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Drivers of ammonia volatilization in Mediterranean climate cropping systems

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Abstract

Ammonia (NH_3) volatilization is the major source of nitrogen (N) loss resulting from the application of synthetic and organic N fertilizers to croplands. It is well known that in Mediterranean cropping systems, there is a relationship between the intrinsic characteristics of the climate and nitrous oxide (N_2O) emissions, but whether the same relation exists for NH_3 emissions remains uncertain. Here, we estimated the impact of edaphoclimatic conditions (including meteorological conditions after N fertilization), crop management factors, and the measurement technique on both the cumulative emissions and the NH_3 emission factor (EF) in Mediterranean climate zones, drawing on a database of 234 field treatments. We used a machine learning method, random forest (RF), to predict volatilization and ranked variables based on their importance in the prediction. Random forest had a good predictive power for the NH_3 EF and cumulative emissions, with an R^2 of 0.69 and 0.76, respectively. Nitrogen fertilization rate (N rate) was the top-ranked predictor variable, increasing NH_3 emissions substantially when N rate was higher than 170 kg N ha^{-1}. Soil pH was the most important edaphoclimatic variable, showing greater emissions (36.7 kg NH_3 ha^{-1}, EF = 19.3%) when pH was above 8.2. Crop type, fertilizer type, and N application method also affected NH_3 emission patterns, while water management, mean precipitation, and soil texture were ranked low by the model. Our results show that intrinsic Mediterranean characteristics had only an indirect effect on NH_3 emissions. For instance, relatively low N fertilization rates result in small NH_3 emissions in rainfed areas, which occupy a very significant surface of Mediterranean agricultural land. Overall, N fertilization management is a key driver in reducing NH_3 emissions, but additional field factors should be studied in future research to establish more robust abatement strategies.

Keywords

Ammonia emissions; Mediterranean cropping systems; Random Forest; Nitrogen use efficiency; Crop management; Meteorological conditions.

1. Introduction

Nitrogen (N) -fertilized soils are a primary source of ammonia (NH_3) volatilization to the atmosphere (Bouwman et al., 2002). Globally, this volatilization increased by 78% between 1980 and 2018 (Liu et al., 2022). Ammonia is a gaseous reactive N compound that contributes to the formation of fine particulate matter, with an impact on both human health and air quality (Ma et al., 2021; Zhan et al., 2021). It returns to the soil surface through deposition (dissolved in the rain or attached to particulate matter), causing acidification, eutrophication, and loss of biodiversity (Cameron et al., 2013; Xu et al., 2019), as well as indirect nitrous oxide (N_2O) emissions (IPCC, 2019). Moreover, the loss of N reduces fertilizer efficiency, potentially incurring an extra cost for farmers (Pan et al., 2016). Ammonia volatilization from croplands is generated mainly due to the application of ammonium-based fertilizers (including urea), both synthetic and organic, to soils (Bittman et al., 2014; Ma et al., 2021). Recent global studies have reported that, on average, between 13 and 18% of N from fertilizers is lost as NH_3 (Pan et al., 2016; Ma et al., 2021; Zhan et al., 2021), but with substantial variability depending on the N source and place, as well as the type of crop.

Volatilization is a physicochemical process influenced by soil characteristics (e.g. texture, pH, and cation exchange capacity), meteorological conditions (wind speed, temperature, and precipitation), and the management of N fertilization (source, rate, time, and placement) (Bouwmeester et al., 1985; Li et al., 2022). Nevertheless, there are strategies to abate NH_3 emissions, e.g., incorporating the fertilizer into the soil, using enhanced-efficiency fertilizers (coated or slow-release urea, urease inhibitors), and applying the fertilizer under specific weather conditions (e.g., before rain events or at low temperatures) (Bittman et al., 2014), most of them are influenced by regionally adapted crop management and edaphoclimatic conditions. Indeed, specific climates such as the Mediterranean climate present singular characteristics that could affect the efficiency of the abatement strategies (Sanz-Cobena et al., 2017; Lassaletta et al., 2021). This is the case with N_2O emissions, as the meta-analysis conducted by Cayuela et al. (2017) determined that the average N_2O emission factor (EF) in Mediterranean cropping systems was 50% less than the IPCC tier 1 default value (IPCC, 2006), information that is currently included in the IPCC update

(IPCC, 2019). However, unlike NH_3, N_2O emissions are driven by microbiological processes (e.g., nitrification and denitrification), making it necessary to explore whether Mediterranean conditions also influence NH_3 volatilization.

In recent years, NH_3 volatilization studies in Mediterranean regions have focused on evaluating different strategies to reduce these N losses, e.g., N application rate, placement, and source (including the use of urease inhibitors) (Bosch-Serra et al., 2014; Fangueiro et al., 2018; Lam et al., 2019; Sanz-Cobena et al., 2019; Guardia et al., 2021). Nevertheless, no research has quantitatively consolidated the results of these independent studies. Moreover, most previous NH_3 synthesis studies have focused on long-term climatic conditions (Ma et al., 2021) rather than on the weather conditions in the first week after N application, when most of the cumulative NH_3 losses occur (Salazar et al., 2012, 2014; Recio et al., 2018, 2020). Nevertheless, in recent years and as a result of a very significant work of synthesis and data collection, the DATAMAN database (Beltran et al., 2021) includes some measurements of air temperature (24 hours and 30 days after application) as well as rainfall/irrigation (1 hour, 6 hours, and 30 days after application), but these meteorological conditions in croplands still need to be synthesized and quantified statistically. This may be particularly relevant in semi-arid regions such as the Mediterranean, subjected to:

i) The Irregular distribution of precipitation and, therefore, a greater probability of dry periods (and low temperatures) after fertilization in winter rainfed croplands (Lassaletta et al., 2021).

ii) A large proportion of calcareous soils which favour the dominance of NH_3 over NH_4^+ (Kissel and Cabrera, 2005; Ryan et al., 2009).

iii) Intense nitrifying activity (Aguilera et al., 2013; Guardia et al., 2018).

iv) Limited soil organic matter content, which affects the cation exchange capacity (CEC) and, thus, the ammonium adsorption to the colloid (Aguilera et al., 2013).

In contrast, summer crops in Mediterranean areas normally require irrigation and experience higher air temperatures, which could stimulate volatilization rates. However, the use of water favours the infiltration of urea or NH_4^+-N into the soil immediately after or during its application, thus drastically reducing the chances for NH_3 emission (Sha et al., 2021). As a result, specifically analyzing the NH_3 volatilization dynamics and the main determining factors in the Mediterranean basin is pivotal to determine regional-specific mitigation practices.

Multiple regression, meta-analysis, and simulation models are commonly used to address the main determinants of NH_3 emissions after N fertilization in agricultural soils (e.g., Pan et al., 2016; Ti et al., 2019; Xu et al., 2019; Ma et al., 2021; Sha et al., 2021; Zhan et al., 2021). All these approaches, however, have certain limitations, e.g., meta-analyses do not work well with heterogeneous datasets (Walker et al., 2008), and in simulation models the calibration is challenging (Villa-Vialaneix et al., 2012). In the last few years, and in part to overcome the abovementioned problems, machine-learning technique random forests (RF, Breiman, 2001), which build an ensemble of regression (or classification) trees from a set of binary decision rules based on the predictor (i.e., input) variables, has become a popular and widely used tool for non-parametric regression in many scientific areas, such as environmental pollution (e.g., Kamińska, 2018; Song et al., 2020), ecology (e.g., Lawler et al., 2006; Prasad et al., 2006), and agriculture (e.g., Jeong et al., 2016; Cai et al., 2023). Random forest has several advantages over traditional regression models, such as a strong predictive and explanatory power without overfitting the data (Breiman, 2001; Prasad et al., 2006; Cutler et al., 2007), and the potential to manage data with highly correlated predictors, missing values, outliers, and non-linear relationships between the response and the predictor variables (Olden et al., 2008; Strobl et al., 2008; Philibert et al., 2013; James et al., 2013).

We hypothesized that Mediterranean conditions (i.e., low N rates, irrigation in summer crops, and meteorological conditions after fertilization in rainfed crops) would be key drivers for volatilization rates and smaller NH_3 EFs in Mediterranean climate agro-ecosystems. The objective of this study was to assess if (and how) agri-environmental factors influence NH_3 volatilization in Mediterranean climate cropping systems using field data available in scientific articles, as a basis for tailoring abatement strategies. We applied RF to (i) predict NH_3 cumulative emissions and the EF following N fertilization, (ii) rank in order of importance the edaphoclimatic and crop management predictor variables, and (iii) assess the behavior of the predictor variables with the main factor that affects volatilization.

2. Materials and Methods

2.1 Study area and data collection

We used the map provided by Olson et al. (2001) to delimitate those regions of the world with a Mediterranean biome (Fig. 1). The Mediterranean climate is characterized by mild-wet winters and warm-dry summers (Lionello et al., 2006). In winter, the average temperature is below 15°C, and temperatures lower than 0°C are usually rare (Aschmann, 1973). Mean annual precipitation ranges from 275 to 900 mm, with a clear dry period in summer. The largest area with this type of climate is the Mediterranean Basin, but it is also found in Central Chile, coastal California (USA), South and Southwest Australia, and the Cape region of South Africa (Olson et al., 2001). Within these zones, there are variations in temperature and precipitation, with sub-Mediterranean climates ranging from semi-arid to humid (Cayuela et al., 2017).

To set up the database of our model, we searched for peer-reviewed field studies in which NH_3 volatilization was measured after N fertilization in this area and in which the region of study was defined as Mediterranean by the authors. We detected these studies through consulting different on-line repositories such as Web of Science, ScienceDirect, and Google Scholar, and the reference list of the articles reviewed. Finally, the articles selected had to include information on:

(i) Edaphoclimatic data, such as mean temperature and precipitation during the field experiment, soil texture, soil organic matter (SOM), and soil pH.

(ii) Crop management information, at least the type of N fertilizer, the N rate, the application method, the crop type, and water management.

(iii) Measurement technique used to estimate NH_3 volatilization.

Ammonia emissions are studied in this paper using cumulative NH_3 emissions (cumNH_3) and the EF as dependent (response) variables in the RF model, in both cases we only used mean values for each treatment in the model. Cumulative NH_3 is the sum of NH_3 fluxes during the measurement period after N fertilization. Some studies represented cumulative emission data graphically. In those cases, *GetData Graph Digitizer* v.2.26 software was used to extract the information needed. The EF is the percentage of N applied as fertilizer that is emitted as NH_3. It is calculated as the difference between the NH_3 emissions from a fertilized treatment (kg NH_3-N ha^{-1}) and a control or a non-fertilized treatment (kg NH_3-N ha^{-1}) divided by the N fertilizer (kg N ha^{-1}) applied. In the cases of no control, the mean value of NH_3 background concentrations was used as a reference, measured with the micrometeorological mass balance integrated horizontal flux (IHF) technique, assuming zero emissions for the control plots.

The predictor variables were classified into edaphoclimatic, crop management, and NH_3 measurement technique. We registered the mean temperature and the precipitation (including irrigation events) considering the periods mentioned by Villalobos & Fereres (2016), i.e., the first two days after fertilization and the third to seventh days after fertilization. When publications did not report information on these variables, we contacted the authors of the study and requested the missing information. Soil cation exchange capacity (CEC), which plays an important role in NH_3 volatilization (Fenn & Kissel, 1976; Kim et al., 2012; Cameron et al., 2013), was only registered in 41% of the studies. As a result, we decided to incorporate soil texture and soil organic matter (SOM, %) as drivers of CEC. Fertilizer application time (i.e. at seeding/at top-dressing) was not included as a predictor variable, as each fertilization event was a new observation in the database. Twenty-six studies with 234 observations (Table 1), two response variables, and 13 predictor variables (Table 2) composed the database used in the RF statistical model.

2.2 Variable selection

Although RF methods can handle complex datasets, the inclusion of many predictor variables may increase the probability of a correlation between them, which can in turn lead to establishing incorrect relationships between the predictor and response variables. Erroneous selection of the predictor variables used to build the component regression trees may reduce the predictive accuracy of the final model (Strobl et al., 2008). Therefore, to improve RF performance, we first detected those variables that were more closely related to the highly influential predictors and removed them (Lee and Kim, 2020). Specifically, we performed:

(i) A Spearman rank correlation test among all predictor variables, to identify pairs that were strongly (Pearson $R \geq 0.50$) and significantly ($P \leq 0.05$) correlated.

(ii) A principal component analysis (PCA) to detect, on each pair, the predictor with the greatest factor loading on the principal components (i.e., contributing most to defining the variability in the data). We selected this predictor for the RF.

We obtained a strong correlation between the AT_02 and AT_37, and PI_02 and PI_37, and among them, AT_02 and PI_37 (hereafter AT and PI, respectively) had the greatest factor loadings, so they were finally selected. Thus, initially, we considered 13 predictor variables, but after the selection process, we only worked with 11. An overview of the working dataset, detailing the number of observations (N), mean and standard deviation values of cumNH_3 and EF for all predictor variables finally selected is given in Supplement 2.

2.3 Random Forest

Random forest is a machine-learning technique based on decision tree algorithms, which apply a series of if-then statements in the predictor variables and successively partition the entire set of values of the response variable into a set of nodes and branches (Breiman, 2001; Prasad et al., 2006; Kuhn & Johnson, 2013; Supplement 1). We used RF to predict cumNH_3 and EF from the selected variables (Table 2). Performing a RF also involves identification of the suitable values of certain parameters (i.e., hyperparameters), controlling the structure of individual trees (i.e., the minimum size of the nodes; *nodesize*), the structure and size of the forest (i.e., the total number of trees; *ntrees*) and its randomness (i.e., the number of candidate predictor variables considered at each split; *mtry*). This process, known as hyperparameter tuning (Probst et al., 2019), usually improves the performance of the selected models (i.e., trees), compared to the usage of the default values provided by standard R packages. After performing hyperparameter tuning, we set *mtry* = 3 for cumNH_3 and = 8 for EF, and *nodesize* = 2 and *ntree* = 1000 for both response variables. We built each individual tree by randomly dividing the dataset into two sets: the training data (used to fit the model parameters) and the test data (for validating the model).

To evaluate the performance of the model, we used three statistics (Supplement 1); (1) the root mean square error (RMSE), (2) the coefficient of determination (R^2), and (3) the index of agreement or the Willmott index (*d*). We also obtained the plots showing the relationships between the values observed and those predicted by the resulting models (hereafter the observed vs predicted plots), to obtain a rapid visualization of the model's performance and accuracy. Additionally, we estimated the linear regression between the observed and predicted values. The slope of the linear regression equation gives us how far the predicted values are from the observed ones, which also helps to know the consistency of the model. For a better interpretation of the resulting model, we assessed the variable importance and partial dependence plots. Variable importance ranks the predictor variables according to their significance in the output prediction. It measures the percentage increase in the mean square error (%IncMSE) when a specific predictor variable is not used in the RF model. The partial dependence plot is a graphical representation of how a predictor variable influences the predicted outcome of the response variable (Friedman, 2001). The Y-axis value of a partial dependence plot is determined by the average of all the possible model predictions of the response variable values with the training data for each of the observed values of a specific predictor variable (on the X-axis), excluding the effect of the other predictor variables (Jeong et al., 2016). We used R (4.1.2) packages *randomForest* (Liaw and Wiener, 2002) to perform RF analyses, and *tuneRanger* (Probst et al., 2019) to obtain the optimal hyperparameters for them.

2.4 Crop-country fertilization dataset

To compare average fertilization rates of Mediterranean climate and temperate countries, we gathered information on N fertilization (organic and synthetic) per crop and surface. We split the data into rainfed and irrigated crops for Spain as an example of an agriculturally diverse Mediterranean country using the dataset of Aguilera et al. (2021). We compared these data with those obtained by combining crop-specific synthetic (Mueller et al., 2012) and manure (West et al., 2014) N rates for temperate countries: France, Denmark, Netherlands, and the United Kingdom. We selected the year 2015 as reference because it is the most recent period with data available for all these countries. We also scaled N rates so that the total amount matched the FAOSTAT agricultural N application values of each country in 2015.

3. Results

The mean cumulative NH_3 emission (cumNH_3) from the 234 observations, which ranged from 0.09 to 157.9 kg NH_3 ha^{-1}, was 12.2 kg NH_3 ha^{-1}. The EF values varied from 0 to 55.3%, with a mean of 9.5%. The mean and standard deviation (SD) of all the input variables used in the model are reported in Table A.1 (Supplement 2). Random forest accurately predicted the cumNH_3 and EF after N fertilization in Mediterranean regions (Fig. 2). In both cases the slope was close to one (i.e., 0.94 and 1.03 for cumNH_3 and EF, respectively), which indicates a small rate of change between the observed and predicted values.

There was little deviation between the observed values and those predicted by the model for both variables (i.e., RMSE = 6.7 kg NH_3 ha^{-1} for cumNH_3 and RMSE = 5.6 % for EF). Both models also explained a large proportion of the variance in the response variable (i.e.,

R^2 = 0.76 and 0.69 for cumNH_3 and EF, respectively) and they had a very good performance (i.e., d = 0.93 and 0.9 for cumNH_3 and EF, respectively).

Regarding variable importance, the N rate and the soil pH before fertilization (pH) were the most influential variables for cumNH_3, with an increase in MSE (hereafter IncMSE) of 22.4% and 22.1%, respectively. Fertilizer type, crop type, and N application method were ranked third, fourth, and fifth, with an IncMSE between 15 and 15.5 % (Fig. 3a). For the EF, there was little change in the ranking other than a large decrease in importance for the N rate variable (with the greatest influence in cumNH_3 but third from bottom for EFs). Soil pH had the greatest explanatory power (IncMSE, 35%) followed by crop type (IncMSE, 34%). The other top-ranked predictor variables were AT (mean temperature), fertilizer type, and SOM, with an IncMSE of 22.4-25.4% (Fig. 3b). In contrast, soil texture had relatively little importance in both response variables, as was also the case with the NH_3 measurement technique for the cumNH_3 variable.

The partial dependence plots of cumNH_3 for the top-ranked predictor variables (Fig. 4a), show that for the N rate the NH_3 emissions increased substantially when the N application rate was greater than 170 kg N ha^{-1}, showing a maximum of 41 kg NH_3 ha^{-1} when the N rate was above 450 kg N ha^{-1}. Additionally, for pH (Fig. 4b), volatilization was greater in alkaline soil, especially those soils with a pH between 8.2 and 8.4. The fertilizer type indicated that cattle and pig slurries (ROL, according to Table 2) had the greatest emissions values (14.7 kg NH_3 ha^{-1}; Fig. 4c), followed by synthetic fertilizers with nitrification inhibitors (NIs) and urea (U), while treated slurries (TROL-N) had the smallest values, 10.7 kg NH_3 ha^{-1}. All crop types, ranged from 12 to 13 kg NH_3 ha^{-1}, except the industrial/oleaginous crop types. which had the greatest values (16.5 kg NH_3 ha^{-1}; Fig. 4d). Lastly, the N application method showed a clear increase in NH_3 emissions when the organic fertilizer was broadcast (Fig. 4e). Incorporation, injection, and surface application with no incorporation were also assessed, separating synthetic from organic fertilizers in the analysis. However, the results were very similar in both synthetic and organic sources for all fertilizers placement strategies (data not shown), so they were grouped into the same categories. Considering EF as the response variable, the partial dependence plots indicated that it was close to 8.0% in neutral to acidic soils but increased to 19.2% when pH was 8.2 (Fig. 4f). For the crop type (Fig. 4g), the variable had a similar trend to that cumNH_3, with the greatest EF values in the industrial/oleaginous crops. In the case of AT (Fig. 4h), the maximum EF estimated by the model occurred when the temperature was below 3°C; above this temperature, the EF varied between 9.6 and 10.8%. For the fertilizer type variable (Fig. 4i), the plot shows, as when considering cumNH_3 as the response variable, that TROL-N was the fertilizer with the lowest EF, near 8.2%, while U and NI had the greatest values, above 11%. The plot for the fifth ranked variable, SOM (Fig. 4j), indicated that when it was above 14% the EF values increased. The partial dependence plots for the bottom-ranked predictor variables are given in Supplement 3 (Fig. A.1).

4. Discussion

4.1 Model performance

Overall, these results demonstrate that random forest is a robust tool capable of handling complex data, in accordance with previous studies conducted by Jeong et al. (2016), when estimating crop yields at the global and regional scales, and by Philibert et al. (2013), when predicting N_2O global emissions. However, in contrast to the results of Philibert et al. (2013), the inclusion of a smaller number of input variables (11 rather than 14), as well as setting the hyperparameter values based on the data structure (Probst et al., 2019), clearly improved the performance of RF (e.g., Lapointe & Light, 2012). These findings can be explained by the fact that, in our dataset, certain independent variables were highly correlated with others that did not significantly contribute to the variability of the response variable.

4.2 Impact of measurement technique

One of the novelties of this study is that it assesses the incidence of the NH_3 measurement technique on the resultant cumulative fluxes. This was also performed by van der Weerden et al. (2021) but only including results from animal excreta and livestock manure under tropical climatic conditions. Recently, Zhang et al. (2022) found that wind speed is the principal cause of NH_3 quantification variations, mainly at > 1.5 m s^{-1}. Static chambers do not allow air movement and tend to underestimate emissions (Miola et al., 2015), while in dynamic chambers (e.g. wind tunnels) the air is drawn through the chamber at a constant rate and may not fully match the ambient conditions (Sanz-Cobena et al., 2011; Scotto di Perta et al., 2019). Micrometeorological methods are considered the most reliable techniques for on-site determinations (Sommer et al., 2004), and indeed led to 57% and 8% greater average EFs than static and dynamic chambers, respectively (Supplement 2, Table A.1). In agreement, van der Weerden et al. (2021) also found lower NH_3 EFs from static chambers than from other measurement techniques. The integrated horizontal flux method (IHF) has been presented as a reference technique, which is cost-effective and very robust in the quantification of fluxes (e.g., Sommer et al., 2004; Sanz-Cobena et al., 2008; Herrero et al., 2021). However, for the Mediterranean climate, the RF model indicates that the variations between the techniques are small, with measured emissions ranging from 12.3 to 13.8 kg NH_3 ha^{-1}. This is probably because the measurements of our database were taken mainly during calm periods (i.e., atmospheric stability) of wind, highly common in Mediterranean summer and winter, which limited volatilization (Theobald et al., 2015).

4.3 Crop management factors

In the Mediterranean climate, NH_3 volatilization – as well as N leaching in irrigated agroecosystems - is the main pathway of reactive N loss from fertilized crops (Lassaletta et al., 2021), so the independent variables related to fertilizer management are expected to be key drivers in the model's predictions. The study reported by Cai et al. (2023), who also used RF to rank the predictor variables, found that the N rate was the leading factor contributing to yield-scaled NH_3 emissions in paddy rice in China. Additionally, Ma et al. (2021) established that, globally, there is a strong positive correlation between soil NH_3 emissions after fertilization of cropping systems and the N input rate, which is in concordance with the tendency showed in our partial dependence plot (Fig. 4a). However, this behavior is not linear since the emission rate increased less when the N rate was below 170 kg N ha^{-1}. The nonlinearity between these variables shows that constant values for the EF cannot be assumed and depend on the N rate, as also mentioned by Jiang et al. (2017).

The influence of fertilizer type on NH_3 emissions in the Mediterranean climate has been widely studied (Turner et al., 2012; Bosch-Serra et al., 2014; Salazar et al., 2014; Verdi et al., 2018; Scotto di Perta et al., 2019; Vilarrasa-Nogué et al., 2020), so it is not surprising that the third- and fourth-ranked variables contributed to the variation of NH_3 emissions and EF, respectively. The partial dependence plots showed that pig slurries (ROL) had the greatest emissions when considering cumNH_3 (Fig. 4c), but urea had the greatest EF (Fig. 4i). Urea and slurries must be managed adequately; otherwise, the risk of NH_3 volatilization increases (Sutton et al., 2022). For urea, the mitigation strategies include the use of urease inhibitors (UIs), which, according to the RF model, reduced NH_3-EF by 20–23% under Mediterranean conditions, values far below the 45–80% found in other studies (Sanz-Cobena et al., 2008; Abalos et al., 2012; Lam et al., 2019). A complete and more updated database and a robust tool (RF) could explain these differences while pointing out the scientific soundness of the new emission values and mitigation efficacies. Besides, we obtained a relatively low EF for urea under Mediterranean conditions (11%, Fig. 4i), lower than the average value reported by Pan et al. (2016) or that obtained for urea (14.5%) in Ma et al. (2021). It is well known that when environmental or management conditions lead to low emissions rates, the relative efficacy of the mitigation practices such as UIs is masked (Abalos et al., 2014). This was also observed in Montoya et al. (2021), with intense rainfall during the first week after urea application. Lastly, a potential interaction between fertilizer sources and the measurement technique (with an influence on quantitative NH_3 volatilization rates) should not be discarded. Other strategies, such as other enhanced efficiency fertilizers (OEEF), had potential NH_3 mitigation effect. Yet caution must be taken since this category has few observations in the database. The use of UIs is also a strategy for ROL (Rodriguez et al., 2021), as well as the acidification of the slurry before application (TROL-N), reducing in both cases the EF by 16%, a small reduction compared to those (> 85%) reported by Fangueiro et al. (2015, 2018). The use of NIs, which increased NH_3 volatilization in our study (4–20% for synthetic fertilizers, Fig. 4c), delays the nitrification process and prolongs the retention of $NH4^+$ in the soil, increasing the risk of NH_3 volatilization (Qiao et al., 2015; Pan et al., 2016). However, some field studies and even global meta-analyses have not seen a significant effect of NIs on NH_3 emissions (Tufail et al., 2022). The field studies in which NIs did not increase NH_3 losses (Recio et al., 2020; Vilarrasa-Nogué et al., 2020) were performed under irrigated conditions, in which the incorporation of fertilizers with substantial amounts of water is expected to decrease NH_3 volatilization even with the application of NIs.

With regard to the N application method, a few of them such as incorporation and injection are expected to reduce NH_3 emissions, as they in turn reduce the exposure of the fertilizer to the atmosphere (Sanz-Cobena et al., 2014; Ti et al., 2019). However, N application method ranked fifth in importance for cumNH_3 and sixth in importance for EF (Fig. 3), which may suggest that selection of the best N application methods must be combined with other practices (e.g., N adjustment to crop needs) to enhance NH_3 abatement (Sanz-Cobena et al., 2023). Compared to broadcast, incorporation and injection have greater mitigation potential for organic (35–44%) than synthetic fertilizers (2–15%, Fig. 4e). The moderate effectiveness of these N placement strategies under Mediterranean conditions in comparison with those in NW Europe (Webb et al., 2014) could be associated with the relatively low NH_3 EF found in our study (10.5-11.7% for broadcast application, Fig. 4e) in comparison with those reported in other climatic conditions (e.g., 24.2% in van der Weerden et al., 2021). Moreover, incorporation and injection are not suitable when the crop is established (i.e., top-dressing) or in stony, compacted, and dry soils (Sutton et al., 2022). On the other hand, surface application with no incorporation showed a higher potential for NH_3 emission reduction than incorporation. This is probably because some observations of the database do not incorporate the fertilizer immediately, especially organic liquid fertilizer, with a delay between 6 and 24 hours, thus decreasing the efficacy of this mitigation practice.

The crop type also influenced the predictions of our two response variables. In the present study, rainfed crops such as oleaginous and winter cereals had the greatest emission rate, possibly due to the low rainfall amounts, which were sufficient to solubilize the fertilizer but not to incorporate it (Sanz-Cobena et al., 2011), or the common top-dressing applications, which make incorporation difficult. The crops requiring irrigation, such as maize and rice, have low cumulative NH_3 emissions and EFs, since water addition favours N incorporation within the upper soil, thus limiting the contact between NH_4^+ and the soil surface (Barakat et al., 2016).

4.4 Environmental factors

Our results showed that soil pH is the most influential environmental factor for NH_3-EF and its cumulative emissions, ranked first and second, respectively. The values of both response variables increase when soil pH is higher than 7 (especially above 8). This relationship has been widely studied by many authors, showing an increase in volatilization rates if soil pH increases, mainly due to the dominance of NH_3 over NH_4^+ (Bouwman et al., 2002; Cameron et al., 2013; Powlson & Dawson, 2022). These findings are important since a significant proportion of Mediterranean soils are calcareous, which have a pH above 7 (Kissel and Cabrera, 2005; Ryan et al., 2009).

So far, all meta-analysis studies addressing the influence of management and environmental factors on NH_3 volatilization (e.g., Xu et al., 2019; Ma et al., 2021; Cai et al., 2023) have considered climatic rather than meteorological conditions. This could have yielded a potential bias to the results of such studies due to the critical influence of specific conditions (wind, rain, temperature) after N application (mainly during the first week). To our knowledge, the present study is the first data synthesis study that has considered the meteorological conditions after fertilization as a possible determinant of cumNH_3 and EF. Within these meteorological factors, the mean temperature (from fertilization to the seventh day of measurements, AT) was the most important variable, ranking third in explaining EF. The partial dependence plot for AT indicates that EF ranges from 9.6 to 10.8% when the mean temperature is > 3°C. Although this behavior is in concordance with some studies in Mediterranean areas (Dinuccio et al., 2012; Salazar et al., 2012; Vilarrasa-Nogué et al., 2020), according to our results, neither cumNH_3 nor EF varied significantly as AT increased. Moreover, the maximum EF values (13%) occurred when the temperatures were low (2–3°C). In our database, the treatments with the lowest temperature registered are for broadcast ROL and by-hand synthetic fertilizer application. In the case of surface-applied synthetic fertilizers, Bosch-Serra et al. (2014) and Perin et al. (2020) found that low temperatures and high soil water content (SWC) may favour the solubilization of fertilizer granules, thus, leading to an increase in NH_3 volatilization rates. While for broadcast ROL, Bosch-Serra et al. (2014) and Sommer & Hutchings (2001) observed that when the infiltration slurry rate is low, the NH_3 emissions may continue for a prolonged period under low temperatures. Therefore, although the mean temperature was an important variable, its interaction with other environmental and crop management factors should be evaluated.

One of the ways to incorporate fertilizer is through rainfall or irrigation (PI variable), but it should be incorporated in the proper amount to avoid fertilization loss by leaching (Sutton et al., 2022). Although PI ranked ninth for NH_3 emissions predictions, it can reduce the NH_3-EF from 11% to 9% if it is the only mitigation practice to be used (Fig. A1). Sanz-Cobena et al. (2011) found that to incorporate urea properly, and achieve significant volatilization abatement, an irrigation rate > 7 mm is necessary. Moreover, for slurry (ROL), Sanz-Cobena et al. (2019) observed that NH_3 emissions significatively decrease when the fertilizer is applied just before rainfall events. According to our results, the greatest emissions occur when there is no water addition onto the soil during the first seven days after fertilization, which is a plausible scenario, especially for rainfed Mediterranean crops.

Soil organic matter and soil texture had a medium to little relevance in explaining cumulative NH_3 and EF. The partial dependence plot for SOM shows that the greatest EFs (approximately 12%) occur when the organic matter is greater than 13%. In our database, the only place where large SOM values are found is in Chile. Our results contradict some of the literature since soils with a large content of organic matter or clay (negatively charged ions) can retain NH_4^+ ions, removing them from the soil solution and thus reducing the volatilization possibilities (Kim et al., 2012; Cameron et al., 2013). Nevertheless, Cai et al. (2023) and Jing et al. (2020) suggested that large SOM content may increase soil urease activity and the N decomposition rate, which results in greater NH_3 emissions. These findings are in concordance with the results reported by Verdi et al. (2018), who found that after urea fertilization NH_3 emissions were higher when the SOM content was greater.

4.5 NH_3 vs N_2O from Mediterranean fertilized agroecosystems

The principal factors influencing NH_3 volatilization are not determined by the intrinsic Mediterranean characteristics, as with N_2O emissions. This is mainly because the Mediterranean climate particularities deeply affect the microbiological processes that govern N_2O, but not the physicochemical processes that generate NH_3 losses. Even so, the N rate (top-ranked factor for predicting cumulative NH_3 emissions) is indirectly influenced by the characteristic soil and climatic conditions of Mediterranean agroecosystems. Taking Spain as an example of a Mediterranean climate, Lassaletta et al. (2021) found a direct relationship between water input and the N rate in rainfed crops, as well as a significantly greater N rate in irrigated than in rainfed crops. The water supply limitation in Spain (little annual precipitation and drought events in summer) implies that most of the cultivated area has rainfed crops (83% in 2015, Supplement 4). The predominant N fertilization rate is between 17 and 102 kg N ha^{-1} (75% of the total cultivated area), with most N application rate below the threshold of 170 kg N ha^{-1} from above which the NH_3 emissions increase substantially according to our model (Fig. 4a). These rates contrast with those of temperate European countries, such as Denmark, the Netherlands, France, and the United Kingdom, where N rates applied to crops ranged between 100 and 320 kg N ha^{-1}. Although the relationship between NH_3 losses and N rates might differ from Mediterranean conditions, one may consider differences in N rates as an important feature distinguishing NH_3 patterns in Mediterranean and temperate agroecosystems.

This is the first study that assesses the behavior of NH_3 emissions in a Mediterranean climate zone, considering the influence of the measurement technique or the short-term meteorological conditions. However, soil and meteorological variables such as wind speed or the CEC were not included in the RF model because most of the studies comprising our database did not measure these parameters (even though we used the SOM content and soil texture as components of the CEC). In the crop management factors, most of our variables focused on fertilizer management. However, various meta-analyses reported an influence in NH_3 volatilization when tillage intensity varies (Sha et al., 2021; Cai et al., 2023) and/or when crop residues are left on the soil surface (Ti et al., 2019). This suggests that future studies should also give priority to these factors and evaluate how they behave depending on the crop type in the Mediterranean climate. Moreover, a limited dataset on water management (i.e., only 13% of the studies of our dataset were focused on irrigated crops), particularly high-frequency irrigation systems (e.g., micro-sprinkling and surface/subsurface drip irrigation) and systems promoting the incorporation of fertilizer into the soil (furrow irrigation), did not allow us to compare these strategies with other irrigation systems. Drip irrigation is a promising strategy to improve the timing and placement of N supply, as it is an effective N_2O mitigation strategy (Kuang et al., 2021) and it facilitates the application of fertilizers through fertigation. More research is needed to determine the potential of NH_3 emission abatement by applying N fertilizer via fertigation (especially urea) compared to other traditional practices. Our database also suggests that more field experiments should be conducted in maize and perennial crops to improve the robustness of the NH_3 volatilization factors and mitigation in these highly relevant agroecosystems (surface and economic value of the production) in Mediterranean countries. Finally, crop yield was not included in the model because this variable had a reduced sample size, limiting the estimation of NH_3 emission per unit of crop production (i.e., yield-scaled NH_3).

5. Conclusions

This study used the random forest technique to evaluate the NH_3 emissions in Mediterranean climate cropping systems, using a complex dataset that includes an NH_3 measurement technique, as well as edaphoclimatic and crop management data as predictor variables. The results showed good performance of the RF prediction model. The main drivers that affect NH_3 volatilization were not directly influenced by intrinsic Mediterranean characteristics, as is the case of N_2O emissions. For this study, the most significant factor was the N fertilization rate, and we determined that NH_3 emissions increase rapidly when the N rate surpasses the 170 kg N ha^{-1} threshold. This scenario, however, is not common in Mediterranean environments, where most of the cultivated area is occupied by rainfed systems in which the N rate is usually less than those applied to the irrigated crops or in rainfed cold-temperate agroecosystems. Other crop management factors, such as fertilizer type, crop type, and the N application method are dominant factors that contribute to the variations in NH_3 emissions. Soil pH and mean temperature during the field experiment were the most influential edaphoclimatic variables. These findings suggest that the mitigation of NH_3 emissions from Mediterranean agriculture should be focused mainly on N fertilization management. For instance, we obtained a more than 2-fold increase in volatilization rates and EFs using nitrification inhibitors. Other well-known NH_3 mitigation practices- such as the urease inhibitors, incorporation, or injection resulted in moderate mitigation efficacies compared with previous literature findings. For more robust mitigation strategies it is necessary that future field studies evaluate additional field management factors, such as different irrigation systems and tillage intensity.

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TABLES AND FIGURES

Table 1. Geographical distribution of the studies included in the random forest model.

Region	Country	Studies
Australia	Australia	Lam et al., 2019; Turner et al., 2012
California	USA	Chuong et al., 2020
Chile	Chile	Martínez-Lagos et al., 2013; Salazar et al., 2012, 2014
Mediterranean Basin	Italy	Badagliacca et al., 2018; Rana and Mastrorilli, 1998; Scotto di Perta et al., 2019; Verdi et al., 2018
	Portugal	Fangueiro et al., 2015, 2018
	Spain	Abalos et al., 2012; Abascal et al., 2019; Bosch-Serra et al., 2014; Corrochano-Monsalve et al., 2021; Guardia et al., 2021; Montoya et al., 2021; Recio et al., 2018, 2020; Sanz-Cobena et al., 2008, 2019; Viguria et al., 2015; Vilarrasa-Nogué et al., 2020; Yagüe et al., 2019; Yagüe and Bosch-Serra, 2013

Table 2. Predictor variables used in the random forest model to assess the main determinants of cumulative ammonia emissions (cumNH_3, kg NH_3 ha^{-1}) and the emission factor (EF, %) in Mediterranean environment areas.

Variable	Type[a]	Number of categories	Description
AT_02	Q	---	Average temperature after N fertilization to the second day after measurements (°C)
AT_37	Q	---	Average temperature from the third day to the seventh day of measurements (°C)
PI_02	Q	---	Average precipitation and irrigation after N fertilization to the second day after measurements (mm)
PI_37	Q	---	Average precipitation and irrigation after N fertilization to the second day after measurements (mm)
pH	Q	---	Soil pH before fertilization
SOM	Q	---	Soil organic matter (%)
Soil texture	C	3	Coarse, medium, or fine[b]
Crop type	C	7	Grassland/meadow, maize, industrial/oleaginous, perennial, rice, winter cereal, non-crop[c]
Water management	C	4	Rainfed or irrigated: flood, sprinkler, rainfed < 460 mm, rainfed > 460 mm[d]
Fertilizer type	C	10	AM, NI, UI, BI, OEEF, OS, ROL, TROL-N, TROL-O, U[e]
N rate	Q	---	Amount of N fertilizer applied (kg N ha^{-1})
N Application method	C	5	Broadcast organic fertilizer, by-hand synthetic fertilizer, incorporation, injection, surface no incorporation[f,g]
Measurement technique	C	3	Method used to measure NH_3: dynamic chambers, micrometeorological, static chambers

a Q = quantitative variable, C = categorical variable.
b coarse = sandy loam, sandy clay loam, loamy sand; medium = clay loam, loam, silty loam, silt; fine = clay, silt clay, sandy clay
c non-crop = includes bare soil, plowed soil before sown, soil with stubble.
d rainfed < 460mm = rainfed with an annual precipitation less than 460 mm, rainfed > 460mm = rainfed with an annual precipitation above 460 mm.
e AM = synthetic ammonia -base, NI = nitrification inhibitor in synthetic fertilizers, UI = urease inhibitor in synthetic fertilizers, BI = synthetic fertilizer combined with NI and UI, OEEF = other enhanced efficiency fertilizer (e.g., polymer-coated urea), OS = organic solid, ROL = raw organic liquid (cattle and pig slurry), TROL-N = treated ROL to reduce NH_3 emissions (e.g., slurry acidification or UI in the slurry), TROL-O = treated ROL to reduce other emissions (e.g., NI applied in the slurry or liquid separate digestate), U = urea.
f incorporation, injection and surface no incorporation includes both organic and synthetic fertilizer.
g Surface no incorporation includes band spreaders (no sufficient data to separate into trailing hose and trailing shoe) and treatments that incorporated fertilizer after 24 hours.

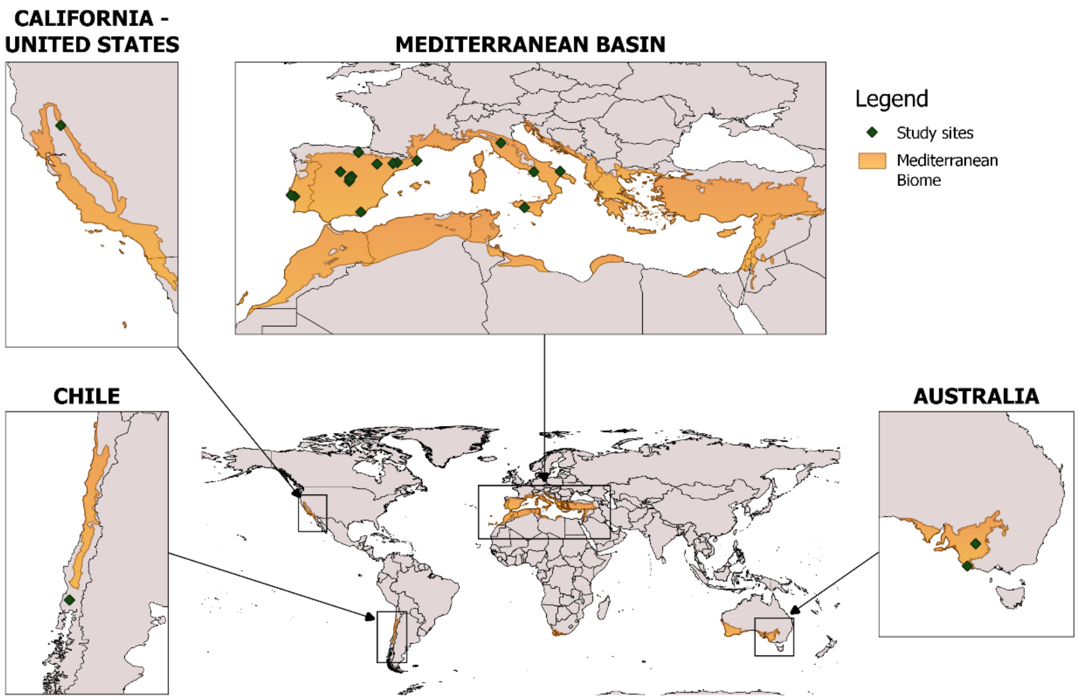
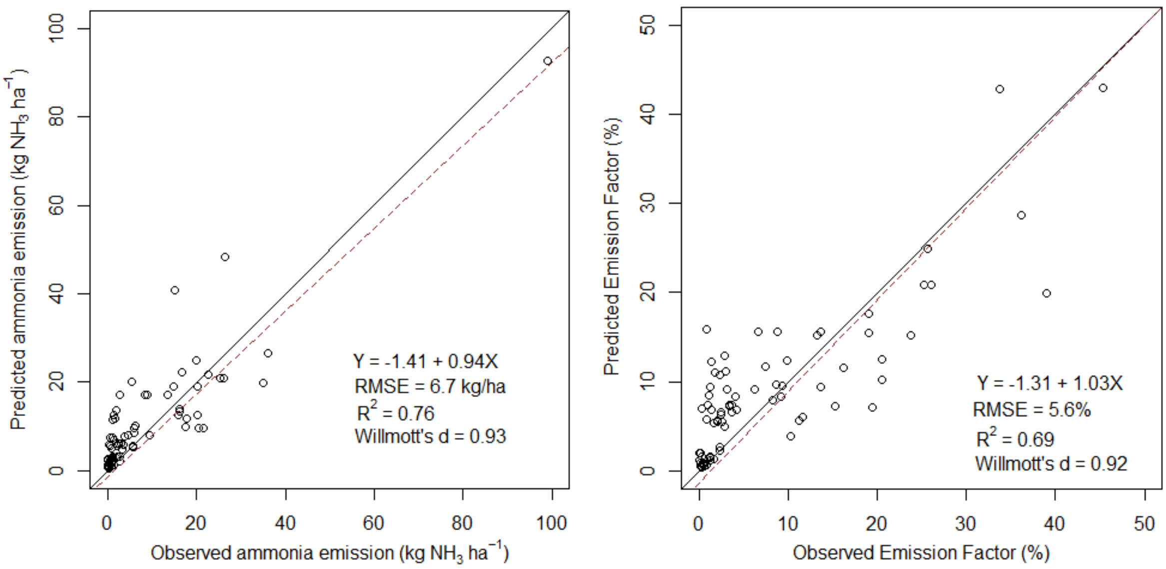


Fig. 1. Localization of the studies included in the random forest model within the Mediterranean biome, brown area.



The solid line is the 1:1 relationship between the observed and predicted values. The dashed line indicates the linear regression between the values. The final model equation, as well as the root mean squared Error (RMSE), the coefficient of determination (R^2) and Willmott's d (d) are also indicated.

Fig. 2. Observed vs predicted (a) cumulative NH_3 emissions and (b) ammonia emission factor with random forest.

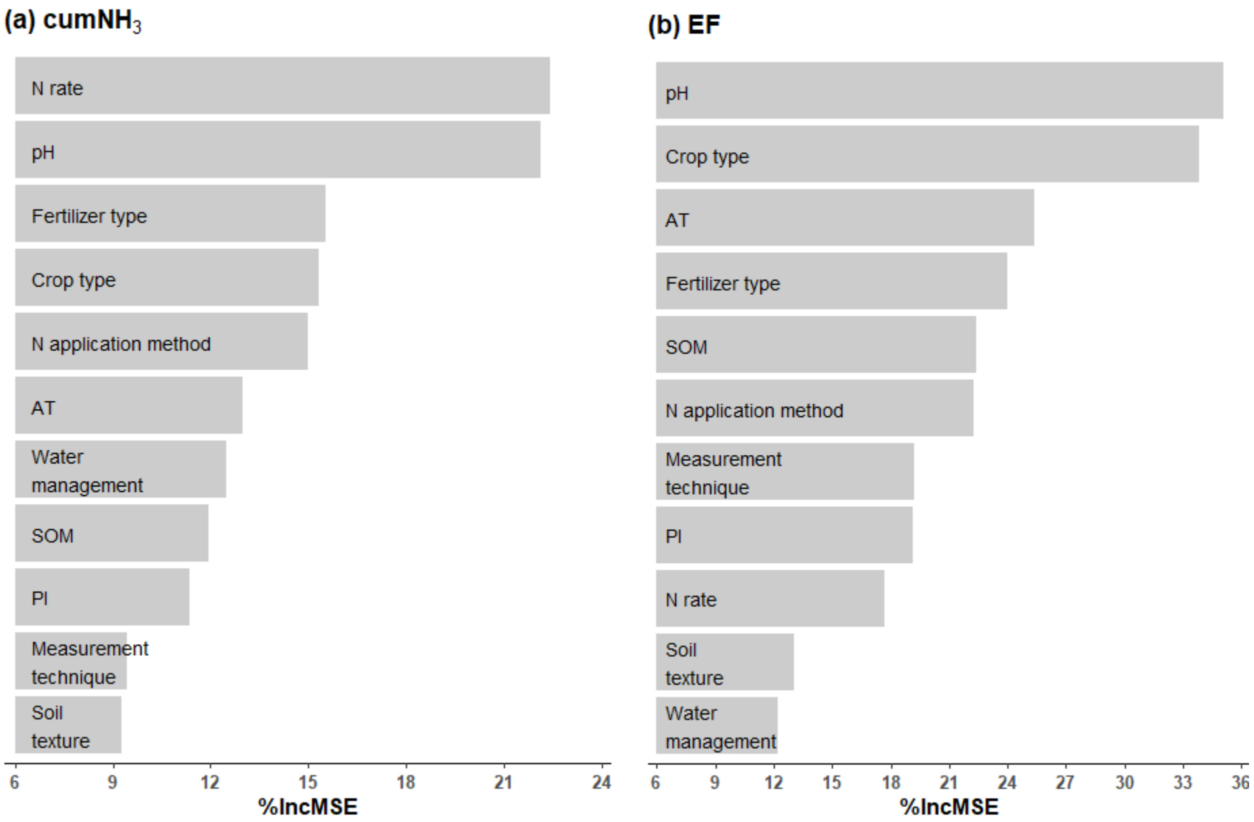


Fig. 3. Importance of the predicted variables in the estimation of (a) cumulative NH_3 emissions and (b) emission factor. Sorted in decreasing order of importance.

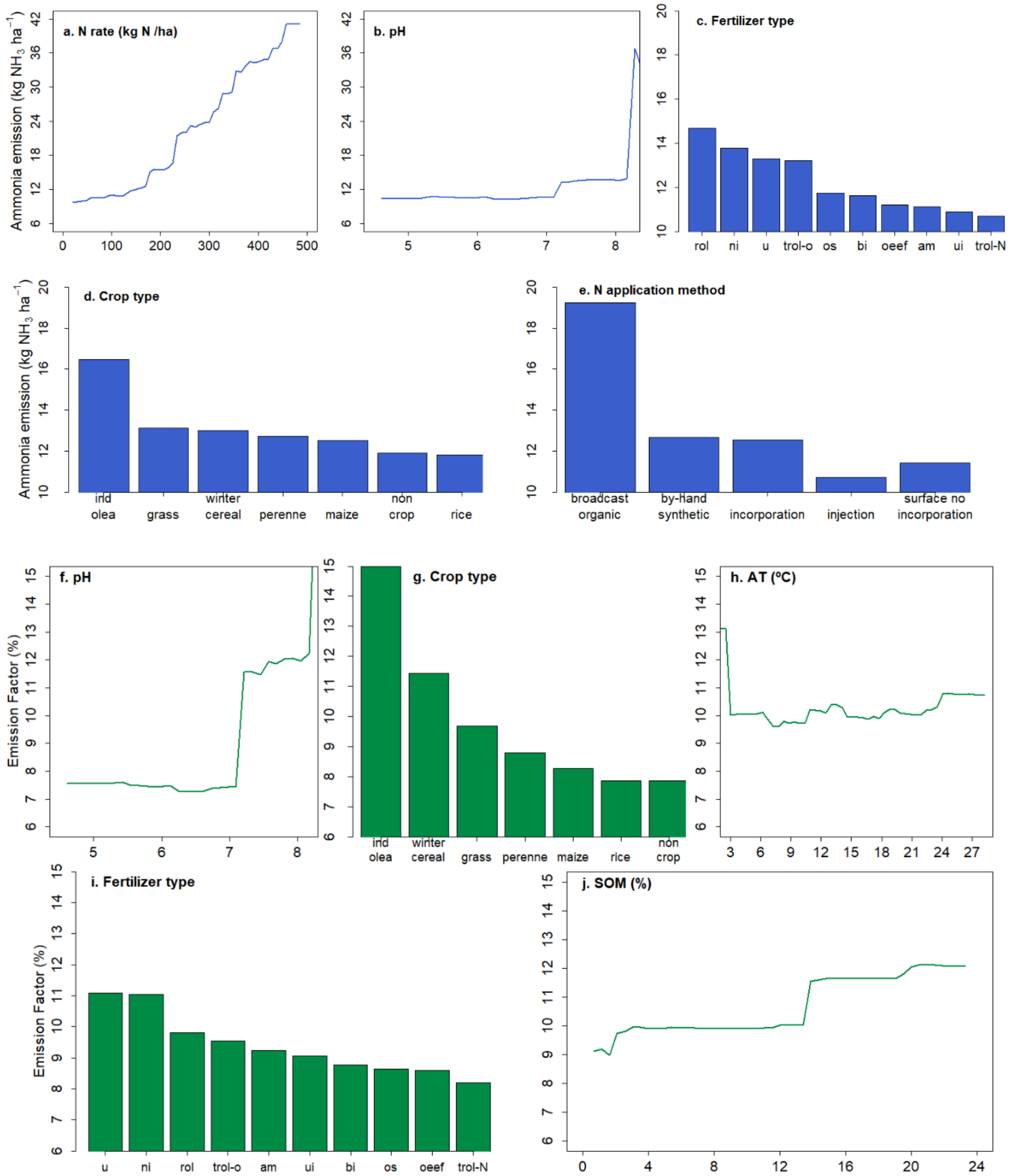


Fig. 4. Partial dependence plots for the five top-ranked predictor variables; (a) N rate, (b) soil pH, (c) fertilizer type, (d) crop type, and (e) N application method considering the cumulative ammonia emissions (cumNH_3) as the response variable, and (f) soil pH, (g) crop type, (h) mean temperature, (i) fertilizer type, and (j) SOM, considering the emission factor (EF) as the response variable. U = urea, NI = nitrification inhibitor in synthetic fertilizers, ROL = raw organic liquid slurry, TROL-O = treated ROL to reduce other emissions (e.g., NI applied in the slurry or liquid separate digestate), AM = synthetic ammonia-base, UI = urease inhibitor in synthetic fertilizers, BI = synthetic fertilizer combined with NI and UI, OS = organic solid, OEEF = other enhanced efficiency fertilizer (e.g., polymer-coated urea), TROL-N = treated ROL to reduce NH_3 emissions (e.g., slurry acidification or UI in the slurry).