the two separate years and thresholds for u_* .

Appendix C. Model evaluation (DEPAC)

C.1. Model description

DEPAC is a module of air quality models that are used in the Netherlands to calculate, among others, NH_3 surface exchange fluxes (Sauter et al., 2023; Manders et al., 2017). It can also be used as an one-dimensional inferential model to compare model output against observations. Deposition of atmospheric compounds is often modeled using the resistance analogy, with in series the aerodynamic resistance (r_a), the quasi-laminar boundary layer resistance (r_b) and the canopy resistance (r_c). r_a describes turbulent transport between surface and atmosphere and is calculated from observations. r_b is due to the thin layer above the surface where molecular diffusion dominates over turbulent transport, for which we used the parameterization of Hicks et al. (1987). Finally, r_c is calculated from three parallel pathways: (i) A stomatal pathway (r_s) with compensation point (χ_s), (ii) an external leaf pathway (r_w) with compensation point (χ_w) and (iii) a soil pathway (r_{soil}) with a compensation point set to zero. In case of forests, the soil pathway is in series with an in-canopy resistance (r_{inc}), which combined gives the effective soil resistance ($r_{soil,eff}$) (van Zanten et al., 2010; Wichink Kruit et al., 2010). The flux is then calculated as:

$$F_{NH_3} = ([NH_3] - \chi_c) \cdot \left(\frac{1}{r_a + r_b + r_c} \right), \quad (\text{C.1})$$

where r_c is the total canopy resistance, given by $1/r_c = 1/r_s + 1/r_w + 1/r_{soil,eff}$. The canopy compensation point (χ_c) is calculated as sum of

the relative contribution of each path:

$$\chi_c = r_c/r_s \cdot \chi_s + r_c/r_w \cdot \chi_w. \quad (\text{C.2})$$

The compensation points χ_s and χ_w are calculated from the respective emission potentials Γ_s and Γ_w , taking into account the solubility of NH_3 as a function of the surface temperature (T_{surf} ; using Henry's law for equilibrium) and the dissociation equilibrium of in water dissolved NH_3 . In turn, Γ_i are calculated using the empirical relations from Wichink Kruit et al. (2010) dependent on ambient $[NH_3]$ and T_{surf} . Here, Γ_s is assumed to be in equilibrium with the moving-average atmospheric $[NH_3]$ during the past 31 days, and for Γ_w we assume instantaneous equilibrium with $[NH_3]$. χ_s and χ_w can be derived from atmospheric observations using appropriate filtering conditions to isolate moments where a single exchange pathway dominates (e.g. Melman et al., 2025; Wichink Kruit et al., 2010). In this study, we derived χ_s by filtering, in addition to the filters listed in Table 1, for $RH < 60\%$, global radiation (R_g) $> 10 W m^{-2}$ (as in Fig. 7a and Table 2), $\zeta < 0.1$ and $|F_{NH_3}| < 0.02 \mu g m^{-2} s^{-1}$. These filters make sure that the dominant exchange path is through the stomata (dry and daytime), that ambient $[NH_3]$ is equal to the compensation point χ_s and that there is sufficient turbulent mixing. Using similar filters for χ_w results in too few data points to calculate a representative value. Therefore, we use an alternate approach, where we use the modeled r_a , r_b and r_w to calculate χ_s : we first filtered for situations where the stomatal path and soil path are assumed to be not relevant ($RH > 60\%$, $R_g < 10 W m^{-2}$, $\zeta < 0.1$). Subsequently, χ_w can be calculated by rewriting Eq. (C.1) (see also Wichink Kruit et al. (2010)).

$$\chi_w = [NH_3] + F_{NH_3} \cdot (r_a + r_b + r_w), \quad (\text{C.3})$$

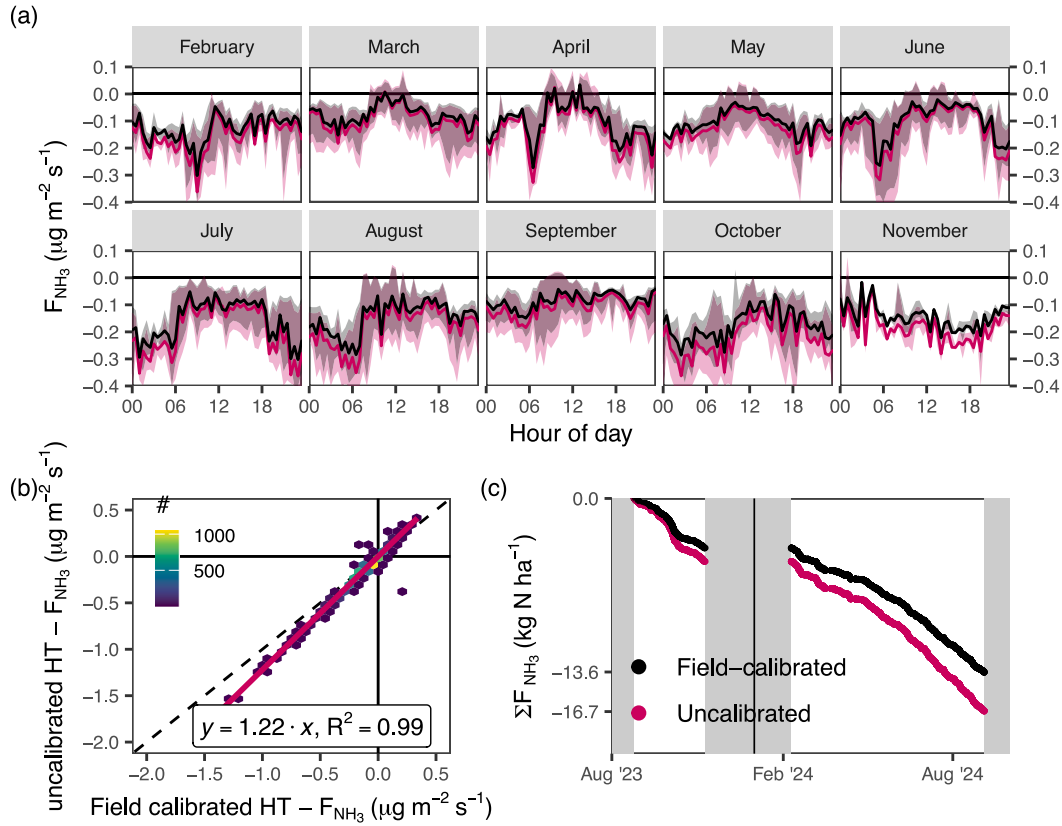


Fig. A.2. Comparison of fluxes calculated with (black) corrected and (red) uncorrected HT [NH_3] for (a) median (+inter-quantile range) diurnal variability, (b) direct comparison and (c) cumulative sum. Shaded areas in (c) indicate periods where the HT was not deployed.

where r_s and $r_{soil,eff}$ are omitted because they are assumed to be negligible under the filtered conditions. From χ_s and χ_w , we calculate Γ_s and Γ_w with:

$$\Gamma_i = \chi_i \cdot \left(\frac{2.75 \cdot 10^{25}}{T_s} \exp \left(\frac{-1.044 \cdot 10^4}{T_s} \right) \right)^{-1} \quad (C.4)$$

For more detailed information on DEPAC see also [van Zanten et al. \(2010\)](#).

The DEPAC reference run is fed with $[NH_3]_{HT}$, turbulent parameters measured by the sonic anemometer (friction velocity u_* , Obukhov length L), and top level (38.2 m) measurements of wind speed (U), T_{air} , RH and Rg. Furthermore, we used locally derived site parameters such as the roughness length ($z_0 = 1.0$ m), displacement height ($z_d = 15.5$ m), canopy height ($h_c = 21$ m) and leaf area index ($LAI = 2.3$ – 2.8 , see [Fig. 3](#)). Finally, we used observations of $[SO_2]$ of two nearby LML-stations (available on ; last access 2025-07-09) to account for co-deposition. With easterly winds ($0 \leq WD < 180$) we use observations from the Eibergen site (≈ 60 km to the east) and with westerly winds ($180 \leq WD < 360$) we use observations from the Cabauw site (≈ 60 km to the west). On average, $[SO_2]$ was higher east of Loobos (Eibergen; $1.0 \mu g m^{-3}$) compared to west of Loobos (Cabauw, $0.2 \mu g m^{-3}$).

C.2. Results & discussion

[Fig. C.1](#), shows the median diurnal cycle of F_{NH_3} for each month for both the observations and the DEPAC reference run (DEPAC_{ref}). In general, the diurnal cycle is captured well for most months; this is in line with earlier results ([Vendel et al., 2023](#); [Jongenelen et al., 2024](#)). [Jongenelen et al. \(2024\)](#) investigated the accuracy of three different state-of-the-art NH_3 exchange models for a dune ecosystem. They report that, although DEPAC has a larger bias in the deposition

flux value than the models of [Zhang et al. \(2010\)](#) and [Massad et al. \(2010\)](#), it outperforms the other two models in modeling the shape of the diurnal cycle. This indicates that an accurate prediction of the annual load does not necessarily mean an accurate prediction of the temporal behavior of the flux on shorter timescales like the diurnal cycle. Though DEPAC predicts the temporal behavior reasonably well at Loobos, it underestimates the flux during the majority of the months and cumulatively with approximately 44%.

From [Fig. C.1](#), it is clear that underestimation of the flux by DEPAC_{ref} is not constant throughout the year. During the summer season, the underestimation becomes stronger towards peak summer (July). This suggests that the seasonal dependency as described in Sections 3.5 and 3.4.2 is not captured in DEPAC. [Fig. C.2](#) shows the response of DEPAC_{ref} to increasing $[NH_3]$ under different conditions. In general, the observed flux has a higher response to increasing $[NH_3]$ than the DEPAC_{ref} modeled flux, indicating that the modeled deposition for all paths should be increased. To compare DEPAC_{ref} to the observations, we calculated the Nash–Sutcliffe model efficiency (NSE, [Nash and Sutcliffe, 1970](#)) as:

$$NSE = 1 - \frac{\sum (F_{NH_3,obs} - F_{NH_3,DEPAC})^2}{\sum (F_{NH_3,obs} - \overline{F_{NH_3,obs}})^2} \quad (C.5)$$

The NSE shows the model efficiency compared to the mean observed flux, where 1 would mean a perfect model, 0 means that the model is as good as the mean and negative values indicate that the model does worse in predicting the flux than the mean. The NSE as well as other statistical metrics are summarized in [Table C.1](#). It can be seen that DEPAC underestimates both the mean and median flux (and thus has a positive mean bias). However, with an NSE value between 0 and 1, the model performs better than simply using the mean flux, indicating that it captures some of the diurnal variability.

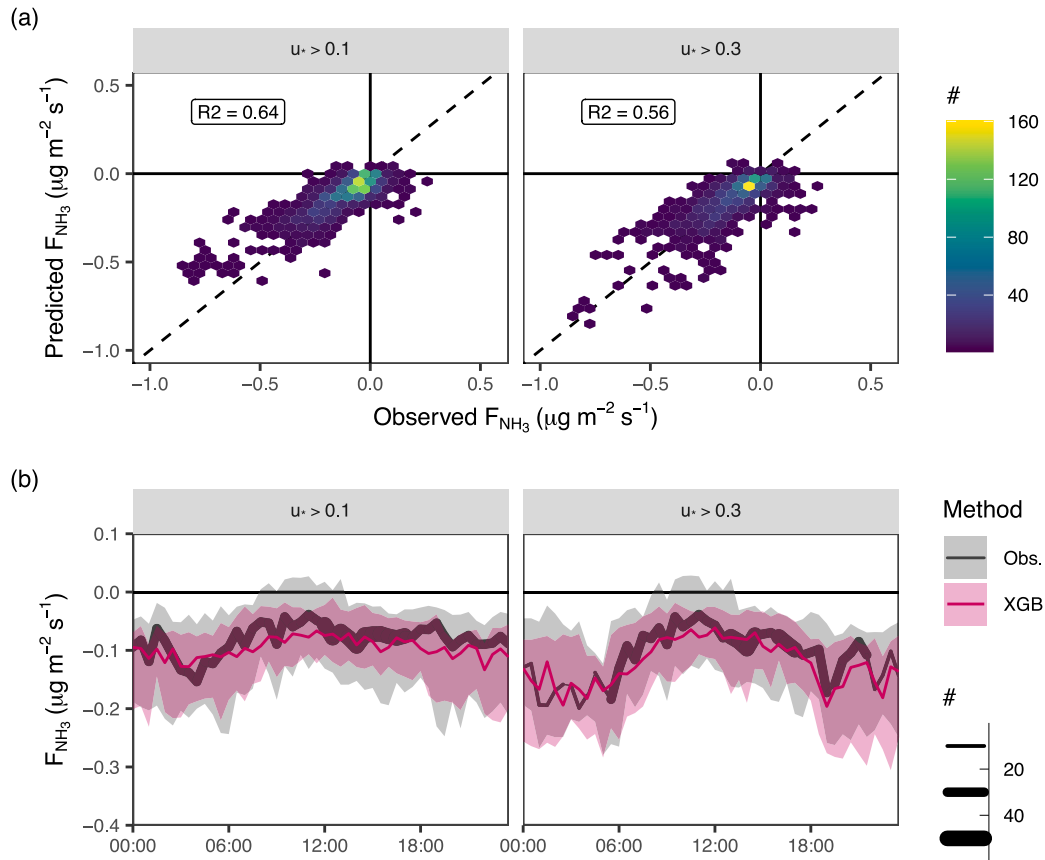


Fig. B.1. For both the low- and high- u_* thresholds: (a) Comparison of observed and XGB-predicted F_{NH_3} for the training set only, the color represent the number of observations in each hexagon (#). (b) median diurnal cycle of observed and XGB-predicted F_{NH_3} for the training dataset only. The shaded area indicates the 25th-75th percentile and linewidth indicates the number of observations (#)

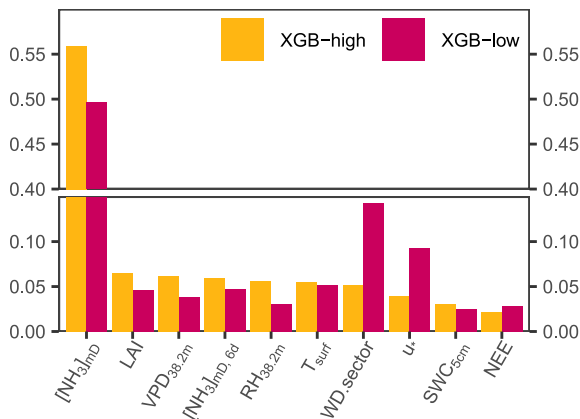


Fig. B.2. Feature importance of the XGB models.

Fig. C.1 shows that during most months daytime fluxes (where stomatal exchange is dominant) are underestimated, where DEPAC_{ref} in some cases even predicts emission, while the observations show deposition (e.g. June/July). Simultaneously, Fig. C.2a shows that the zero-crossing of DEPAC_{ref} is at much higher concentrations than observed. Altogether, this indicates that Γ_s is overestimated in DEPAC. Unfortunately, we do not have enough observations to derive a seasonal course in Γ_s . Therefore, we derived a single Γ_s for the entire dataset.

Table C.1

Performance overview of the different DEPAC runs for half hours that passed filter criteria in Table 1. Fluxes are given in $\mu\text{g m}^{-2}\text{s}^{-1}$. RMSE denotes the root mean squared error, MB the mean bias and NSE the Nash–Sutcliffe model efficiency.

	Observed	DEPAC _{ref}
Mean F_{NH_3}	−0.13	−0.07
Median F_{NH_3}	−0.10	−0.07
RMSE		0.14
MB		0.06
NSE		0.16

The median value of 118 observations gives $\Gamma_s = 716$, which is a much lower value than expected compared to previous results reported in literature (see Fig. C.3).

It is outside the scope of this study to improve the model, but based on our analysis we can make some recommendations: (i) The modeled response in F_{NH_3} to increasing $[\text{NH}_3]$ is far too small for all exchange processes, meaning that either the respective resistance or the emission potential should be decreased. Based on the difference in zero-crossing and slope between observations and DEPAC_{ref} in Fig. C.2, we find it most likely that solution should be found decreasing Γ_i . (ii) The seasonal course in Γ_s could be modeled using GPP as a proxy, or another seasonal tracer such as daytime length. Moreover, the averaging window to calculate Γ_s might be seasonally dependent (see also Sections 3.5 and 3.4.2).

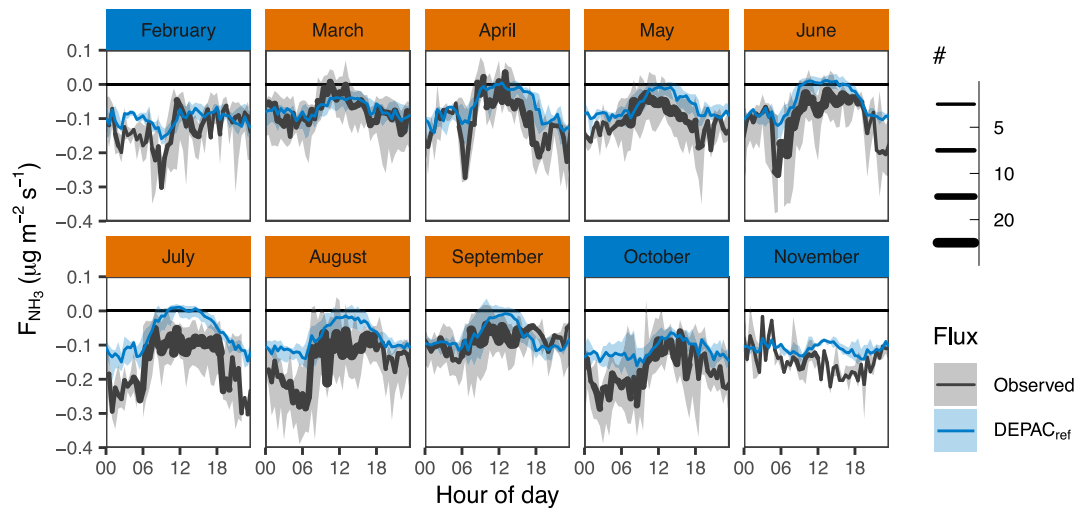


Fig. C.1. Observed and DEPAC-modeled diurnal median and 25th-75th percentiles of F_{NH_3} for each month. The linewidth of the observed dataset shows the number of observations for each respective value.

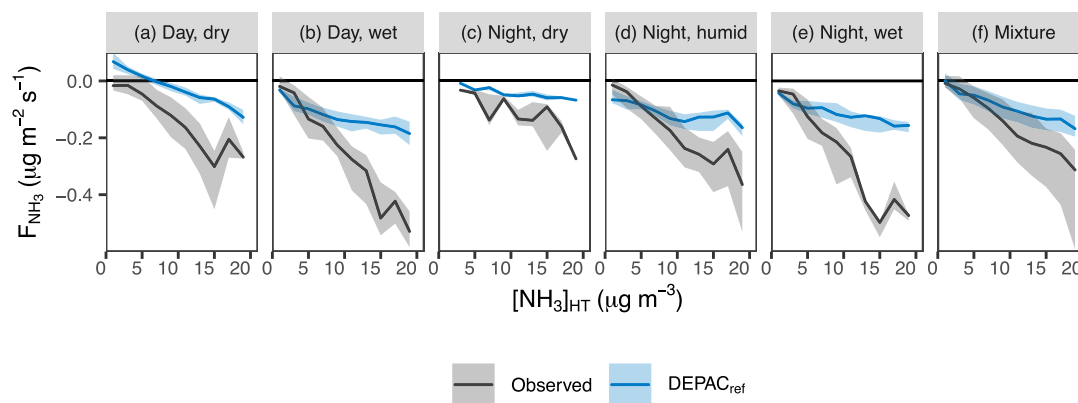


Fig. C.2. Median and 25th-75th percentiles of the observed and DEPAC modeled F_{NH_3} for bins of $2 \mu\text{g m}^{-3}$. Each panel represents different filtering conditions; see Table 2 for filter criteria and number of observations in each panel.

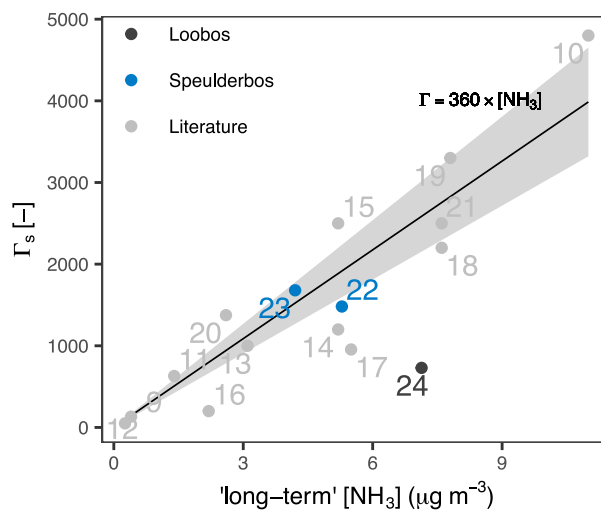


Fig. C.3. Γ_s versus the 'long-term' $[\text{NH}_3]$. The gray dots denote literature reported values, derived using the micrometeorological method, and their numbers correspond to the references in Tab. 5 from Wichink Kruit et al. (2010). The blue dots (nr. 22 and 23) denote the results from the nearby site Speulderbos (Melman et al., 2025) and the black dot (nr. 24) denotes the result of this study. The black line shows a linear fit through all literature reported values, with fixed intercept $y = 0$ (not including Loobos).

Appendix D. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.agrformet.2026.111358>.

Data availability

The data presented in this manuscript can be downloaded from <https://zenodo.org/records/20666694>, and code necessary to reproduce the presented figures and tables can be found at <https://github.com/rivm-syso/loobos2324-nh3-flux-code>.

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