

Article

Interpretable Machine Learning Identifies Nitrogen Turnover Signatures in Soil Ammonia Emissions

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Abstract

Soil ammonia (NH₃) emissions are a major pathway for reactive nitrogen loss, but their spatial variability is difficult to explain using equilibrium-based approaches alone. This study evaluated whether machine learning can improve the interpretation of NH₃ flux by identifying informative soil predictors. NH₃ flux, soil temperature and volumetric water content (approximately 0–6 cm) were measured at 20 sampling points on bare agricultural soil, while NH₄⁺, NO₃[−], total nitrogen, humus content and pH were determined at three soil depths. Five regression models were evaluated using leave-one-out cross-validation. Pairwise correlations showed that no single measured variable exhibited a dominant linear relationship with NH₃ flux. Nevertheless, Random Forest achieved the best cross-validated performance ($R^2 = 0.418$), suggesting that the observed spatial variability was better represented by multivariate and potentially nonlinear relationships among soil properties than by individual linear associations. Partial Least Squares Regression provided complementary information on the multivariate soil gradients. Within the Random Forest model, NO₃[−] concentration at 10–20 cm and near-surface soil moisture had the highest permutation importance. These findings indicate that small-scale spatial variation in NH₃ flux was associated with the combined statistical information contained in several soil properties rather than with a single dominant linear predictor. The importance of NO₃[−] represents a dataset-specific statistical association and should not be interpreted as evidence of direct causal control or nitrification intensity.



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1. Introduction

Ammonia (NH₃) volatilization from soils represents a major pathway of nitrogen loss and contributes to the atmospheric transport and deposition of nitrogen, thereby propagating the nitrogen cascade and promoting ecosystem eutrophication and secondary

particulate matter formation [1–3]. Soil NH_3 volatilization is strongly influenced by NH_4^+ availability, soil pH, temperature, moisture and gas-transfer conditions. Microbial processes may additionally affect NH_3 emission indirectly by modifying the production and consumption of soil NH_4^+ [4–8]. The concept of the soil compensation point concentration describes the equilibrium concentration of NH_3 in the atmosphere above the soil surface, which depends mainly on the ratio of NH_4^+ to hydrogen ions (H^+) in soil solution. According to thermodynamic considerations, NH_4^+ availability and soil acidity are therefore expected to be the primary drivers of NH_3 volatilization [5–8].

However, field observations often reveal more complex relationships between soil nitrogen pools and NH_3 emissions than expected from equilibrium chemistry alone. Nitrate (NO_3^-) concentrations may contain indirect information about the soil N state, although the observed NO_3^- pool cannot be attributed to nitrification alone. As a result, variables that integrate microbial nitrogen transformation processes may emerge as important statistical predictors of NH_3 flux even though they do not directly control the $\text{NH}_4^+/\text{NH}_3$ equilibrium. Nitrification may indirectly regulate NH_3 volatilization by controlling the transformation rates between different nitrogen species [9–12]. In this context, NO_3^- concentration should not be interpreted as a direct chemical driver of NH_3 volatilization or as a direct proxy for nitrification rate, because its concentration reflects the combined effects of multiple N-transformation and transport processes.

Process-based approaches have long been used to simulate soil NH_3 volatilization. For example, Jayaweera and Mikkelsen [13] developed a mechanistic model for flooded soils based on aqueous $\text{NH}_4^+/\text{NH}_3$ equilibria and mass-transfer processes, whereas the SURFATM- NH_3 model combined surface energy balance calculations with resistance-based bidirectional NH_3 exchange at the field scale [14]. These approaches established the importance of thermodynamic, meteorological and transport controls but generally require detailed process-specific parameterization. More recently, data-driven methods have been applied to evaluate whether nonlinear combinations of soil, meteorological and management variables can improve empirical prediction of NH_3 losses.

Recent advances in machine learning provide new opportunities to identify statistical relationships in complex environmental datasets where multiple interacting drivers control ecosystem processes. Machine learning models are increasingly used to identify nonlinear interactions in complex soil systems that are difficult to detect using traditional statistical approaches. In soil science and biogeochemistry, such methods are increasingly used to analyse soil processes characterized by multiple interacting drivers [15,16].

Applications of machine learning to agricultural NH_3 volatilization remain relatively limited, but recent studies demonstrate their potential to identify nonlinear relationships among soil, meteorological and management variables. Hurtado et al. [17] applied Random Forest to 234 field treatments from Mediterranean cropping systems and obtained R^2 values of 0.69 for the NH_3 emission factor and 0.76 for cumulative NH_3 emissions. Nitrogen application rate was the strongest overall predictor, with a marked increase in volatilization above approximately 170 kg N ha^{-1} , while soil pH was the most influential edaphoclimatic variable, with particularly high emissions above pH 8.2. Fertilizer type, crop type and application method also contributed substantially, whereas precipitation, water management and soil texture had comparatively low importance. These results indicate that climatic conditions affect NH_3 losses mainly indirectly, through their interactions with fertilization and cropping practices, rather than acting as dominant predictors independently [17].

More recently, Favrot et al. [18] used 5939 emission observations from 538 experiments in the ALFAM2 database to predict cumulative NH_3 volatilization during the first 72 h after slurry application. Random Forest provided the best performance on an independent test dataset ($r = 0.94$, RMSE = 4.51 and MAE = 3.28), followed by gradient boosting. Their

analysis demonstrated that NH_3 losses were jointly influenced by slurry characteristics, meteorological conditions, application method and the timing of slurry incorporation. Depending on these interacting conditions, alternative application and incorporation techniques reduced predicted emissions by approximately 13.6–61.7% relative to broadcast application [18].

These previous studies primarily addressed cumulative fertilizer- or slurry-derived NH_3 losses across multiple experiments and management conditions. In contrast, it remains unclear whether soil physicochemical properties measured at different depths can provide additional information on the within-field spatial variability of instantaneous NH_3 flux. The present study addresses this narrower question using simultaneously collected, depth-resolved soil measurements.

In particular, we examine whether variables associated with microbial nitrogen transformations may emerge as strong statistical predictors of NH_3 emission even though volatilization is thermodynamically controlled by the $\text{NH}_4^+/\text{NH}_3$ equilibrium.

By comparing linear, regularized, latent-variable and nonlinear models, this study evaluates whether multivariate and potentially nonlinear relationships among depth-resolved soil properties provide additional information on the spatial variability of NH_3 flux. Machine learning was used to rank statistically informative predictors and to explore possible interactions among correlated soil variables, rather than to identify previously unknown microbial mechanisms or establish causality.

The objective of this exploratory study was to compare linear, regularized, latent-variable and nonlinear regression approaches for describing small-scale spatial variation in soil NH_3 flux within a single field on one sampling date. Specifically, we assessed whether physicochemical variables measured at different soil depths contained useful statistical information for predicting the observed variation among the 20 sampling points. The relative importance of individual variables was evaluated only within the present dataset and was not interpreted as evidence of general or causal control over NH_3 emissions.

2. Materials and Methods

2.1. Site and Field Management

Measurements and sampling were conducted in an arable field near Kartal, at the Gödöllő Experimental Farm, on 14 March 2024. the site coordinates were $\varphi = 47^\circ 39' 42.56''$, $\lambda = 19^\circ 31' 43.21''$, at an elevation of 153 m above sea level. The climate is continental, with an average annual precipitation (1991–2020) between 550 and 600 mm year⁻¹. During the two weeks preceding the measurements, the mean daily air temperature was 8.6 °C, with mean daily maximum and minimum temperatures of 12.4 and 5.3 °C, respectively. The mean daily soil temperature was 8.4 °C, and the cumulative precipitation during this period was 16 mm. Measurements were conducted immediately before the fertilizer application and before crop establishment. Consequently, the survey represents pre-fertilization baseline conditions rather than the NH_3 emission pulse following fresh fertilizer application.

The soil was classified as a Haplic Phaeozem (Humic, Pantoloamic) using the World Reference Base for Soil Resources (WRB) classification system of the International Union of Soil Sciences (IUSS). The soil texture clay 32.3%, silt 49.1%, and sand 18.6%, which corresponds to a silty clay loam according to the USDA textural classification. The reported texture represents the field-level soil classification. Clay, silt and sand contents were not determined separately at each sampling point or soil depth; therefore, possible small-scale textural variability within the study area was not quantified and could not be included in the models.

The field was cultivated with corn (*Zea mays* L.) in 2023. At the end of April and the beginning of May 2023, 135 kg N/ha of calcium ammonium nitrate fertilizer was

applied in granular form. The field was ploughed in November 2023, and seedbed preparation was performed on 21 February 2024. Twenty measurement points were designated in the area (Figure 1), and further investigations, such as soil sampling and NH_3 emission measurements, were conducted at these points. Measurements were carried out on bare soil.

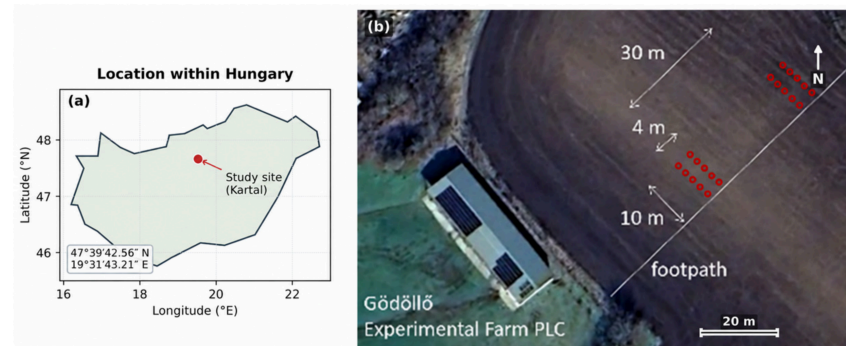


Figure 1. Location of the study site within Hungary (a) and sampling layout at the Gödöllő Experimental Farm near Kartal (b). Red circles indicate the 20 sampling points.

The sampling area was deliberately restricted to a single, uniformly managed field section to examine small-scale spatial associations between simultaneously measured NH_3 fluxes and soil properties under common meteorological, land-use and management conditions. This design reduced between-site variation arising from different soil types and management histories but necessarily limited the spatial representativeness and broader generalizability of the results.

2.2. Soil Physical and Chemical Properties

For soil chemical analyses, three soil samples were collected from each of the 20 sampling points at three depths (0–10, 10–20 and 20–30 cm) immediately after flux measurements. The samples were air-dried and ground using a 2 mm sieve prior to analysis.

Humus content was determined using the modified Walkley–Black method for organic carbon (SOC) [19].

Total nitrogen was determined using the modified Kjeldahl method, involving acid digestion, conversion of organic nitrogen to ammonium, alkaline distillation and titrimetric quantification [20]. Extractable NH_4^+ and NO_3^- were determined using the KCl extraction–distillation procedure of Bremner and Keeney [21]. Air-dried and 2 mm-sieved soil was extracted by shaking for 1 h with 2 M KCl (Merck KGaA, Darmstadt, Germany) at an extractant-to-soil ratio of 10 mL g^{-1} . The extract was subsequently analysed by steam distillation. Magnesium oxide was used for the distillation of NH_4^+ , whereas ball-milled Devarda's alloy was used to reduce NO_3^- to NH_4^+ ; sulfamic acid was added to eliminate interference from NO_2^- . Magnesium oxide, Devarda's alloy and sulfamic acid were obtained from Merck KGaA (Darmstadt, Germany). The released NH_3 was collected in a boric acid–indicator solution (Merck KGaA, Darmstadt, Germany) and quantified by titration with 0.005 N sulfuric acid (Merck KGaA, Darmstadt, Germany). Soil pH(H_2O) was measured potentiometrically in a soil–water suspension using a calibrated MultiLine P4 meter (WTW, Weilheim, Germany), following the Hungarian Standard [22].

These parameters represent key soil chemical properties influencing NH_3 volatilization through their effects on microbial activity and nitrogen transformations in soil.

2.3. NH_3 Soil Flux Measurement

Soil NH_3 fluxes were measured on 14 March 2024 using a Picarro G2103 gas concentration analyser (Picarro Inc., Santa Clara, CA, USA) based on cavity ring-down spectroscopy.

The reported 1 s, 1σ measurement precision of the analyser was 0.19 ppb. Measurements were performed using a cylindrical open dynamic chamber with an internal diameter of 10.5 cm, a height of 20 cm, and an enclosed soil surface area of approximately 86.6 cm². The chamber was positioned within pre-installed collars on bare, vegetation-free soil, ensuring that the measurements represented soil–atmosphere exchange at the designated sampling points without direct plant contributions.

Ambient air entered the open chamber, and the chamber outlet was connected to the gas analyser. Air was drawn through the chamber at a flow rate exceeding 1.5 standard L min^{−1}, referenced to a pressure of 1.013 bar. The NH₃ flux was calculated from the difference between the NH₃ mole fractions in the chamber outlet and incoming ambient air, taking into account the molar airflow rate through the chamber and the enclosed soil surface area. Positive flux values indicate net emission from the soil to the atmosphere.

Measurements were conducted sequentially at all 20 sampling points between 09:52 and 11:53 UTC. Each measurement lasted 90 s.

Soil volumetric water content was measured adjacent to the chamber at an approximate depth of 0–6 cm using an ML3 ThetaProbe Soil Moisture Sensor (Delta-T Devices Ltd., Cambridge, UK). Soil temperature was measured using a Brannan thermometer (Brannan Thermometers & Instrumentation, Cleator Moor, UK) with an accuracy of ± 0.1 °C. The late-morning measurement period was selected because soil temperature during this interval was close to the daily mean, thereby limiting the influence of short-term diurnal temperature variation on the spatial comparisons.

2.4. Analytical Workflow

The overall analytical workflow of the study, from field measurements and laboratory soil analyses to model fitting and interpretation, is summarized in Figure 2. The following sections describe the individual steps of this pipeline, including data preprocessing, model fitting, cross-validation and interpretation of model outputs.

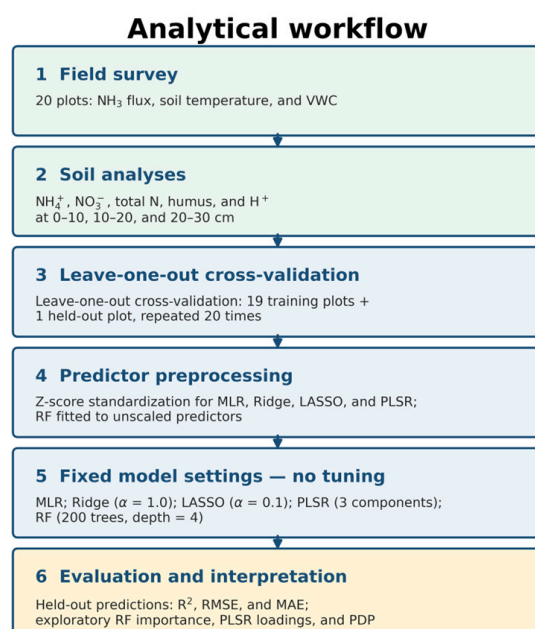


Figure 2. Workflow of the analytical pipeline, from field measurements and laboratory analyses to model fitting, LOOCV evaluation and ecological interpretation. Abbreviations: LASSO = Least Absolute Shrinkage and Selection Operator; PLSR = Partial Least Squares Regression; LOOCV = leave-one-out cross-validation; RMSE = root mean square error; MAE = mean absolute error; PDP = partial dependence plots.

The analysis combined field measurements, laboratory soil analyses and statistical modelling to evaluate which measured variables contained predictive information on the observed within-field spatial variation in NH_3 flux. Permutation importance analysis ranked the measured soil physicochemical variables according to their contribution to the fitted Random Forest predictions. The workflow begins with field measurements of NH_3 flux together with soil temperature (t_s) and volumetric water content (VWC) at multiple sampling points. These observations were complemented by laboratory analyses of soil chemical properties, including NH_4^+ , NO_3^- , total nitrogen, humus content, and pH measured at three soil depths (0–10, 10–20 and 20–30 cm). Hydrogen ion concentration was calculated from the measured pH as $[\text{H}^+] = 10^{-\text{pH}} \text{ mol dm}^{-3}$ and was subsequently converted to nmol dm^{-3} . We chose hydrogen ion concentration instead of pH as the independent variable, because in the equation for the compensation point concentration that determines soil NH_3 flux, it is not expressed in logarithmic form [14,23]:

$$[\text{NH}_3] = K_H \cdot K_A \cdot \left\{ \exp \left[\frac{\Delta G_H^0 + \Delta G_A^0}{R} \left(\frac{1}{298.15} - \frac{1}{T} \right) \right] \right\} \cdot \frac{[\text{NH}_4^+]}{[\text{H}^+]}, \quad (1)$$

where K_H and K_A are the Henry's constant for NH_3 between the soil aqueous phase and the atmosphere, and the dissociation constant, respectively; ΔG_H^0 and ΔG_A^0 are the corresponding standard Gibbs free energies.

2.5. Data Preprocessing

Soil NH_3 flux was used as the response variable. The 17 candidate predictors comprised volumetric water content and soil temperature, together with NH_4^+ , NO_3^- , total N, humus content and H^+ concentration measured at three soil depths (0–10, 10–20 and 20–30 cm). All analyses were performed in Python 3 using pandas, NumPy and scikit-learn.

Predictors were standardized to zero mean and unit variance before fitting the scale-sensitive models. The standardized value was calculated as $z_i = (x_i - \mu_x) / \sigma_x$, where x_i is the observed value and μ_x and σ_x are the mean and standard deviation, respectively, of the corresponding predictor. Multiple linear regression, Ridge regression, LASSO regression and PLSR were fitted using the standardized predictors. All analyses were performed using Python 3.12.14 (Python Software Foundation, Wilmington, DE, USA), with pandas 2.2.3, NumPy 2.3.5 and scikit-learn 1.8.0.

2.6. Model Specification and Optimization

Five regression models representing different modelling strategies were evaluated: ordinary multiple linear regression, Ridge regression, LASSO regression, Partial Least Squares Regression (PLSR) and Random Forest regression [24,25]. Multiple linear regression was fitted by ordinary least squares with an intercept. Ridge regression was fitted with a regularization parameter of $\alpha = 1.0$. LASSO regression used $\alpha = 0.1$, a maximum of 10,000 iterations and an intercept. PLSR was fitted using three latent components. The Random Forest model consisted of 200 regression trees, with a maximum tree depth of four and a fixed random seed of 42. The remaining model parameters were retained at their scikit-learn default values.

No grid search, randomized search or other data-driven hyperparameter optimization was performed. Model parameters were fixed and kept constant across all leave-one-out cross-validation iterations. Hyperparameter tuning was avoided because optimization against validation results would have increased the risk of model-selection overfitting in a dataset containing only 20 observations [26–28]. The objective was to compare representative modelling strategies under identical validation conditions rather than to maximize the apparent predictive performance of each algorithm.

2.7. Model Validation

Model performance was evaluated using leave-one-out cross-validation (LOOCV). Each of the 20 observations was held out once for testing, while the remaining 19 observations were used for model fitting, resulting in 20 training–test iterations. Predictions for all held-out observations were combined to calculate the coefficient of determination (R^2), root mean square error (RMSE) and mean absolute error (MAE).

LOOCV maximized the number of observations available for model fitting and ensured that each observation was evaluated once out of sample. However, LOOCV does not eliminate overfitting, and with only 20 observations, its performance estimates may remain sensitive to individual sampling points [26–28]. The calculated performance metrics were therefore interpreted as exploratory estimates rather than as evidence of independently validated predictive performance.

2.8. Model Interpretation

For predictor interpretation, the Random Forest model was refitted to the complete, unstandardized dataset using the same model parameters. Permutation importance was calculated using 20 repetitions and a random seed of 0. Predictor importance was expressed as the mean decrease in model R^2 resulting from permutation of the corresponding predictor.

Pearson correlation coefficients were calculated to characterize pairwise linear relationships among NH_3 flux and the predictor variables. PLSR loadings were used to describe the multivariate covariance structure of the standardized predictors. Partial dependence was calculated for the highest-ranked Random Forest predictor over 60 evenly spaced values spanning its observed minimum–maximum range, while the remaining predictors retained their observed values. These interpretation procedures describe statistical properties of the models fitted to the complete dataset and were not used as evidence of causal relationships.

3. Results

3.1. Descriptive Statistics of the Measured Variables

The descriptive statistics of the measured NH_3 flux and soil physicochemical variables are summarized in Table 1. The measurements showed substantial spatial variability in NH_3 flux across the 20 sampling points, whereas soil temperature varied within a comparatively narrow range.

Table 1. Mean values and standard deviations of NH_3 flux (ranged from 4.1 to 39.8 $\text{nmol m}^{-2} \text{s}^{-1}$) and soil physicochemical variables across the 20 sampling points. Depth-resolved soil chemical variables are presented as averages across the 0–30 cm soil profile (mean $\pm$ SD).

Variable	Unit	Mean $\pm$ SD
NH_3 flux	$\text{nmol m}^{-2} \text{s}^{-1}$	18.1 ± 11.5
VWC	%	21.9 ± 3.9
Soil temperature	$^{\circ}\text{C}$	9.54 ± 0.51
NH_4^+	mg kg^{-1}	6.51 ± 1.33
NO_3^-	mg kg^{-1}	7.24 ± 2.13
Total N	%(m/m)	0.17 ± 0.02
Humus content	%(m/m)	2.50 ± 0.25
$[\text{H}^+]$ derived from pH	nmol dm^{-3}	11.7 ± 4.8

3.2. Model Performance

The predictive performance of the five regression models was compared using the LOOCV-based R^2 , RMSE and MAE values summarized in Table 2.

Table 2. Predictive performance of the evaluated regression models under leave-one-out cross-validation (LOOCV), evaluated using R^2 , root mean square error (RMSE), and mean absolute error (MAE).

Model	R^2 (LOOCV)	RMSE	MAE
Random Forest	0.418	8.56	6.79
PLSR	0.315	9.28	7.90
Ridge	0.200	10.03	8.82
LASSO	−0.037	11.42	9.85
Linear regression	−43.14	74.52	41.9

The comparison of model performance revealed that nonlinear machine learning approaches improved predictive accuracy relative to classical linear regression methods [24,25].

Random Forest produced the lowest RMSE and the highest predictive accuracy among the evaluated models under LOOCV conditions (Table 2). Regularized linear models such as Ridge and LASSO also produced stable predictions, whereas ordinary multiple linear regression exhibited strong overfitting due to the relatively large number of predictors relative to the number of observations.

Although the predictive power remained moderate, the results indicate that nonlinear interactions among soil variables contribute to explaining variability in NH_3 flux. Given the limited sample size ($n = 20$), model results should be interpreted as exploratory rather than predictive.

The predictive behaviour of the best-performing model is illustrated in Figure 3, which compares observed NH_3 flux values with LOOCV-predicted values from the Random Forest model. The scatter of points indicates moderate predictive skill, reflecting both the small dataset and the inherently high spatial variability of soil nitrogen processes. Nevertheless, the model captures part of the observed variability in NH_3 flux, suggesting that nonlinear interactions among soil properties contribute to the emission dynamics.

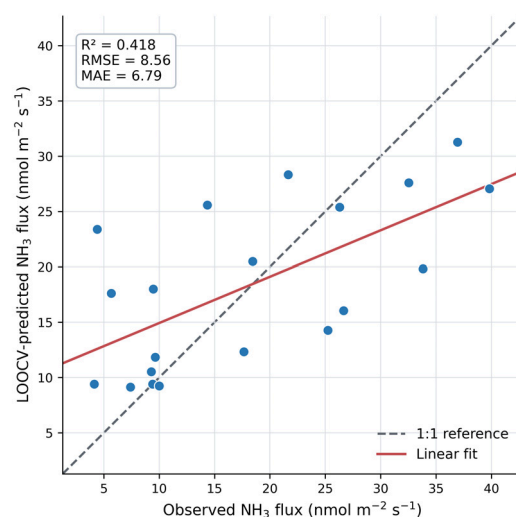


Figure 3. Observed versus leave-one-out cross-validation (LOOCV)-predicted NH_3 flux values for the Random Forest model. Blue dots represent individual observations ($n = 20$).

3.3. Model Interpretation and Predictor Analysis

Permutation importance analysis (Figure 4) ranked the measured soil physicochemical variables according to their contribution to the fitted Random Forest predictions. Within the present dataset, NO_3^- concentration at 10–20 cm had the highest permutation importance, followed by volumetric water content. NH_4^+ concentration at 20–30 cm ranked fifth among

the 17 candidate predictors, whereas H^+ concentration showed negligible permutation importance at all three soil depths.

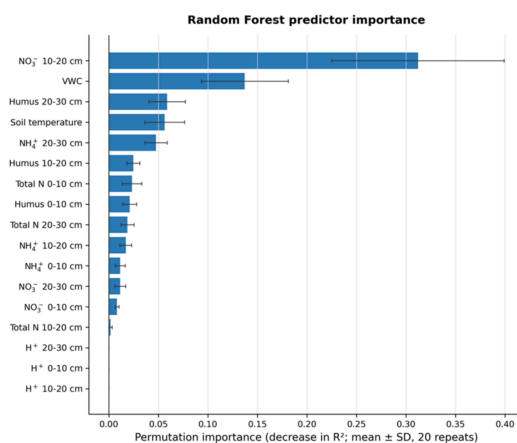


Figure 4. Permutation importance of the predictors in the Random Forest model.

Other relevant predictors included soil moisture, total nitrogen content and humus concentration.

Among the evaluated predictors, NO_3^- concentration at 10–20 cm had the highest permutation importance in the Random Forest model, followed by volumetric water content.

The multivariate relationships among predictors are illustrated in the correlation matrix (Figure 5). The matrix reveals several moderate-to-strong associations between the soil variables and NH_3 flux, although no single predictor clearly dominates the pairwise linear relationships with the response variable.

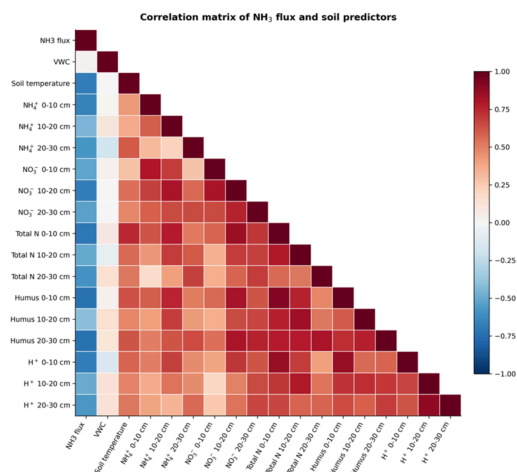


Figure 5. Correlation matrix showing the covariation structure between NH_3 flux and the soil physicochemical predictors across depths.

Further insight into the multivariate structure of the dataset is provided by the PLSR loading plot (Figure 6). The first latent component represents a dominant soil chemical gradient associated with NH_3 flux variability. Variables related to nitrogen availability and soil organic matter load strongly along this component.

The nonlinear influence of NO_3^- concentration is illustrated in the partial dependence plot for NO_3^- (10–20 cm) shown in Figure 7. The plot indicates a nonlinear relationship between NO_3^- concentration and predicted NH_3 flux, with lower NO_3^- levels generally associated with higher NH_3 emissions, while higher NO_3^- concentrations correspond to reduced flux values.

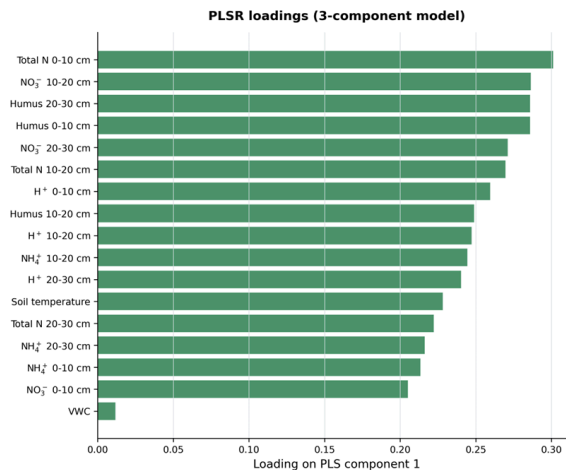


Figure 6. PLSR loadings for the first latent component, illustrating the dominant multivariate soil gradient associated with NH_3 flux variation.

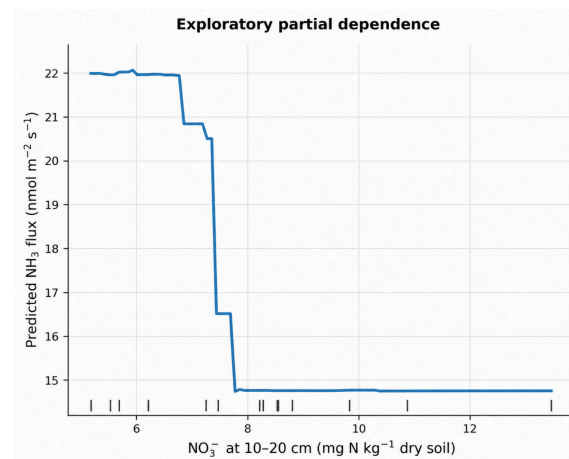


Figure 7. Partial dependence plot for NO_3^- concentration at 10–20 cm, showing the nonlinear contribution of this predictor to the fitted Random Forest response surface. Rug marks along the x-axis indicate the observed predictor values.

4. Discussion

4.1. Magnitude and Context of the Measured Variables

The mean pre-fertilization NH_3 flux was $18.1 \pm 11.5 \text{ nmol m}^{-2} \text{ s}^{-1}$, corresponding to approximately $0.25 \pm 0.16 \mu\text{g N m}^{-2} \text{ s}^{-1}$. This value confirms measurable NH_3 emission from the bare soil before the 2024 fertilizer application, although the spatial variability among the 20 sampling points was considerable. For comparison, a recent field-scale study in southern Finland reported predominantly low pre-fertilization fluxes of $0\text{--}0.02 \mu\text{g N m}^{-2} \text{ s}^{-1}$, whereas manure application generated short-term emissions of up to $1.4 \mu\text{g N m}^{-2} \text{ s}^{-1}$ [29]. The flux observed in the present study was therefore higher than the low background range reported at that site but remained substantially below a major post-fertilization emission peak. This comparison should be interpreted cautiously because soil conditions, climate, previous management and measurement techniques differed between the studies.

Mean total soil N and humus content were 0.17% (1.7 g N kg^{-1}) and 2.50% , respectively. Using the conventional conversion factor of 1.724, the measured humus content corresponds to approximately $14.5 \text{ g organic C kg}^{-1}$. This value is close to the median organic C content of 14.3 g kg^{-1} reported for European croplands in the LUCAS 2015 survey [30]. Total N was of the same order of magnitude as values reported for cultivated mineral topsoils, although it was lower than the overall mean of 2.7 g kg^{-1} reported for the Western Balkan LUCAS

dataset [31]. These comparisons indicate that the investigated field was not exceptional in terms of its total N or organic-matter status.

Mean extractable NH_4^+ and NO_3^- concentrations were 6.51 and 7.24 mg kg⁻¹, respectively. The two mineral-N pools were therefore of comparable magnitude and remained within the order of 1–10 mg kg⁻¹, consistent with a pre-fertilization soil rather than a recent fertilizer-induced accumulation. Soil pH ranged from 7.50 to 8.16, indicating slightly to moderately alkaline conditions. Such conditions favour a larger gaseous NH_3 fraction in the $\text{NH}_4^+/\text{NH}_3$ equilibrium than acidic soils, although the instantaneous flux also depends on NH_4^+ availability, temperature, moisture and atmospheric exchange conditions [5–8].

4.2. Performance and Interpretation of the Machine-Learning Models

An important result of the present study was that no single measured variable exhibited a dominant linear correlation with NH_3 flux. This finding indicates that the observed spatial variation could not be adequately described by an individual soil property acting through a simple linear relationship. The better performance of the nonlinear Random Forest model relative to the linear alternatives is consistent with the presence of combined, potentially nonlinear information among the measured soil variables. However, the present analysis does not demonstrate specific interactions or causal relationships.

Random Forest achieved the highest LOOCV performance, with $R^2 = 0.418$, RMSE = 8.56 nmol m⁻² s⁻¹ and MAE = 6.79 nmol m⁻² s⁻¹. Its predictive performance should be considered moderate: the model explained part, but not most, of the observed variability. PLSR produced the second-best result ($R^2 = 0.315$), followed by Ridge regression ($R^2 = 0.200$). LASSO did not provide useful out-of-sample prediction ($R^2 = -0.037$), while ordinary multiple linear regression showed severe overfitting ($R^2 = -43.14$). The poor performance of unregularized linear regression was expected because the number of candidate predictors ($n = 17$) approached the number of observations ($n = 20$), resulting in unstable coefficient estimates. Regularization and latent-variable reduction improved stability, but their predominantly linear representation could not reproduce the full structure identified by Random Forest.

Random Forest and PLSR provided complementary rather than directly competing interpretations. Permutation importance in the Random Forest model ranked variables according to their contribution to prediction in the fitted nonlinear model, whereas PLSR loadings described the covariance structure shared by the predictors and response. This distinction explains why volumetric water content and NO_3^- at 10–20 cm had high Random Forest importance, while PLSR represented individual variables as components of broader gradients in soil N and organic matter. Similarly, the partial dependence plot described the fitted Random Forest response to NO_3^- at 10–20 cm but did not establish that changing NO_3^- would cause a corresponding change in NH_3 flux.

Previous machine-learning studies of agricultural NH_3 volatilization used considerably larger and more heterogeneous datasets. Hurtado et al. [17] analysed 234 Mediterranean field treatments and identified fertilizer rate, pH, fertilizer type and application method as major predictors of cumulative NH_3 losses. Favrot et al. [18] used 5939 observations from 538 slurry-application experiments and showed that Random Forest and gradient boosting could successfully predict cumulative emissions across different slurry, weather and management conditions. In contrast, the present study addressed small-scale spatial variability within one field, on one date and before fertilizer application. These differences in scale, response variable and experimental context likely explain both the lower predictive performance and the different predictor ranking observed here. Predictor rankings should therefore be regarded as context-dependent rather than as universally applicable controls of NH_3 emissions.

4.3. Depth-Related Patterns in Predictor Importance

The contribution of the measured soil properties depended on both the variable and the sampling depth. The clearest depth-related pattern was observed for NO_3^- ; its concentration at 10–20 cm had the highest permutation importance among all predictors, whereas NO_3^- measured at 0–10 and 20–30 cm contributed substantially less to the Random Forest predictions. Among the other depth-resolved variables, humus content and NH_4^+ concentration at 20–30 cm showed secondary predictive importance, while total N at 0–10 cm made a smaller contribution. Hydrogen ion activity derived from pH had little predictive importance at any of the investigated depths.

The models were not designed to simulate nitrogen migration or solute transport through the soil profile. The depth-resolved variables were included only to evaluate whether soil properties measured in different layers contained distinct statistical information about the simultaneously measured surface NH_3 flux.

No consistent monotonic increase or decrease in predictor importance with depth was observed. Instead, the results indicate variable- and depth-specific predictive patterns, with the intermediate layer being particularly informative for NO_3^- . The prominence of NO_3^- at 10–20 cm does not demonstrate that this layer directly controlled surface NH_3 emission. Subsurface N pools may be associated with vertical redistribution, previous fertilizer incorporation and spatial differences in soil N status, but these processes were not measured directly. The result should therefore be interpreted as a statistical association specific to the present dataset.

Soil organisms may also influence the vertical distribution of mineral N through their effects on soil structure. Earthworm burrows, other faunal channels and decaying root pathways can form connected macropores that promote preferential water flow and solute transport. Soil–faunal activity, root-channel density and macropore continuity were not measured in this study. Although mouldboard ploughing in November 2023 and subsequent seedbed preparation may have disrupted or reorganized part of the biogenic pore network, the persistence of preferential pathways cannot be excluded. Therefore, the observed depth-resolved NH_4^+ and NO_3^- patterns cannot be attributed specifically to matrix flow, preferential transport or biological activity.

The use of depth-resolved measurements nevertheless provided information that would have been lost if the soil chemical data had been averaged across the 0–30 cm profile. This finding supports the inclusion of depth-specific soil sampling in future NH_3 studies. Confirmation will require repeated measurements to determine whether the importance of the 10–20 cm layer persists across seasons, fertilization events and different soil moisture conditions.

4.4. Biogeochemical Interpretation, Limitations and Implications

The transformation of organic N to NH_4^+ through ammonification and the subsequent oxidation of NH_4^+ to NO_3^- through nitrification are established components of soil N cycling [9–12,32]. The present study did not directly measure ammonification, nitrification, microbial biomass or microbial activity. Consequently, the high permutation importance of NO_3^- cannot be considered evidence of nitrification intensity or microbial control of NH_3 emission. A more restricted interpretation is that NO_3^- at 10–20 cm contained statistical information about the soil N state that was not represented by individual linear relationships with the instantaneous NH_3 flux.

Although NO_3^- concentration at 10–20 cm had the highest permutation importance in the Random Forest model, nitrification was not measured directly in this study. NO_3^- concentration therefore cannot be interpreted as a measure of the current nitrification rate. The observed NO_3^- pool represents the net outcome of multiple production, consumption

and transport processes, including nitrification, microbial immobilization, denitrification and leaching, as well as previous fertilizer and crop-management history [9,12,32]. Previous studies using nitrification inhibitors have demonstrated that experimentally modifying microbial N transformations can affect gaseous N losses [10,11]; however, no such experimental manipulation or direct process-rate measurement was included in the present study. Accordingly, the association between NO_3^- and NH_3 flux indicates only that NO_3^- contained additional statistical information about spatial variation in the soil N state within the present dataset; it does not demonstrate that nitrification controlled NH_3 emission. Direct determination of nitrification rates using incubation-based or isotope-tracer methods would be required to test this hypothesis. These distinctions are summarized in the interpretive framework shown in Figure 8.

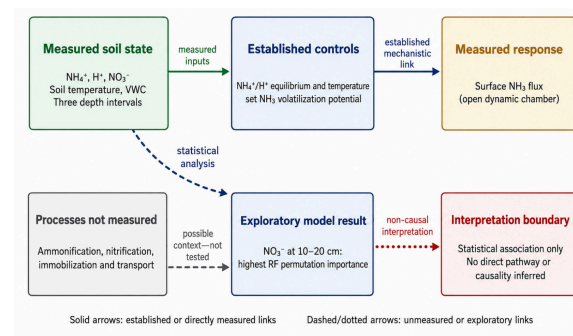


Figure 8. Interpretive framework distinguishing the established thermodynamic controls of soil NH_3 volatilization from the exploratory statistical associations identified in the present dataset. Solid arrows represent established or directly measured relationships, whereas dashed and dotted arrows indicate unmeasured, hypothesized or exploratory relationships. NH_4^+/H^+ equilibrium and temperature determine NH_3 volatilization potential, while NO_3^- concentration at 10–20 cm had the highest Random Forest permutation importance. The statistical importance of NO_3^- does not demonstrate a direct pathway to NH_3 emission, nitrification intensity or causal control. Ammonification, nitrification, immobilization and vertical transport were not measured directly.

Several limitations restrict the interpretation of the models. First, the study comprised only 20 observations and 17 candidate predictors. LOOCV maximized the number of observations available for model fitting but cannot compensate for the limited information content of the dataset. Model performance and permutation-importance rankings may therefore be sensitive to individual sampling points. Second, measurements were conducted within a single field on one date, so the results do not represent temporal variability, post-fertilization emission dynamics or conditions in other soil types and management systems. Third, point-specific soil texture, total porosity, hydraulic conductivity, macroporosity and preferential-flow pathways were not determined. Soil fauna, root-derived biopores and other biologically created flow pathways were also not characterized. Fourth, microbial biomass, microbial activity, microbial-community composition and N-transformation rates, including nitrification, were not measured directly. These omissions restricted our ability to assess small-scale physical and biological controls on NH_3 flux and prevented mechanistic interpretation of the observed vertical mineral-N patterns. Finally, precipitation chemistry and atmospheric N deposition were not measured at the study site. Consequently, the models do not provide a complete mechanistic representation of soil nitrogen dynamics but describe statistical associations between the measured soil-state variables and NH_3 flux under the specific conditions of the survey.

Atmospheric deposition represents an additional source of N to agricultural soils. Kugler et al. [33] reported a net atmospheric N deposition of approximately $12.7 \text{ kg N ha}^{-1} \text{ year}$ for a Hungarian semi-natural grassland, with dry deposition being approximately twice the

wet-deposition component. Although this value cannot be applied directly to the Kartal field, it indicates that atmospheric N input in Hungary can be on the order of 10 kg N ha⁻¹ year. This is substantially smaller than the 135 kg N ha⁻¹ fertilizer application reported for the study field but cannot be assumed to be zero. Because precipitation chemistry and atmospheric deposition were not measured at the study site, their contributions to the mineral-N pools observed on the sampling date cannot be quantified. This omission does not directly affect the statistical model inputs, which consisted of measured soil-N concentrations, but it limits source attribution, construction of a complete N budget and mechanistic interpretation of vertical N transport.

Accordingly, the models should be considered exploratory and hypothesis-generating rather than generally predictive. Their main contribution is not the identification of a new role for NO₃⁻ in soil N cycling, but the demonstration that, within this small pre-fertilization dataset, no single linear predictor described NH₃ flux variability and that a nonlinear multivariate model extracted more predictive information than the evaluated linear alternatives. The results also indicate that retaining the depth resolution of soil measurements may be useful when designing larger NH₃ emission studies.

From a practical perspective, the present models are not sufficiently generalizable for direct fertilizer-management recommendations or regional emission inventories. Nevertheless, the findings help define priorities for subsequent measurements. Larger studies should combine repeated NH₃ flux observations before and after fertilizer application with depth-resolved mineral-N measurements, microbial process indicators, soil hydraulic properties and meteorological variables. Such datasets would allow more reliable testing of model stability, temporal transferability and the added value of nonlinear machine-learning methods for agricultural NH₃ emission assessment.

Independent validation using a larger dataset covering additional sampling dates and environmental conditions will be required to confirm the stability of the model performance and predictor rankings.

5. Conclusions

This exploratory pre-fertilization, bare-soil survey compared five regression approaches for describing small-scale spatial variation in soil NH₃ flux within a single field. No individual measured variable exhibited a dominant linear relationship with NH₃ flux. Random Forest achieved the best LOOCV performance among the evaluated models, although its predictive performance remained moderate ($R^2 = 0.418$). Within the present dataset, NO₃⁻ concentration at 10–20 cm and near-surface volumetric water content had the highest permutation importance. These rankings represent dataset-specific statistical associations and do not demonstrate that NO₃⁻, nitrification or the 10–20 cm soil layer causally controlled NH₃ emission.

The results also demonstrate the distinction between model-specific predictive importance and established mechanistic relevance. NH₄⁺ availability and pH remain fundamental controls of the NH₄⁺/NH₃ equilibrium, even though NH₄⁺ and H⁺ were not the highest-ranked predictors in the present models. The depth-resolved measurements contained statistical information that would have been lost by averaging soil properties across the complete 0–30 cm profile. The principal scientific contribution of the study is therefore the comparative evaluation of different modelling strategies and the identification of candidate variables for subsequent investigation, rather than the identification of new causal mechanisms.

The findings are immediately relevant primarily to soil scientists, environmental-monitoring specialists and developers of agricultural and nitrogen-emission models. They indicate that future assessments of spatial NH₃-emission variability may benefit from combin-

ing surface-flux measurements with soil moisture, temperature and depth-resolved mineral-N information. If confirmed using larger and temporally replicated datasets, such an approach could support the spatial assessment of NH_3 -loss risk and help identify field conditions requiring targeted monitoring or mitigation. It could thereby contribute to the development of improved fertilizer-management strategies and nitrogen-use efficiency. However, the present results do not support specific fertilizer-management recommendations.

From an environmental-protection perspective, improved identification of conditions associated with NH_3 emissions could support the monitoring and mitigation of atmospheric reactive-N losses, secondary particulate-matter formation and nitrogen deposition to sensitive ecosystems. The results may also guide the selection of variables for more comprehensive field-monitoring programmes and process-based NH_3 -emission models.

These implications remain provisional. The dataset comprised only 20 observations collected in a single field on one pre-fertilization date. Point-specific soil texture, porosity, hydraulic conductivity, preferential-flow pathways, microbial-community composition, N-transformation rates and precipitation chemistry were not measured. Consequently, the present analysis does not constitute a validated predictive model, a complete mechanistic representation of soil N dynamics or an operational agricultural decision-support tool. Its practical contribution is the identification of candidate variables and hypotheses for subsequent investigation. A separately designed follow-up study incorporating repeated measurements across fertilization events, crop-development stages, meteorological conditions and additional fields will be required to determine whether the spatial relationships identified in this baseline survey are temporally and spatially transferable.

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