LEX4BIO

Optimising bio-based fertilisers in agriculture

Providing a knowledge basis for new policies

Key LEX4BIO Outputs
E-booklet

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PREFACE

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Optimising bio-based fertiliser in agriculture – Providing a knowledge basis for new policies (LEX4BIO) is a Horizon 2020-project aiming to improve EU´s food security by replacing mineral fertilisers with bio-based fertilizers (BBF) while ensuring food safety, human health, and environmental protection. New Fertilising Products Regulation (2019/1009) sets criteria for CE-labeled fertilisers that can be produced from nutrient-rich side-streams (NRSS), e.g. manures, sewage sludges, biowaste or animal by-products. These nutrient streams constitute a significant source of nitrogen (N) and phosphorus (P) in the EU. However, these nutrient sources are unevenly distributed across the EU and often underutilized in agriculture. Where there is an excessive application, this can result in elevated P concentration in agricultural fields. However, several processing technologies exist for producing BBFs from NRSS with increased nutrient concentration for improving transportability to regions in demand for these nutrients. Improved use of such BBFs by farmers as well as acceptance at large requires knowledge about their agronomic efficiency and potential risks related to their use in various climatic and soil conditions across Europe. Nitrogen and P fertilizers production relies on non-renewable and strategic resources.

Phosphorus is in fact considered a critical raw material in Europe which is mostly imported. Fertilizer market is greatly affected by the unstable geo-political situation. Thus, self-sufficiency in fertilizers needs to be improved and circular economy provides tools for this target. This will contribute to reach ambitious goals set in the Green Deal and Farm to Fork Strategy. Bio-based fertilizers provide great potential for replacing mineral fertilizers and reaching targets set by the EU but their potential in crop production as well as related risks need to be known. In LEX4BIO we have evaluated the potential of BBFs to replace mineral P fertilizers at the EU level by utilizing existing soil P data and fertilization trials. This study showed that majority of crop P demand can be covered with BBFs. Unlike with P, gaseous N losses from fertilizers contribute both to economic losses and environmental deterioration. Laboratory trials showed that potential ammonia losses are affected by the properties of BBFs and soil, and with proper placement methods, ammonia volatilization can be greatly reduced. These studies showed that BBFs have a great potential to replace mineral fertilizers and improve Europe´s self-sufficiency in food production. I hope you enjoy reading these articles published in high ranked journals in 2022.

Assessing the phosphorus demand in European agricultural soils based on the Olsen method

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HIGHLIGHTS

- ***Identification of P-responsive sites is possible using a simple model for the estimation of Olsen P threshold values.***
- ***This will allow for a better allocation of P resources and more accurate estimates of P fertilizer rates.***
- ***Only 27.8% of croplands EU soils were P-responsive.***
- ***Most of the European P demand could be covered with a circular economy approach.***
- ***Results will contribute to agricultural sustainability and environmental performance in the use of P resource.***

ABSTRACT

Overcoming the consequences of future scarcity of P is crucial to ensure agriculture sustainability. This requires decision-making processes depending on data on the P status of agricultural fields, commonly conducted with soil P tests (SPTs), and efficient use of the resource on a societal scale following a circular economy approach. All this will decrease the P losses and the subsequent environmental impact. However, SPTs are not universal and, even for a given SPT, the definition of threshold values for fertilizer response is not accurate. This work aimed to define models to predict Olsen P threshold values, allowing the identification of P-responsive sites at the European scale as a basis for more accurate and sustainable P fertilization schemes based on a circular economy approach. To this end, a data set was compiled based on a literature review that describes the Olsen P threshold values for different crops under field conditions. Subsequently, an analysis of potential P fertilizer requirements was performed on agricultural soils of the European Union (EU) using the data set of the LUCAS project and how this need can be covered with a circular economy approach. Environmental factors were more relevant than crops to explain the variation in threshold values. A regression model involving soil pH and clay content and annual average rainfall as independent variables explained 61% of the variance in Olsen P threshold values. When soil pH and clay content were the only explanatory variables, the explained variance was 49%. This reveals the need to take into account factors related to P buffer and sorption capacity to estimate accurate threshold values. We detected that only 27.8% of EU cropland soils and 42.7% of grassland soils were P-responsive. We can conclude that a more precise allocation of the resource is possible in P-responsive sites and also that most of the European demand for P could be covered by recycling P from manure, wastewater, and municipal solid waste.

KEYWORDS

Fertilizer
Threshold value
Soil P test
Circular economy

ABBREVIATIONS

SPT *(Soil P test)*
GLM *(General Linear Model)*
AIC *(Akaike information criterion)*
RMSE *(Root mean square error)*
MAE *(Mean absolute error)*
LOOCV *(Leave-one-out cross-validation)*

1. Introduction

There is a general consensus in the scientific community on the implications that phosphorus (P), as a finite and highly strategic resource, will have on future agricultural production and food security (Cordell et al., 2009; Keyzer, 2010; Van Vuuren et al., 2010; Cordell and White, 2014; Cordell and Neset, 2014; Helin and Weikard, 2019). This is a particularly relevant issue in Europe, where agricultural production depends on imported P (Ott and Rechberger, 2012; Schoumans et al., 2015; Van Dijk et al., 2016). However, P is inefficiently used in society, and particularly in the food chain. Phosphorus in human diet or animal feed is usually higher than needs, and only a fraction of P is digestible. In fact, 54% of total P losses occur from human consumption, mainly from sequestration of P in sewage sludge and organic waste (van Dijk et al., 2016).

Relevant P losses can also occur in food processing, such as those of animal origin (e.g., bones). Thus, P in manure, food processing and urban waste and sewage sludge may account for a significant portion of P used in agriculture (around 80% according to van Dijk et al., 2016). On the other hand, there is an excessive accumulation of P in agricultural soils, the legacy P, resulting from inappropriate fertilization practices that usually leads to relevant environmental problems (Le Noë et al., 2018; Pavinato et al., 2020; Gatiboni et al., 2020). Thus, ensuring agricultural sustainability and consequently future food security requires more efficient use of the P resource at the societal scales, decreasing losses and increasing the environmental performance in its use (Schröder et al., 2011; Nesme and Withers, 2016; van Dijk et al., 2016). To this end, it is necessary: (i) more efficient P fertilization schemes involving a more accurate estimation of P requirements by crops, and (ii) circular economy approaches in the use of P that should take into account recycled sources of the nutrient.

Efficient P fertilization schemes should rely on a decision-making process involving: (i) data related to soil P status, usually chemical P extraction, the so-called soil P tests (SPT), (ii) interpretation of these data in relation to crop production, and (iii) fertilizer recommendations derived from this interpretation (Neyroud and Lischer, 2003; Delgado and Scalenghe, 2008; Jordan-Meille et al., 2012). Interpreting SPT in relation to crop production requires the definition of threshold values above which no yield increase is expected with P fertilization (Mallarino and Blackmer, 1992; Colomb et al., 2007; Jordan-Meille et al., 2012). This allows the focused application of the P resource to soils where the highest return of fertilization can be achieved, that is, sites responsive to P (Recena et al., 2016). Fertilization schemes recommend increasing P rates at decreasing SPT values (Tunney et al., 2003; Delgado and Scalenghe, 2008; Delgado et al., 2016). The target is to (i) increase the SPT values to a value around or above the threshold value and maintain it by replacing crop exports (“build-up and maintenance” strategy), or (ii) avoid P fertilization above the threshold values (“sufficiency strategy”). This latter option is intended to reduce the environmental risks ascribed to P loss and to improve the use of legacy P (Olson et al., 1987; Delgado et al., 2016; Le Noë et al., 2020). These schemes are essentially empirical, without a mechanistic basis, and are usually described in technical/grey literature more than in scientific literature (Jordan-Meille et al., 2012).

Although this decision-making process is common for P fertilizer recommendations in many regions of the world, the basis for its application, the SPT, is not universal. Many authors have described the reasons for the lack of universality of a given chemical extractant to be used as SPT (Delgado and Torrent, 1997; Delgado and Scalenghe, 2008; Jordan-Meille et al., 2012; Sánchez-Alcalá et al., 2015; Nawara et al., 2017). In summary, the ratio of P uptake to SPT values and the relationship between crop yield and SPT values vary depending on (i) soil properties affecting P dynamics and extractant performance, and (ii) dominant P forms. These reasons also hinder the estimation of the values of a given SPT based on other SPTs in soils that vary widely in their properties. As an example, in a European soil collection, Barberis et al. (1996) observed that the relationship between the Ca lactate method (Schuller, 1969) and Olsen P (Olsen et al., 1954) did not allow an accurate estimation of values of one method based on the other (R2 = 0.35). In this soil set, the ratio of total available P in soil, determined by cumulative P extraction in successive crops until depletion of the available pool, to Olsen P decreased with increasing soil pH (Delgado and Torrent, 1997). In fact, this means that the threshold values will vary for the same SPT depending on the soil properties. In practice, many SPTs have been developed for specific geographic regions, and around 10 official tests have been described in Europe alone (Neyroud and Lischer, 2003; Jordan-Meille et al., 2012). However, even for a given SPT, the ratio of P uptake to SPT value and the threshold values for fertilizer response may vary within a region with relatively homogenous soil types (Sánchez-Alcalá et al., 2014; Recena et al., 2015, 2016; Tandy et al., 2021). Only methods based on near-infinite P sinks seem to provide more homogeneous ratios of P uptake by crops to extracted amounts (Delgado and Torrent, 1997; Tandy et al., 2011; Santner et al., 2015; Recena et al., 2017), but their practical performance in labs is more complex. Additionally, there is less information on the field scale on the threshold values for fertilizer response for such methods. Thus, a conjunction of factors, involving also tradition and legal aspects in fertilization (some extractions are official methods), slows progress in the definition of new accurate and easy-to-apply SPTs.

All this makes it difficult to define a picture on a continental scale, allowing the definition of a general scheme to assess the current status of P in the soil in relation to crop yields and fertilizer demand. Tóth et al. (2014) described the European Union situation based on Olsen P, perhaps the most common SPT used in scientific literature, using the LUCAS project dataset (https://esdac.jrc.ec.europa.eu/projects/lucas). However, this study did not consider that Olsen P fails to identify P-responsive sites for such a large collection of soil samples, as threshold values are affected by soil properties. This can be solved with an estimate of threshold values based on soil properties routinely determined in soil analysis, as proposed by Recena et al. (2016). However, these researchers made a proposal based on pot experiments and with a soil collection with a relatively limited range of properties (e.g., pH ranging from 6.5 to 8.3). To use this approach in the estimation of Olsen P threshold values on the European scale, evidence of its suitability is required in soils that vary widely in their properties. In addition, it is necessary to define the relationship between Olsen P and the yield based on field experiments under a wide range of climatic conditions and crops. We hypothesized that it is possible to accurately estimate the Olsen P threshold value using routinely determined soil properties, climatic conditions, and crop type. Since only a minor part of P in human diets or animal feed is really accumulated in consumers, it can also be hypothesized that there is room for a significant recovery of P from wastes to use this non-renewable resource more efficiently, thus decreasing losses and subsequent environmental impact. The objectives of this work were, on the basis of a literature review, (i) to define a simple model for the estimation of Olsen P threshold values that will allow the identification of P-responsive sites at the European scale, as a basis for a more accurate and sustainable decision-making process in P fertilization, and (ii) to assess the potential of P recycling to cover needs in agriculture at the European scale as a basis for a circular economy-based strategy in the management of the P resource.

2. Materials and methods

2.1. Dataset

The literature review was performed using scientific databases (Web of knowledge and Scopus, Science Direct, University of Minnesota, Rothamsted research, Wiley Online Library, CSIRO, Soil Science Society of America), Google scholar, and Google since the information may also be as technical/grey literature. To this end, the following keywords or their combinations were used: phosphorus, Olsen, threshold value, long-term fertilization, critical soil P, soil test, availability, crop yield, phosphorus status, long-term fertility, fertilizer recommendations, fertilizer use efficiency. The selection of the information was not limited to Europe to encompass a wide variability in crops and environmental conditions.

Articles, book chapters, and congress proceedings were selected if they clearly defined Olsen P threshold values for fertilizer response. This could be done on the grounds of different statistical approaches, usually linear-plateau or linear-linear fittings, Mitscherlich-type fittings (Mallarino and Blackmer, 1992; Black, 1993), or Cate-Nelson method (Cate and Nelson, 1971). For all of these methods, the relationship between relative yield, i.e., the ratio of yield in non-fertilized soil to non-P-limited yield, and the Olsen P values in soil, is established. For linear-plateau or linear-linear, the threshold value is the intersection between the two linear segments. In Mitscherlich, the threshold value corresponds to a yield of 90 or 95% of the maximum attainable yield when P is the only limiting nutrient. In the Cate Nelson, the dataset is graphically separated in two populations (one responsive and another one non-responsive), or it can be estimated as the Olsen P value that maximizes the sum of squares between two populations of Olsen P values (Geng et al., 2014; Recena et al., 2016). The expression of yields on a relative basis in the estimation of the threshold value allows the comparison of results across experiments, sites, and years (Meisinger et al., 1992; Bilbao et al., 2004).

A total of 149 cropland cases providing threshold values for different crops were identified in 37 publications. For grasslands, 69 cases were found in 10 publications. However, only clearly identified crops and sites with soil information (at least pH) were considered (83 for croplands and 28 for grasslands). The references finally used are shown in Table S1. For each selected case/site, available information on soils, including clay content, organic C content of soil, Ca carbonate equivalent, and pH ($CaCl_2$, KCl or water), and average annual rainfall and temperature was compiled. If the average rainfall and temperature were not available in the publication, it was obtained according to geographical coordinates through the web sites of https://es.climate-data.org, and https://weatherspark.com with an average of at least 9 years. To discriminate the most useful data, pH in water or in very dilute electrolytes ($CaCl_2$ in a soil-to-electrolyte ratio of 1:10) was taken into account. For all cases, except those described by Nawara et al. (2017), the pH in water was considered. In the case of Nawara et al. (2017), for soils with neutral pH and low buffer capacity (low clay content), the difference between pH in water and 0.01 M $CaCl_2$ (1:10) is expected to be minimal.

The statistical method for estimation of threshold values may have a large influence, as described by Mallarino and Blackmer (1992). Overall, a different threshold value is expected with different methods, usually in the order Cate-Nelson < Linear-linear/plateau < Mitscherlich 90% relative yield < Mitscherlich 95% relative yield. Thus, it is necessary to bear in mind homogeneous statistical methods for analysing studied cases. In most of them, the Mitscherlich-type model was used to estimate threshold values. In other cases, several statistical methods for estimating the threshold values were used; in that case, Mitscherlich was preferred, since most authors used this method. In general, this method provides the strongest explanation of the variance in relative yields with the Olsen P value (highest R2). If only one method different from Mitscherlich was used, this was considered, but all these cases corresponded to Cate-Nelson. Overall, we took as threshold values those reported by the authors, without any additional calculation or modification, which is not possible, since we do not have access to raw data in most of the cases. Cate-Nelson allows the identification of the non-responsive population when the Mitscherlich or linear-linear/plateau fittings have poor significance. When the authors used the Mitscherlich-type model, among others, for estimating threshold values and the asymptotic limit was clearly below 90% of maximum relative yield, then threshold values for these cases were considered according to other statistical approaches and were checked with a visual Cate-Nelson approach. This occurred in 7 cases described in two studies: (i) Tang et al. (2009) (6 cases for wheat and one for maize) in which the average of the data provided by the authors was considered using linear-linear and linear plateau methods, and (ii) Sandaña et al. (2018) (1 case for potato), in which the visual Cate-Nelson was used to obtain a threshold value based on data provided by the authors in figures. Data from the Ath experiment (Belgium) provided by Nawara et al. (2017) were excluded from the analysis since the threshold values were much higher than the average of other cases (76 for barley and 61 mg kg−1 for potato, around three times the average for other experiments) and the non-fertilized control in this site provided around 95% of the relative maximum yield. The experiments of Poulton with wheat and Gembloux with flax described by Nawara et al. (2017) were also excluded due to the very high threshold values defined (46 mg kg−1 for wheat, around 4 times the average for other cases and 40 mg kg−1 for flax, which cannot be compared with other cases, as it was the only reference with this crop). Taking these assumptions into account, from the 83 cases of croplands mentioned above, a set of 79 cases with soil pH data, rainfall, and temperature was finally considered for statistical analysis (Table S2). Within this set, 60 cases with soil clay content were present and 59 cases included data on soil organic C content. In the case of grasslands, we used the 28 cases mentioned above for the analysis.

2.2. European soil database

We used the LUCAS soil project (https://esdac.jrc.ec.europa.eu/projects/lucas) with the information published for the 2015 sampling campaign. In this database for the EU-28 (including the United Kingdom), the following soil parameters are available: texture, pH, organic C, electrical conductivity, and soil nutrient test, including Olsen P values. We used soil data of agricultural fields with two categories: “croplands” and “grasslands”, with 8946 and 4751 soil samples included, respectively.

2.3. Estimation of P fertilizer needs

Strategies for estimating P needs are described in Table 1, with indication of the calculation method. In both strategies, soils below threshold values have a “build-up component” that is added to crop P exportations. This building component is designed to progressively increase Olsen P in soil until the threshold value is reached avoiding excessive P rates in only one year. However, this increase can take many years and a periodic control of P Olsen in the soil is recommended. For its estimate, the bulk density of soils is necessary, and a soil depth of 25 cm was chosen for the calculations. There is no European data set on soil bulk density. Therefore, we used the pedotransfer function proposed by Hollis et al. (2012) based on a European set of topsoils from 333 croplands. For each LUCAS soil sample, the bulk density was estimated according to this function using organic C and texture data. The estimated average bulk density was 1.38 and 1.23 Mg m−3 for croplands and grasslands, respectively.

Table 1. Table 1. Models for estimating P fertilizer requirements (adapted from Delgado et al., 2016).

Strategy	***Target***	***Estimate of P fertilizer rate***
Build up and maintenance	Soil above threshold value and replace P exportation to maintain the soil P status above threshold value	P rate (kg ha−1) = Exported P + 10 BD Z (POlsent – POlsens) Above threshold value, P rate = Exported P P rate < 100 kg P ha−1 P rate may decrease with increasing soil Olsen P above the threshold value; e.g. by avoiding P fertilization when Olsen P > 2 threshold value
Sufficiency	P fertilization only if SPT < Threshold value (response to P fertilization)	P rate (kg ha−1) = Exported P + 10 BD Z (POlsent – POlsens) P rate < 100 kg P ha−1 No fertilization over threshold value

POlsent, Olsen P threshold value; POlsens, actual soil Olsen P value; BD, bulk density (in Mg m−3); Z, soil depth considered in fertilization of non-mobile nutrients (typically 0.15–0.3 m depending on crops).

The limit of total P fertilization is to avoid the enhancement of P sorption reactions that may decrease the efficiency of applied P in increasing soil available P and P uptake by crops.

The term 10 BD Z (POlsent – POlsens) is assumed the “build up” component intended to progressively increase the available P status of soil. It is estimated on the grounds of assuming that all applied P is transformed in bicarbonate extractable P (Olsen P). However, this does not occur and it has to be considered as an annual fertilizer recommendation till the threshold value is reached (achieved in several years, depending on the P buffer capacity of soil), and the value is defined to avoid excessive P supply for building up the soil available P.

The total P required for the “build-up component” can be estimated on a European scale on the grounds of the agricultural surface ascribed to each P rate class. These classes were calculated based on the current Olsen P value and the estimated threshold for each case. We can assume that the LUCAS project dataset is representative of all cropland and grassland in Europe. The agricultural surface in the European Union (2016, EU-28, including the United Kingdom) accounted for 175.2 million ha in 2015 (https://ec.europa.eu/jrc/en/publication/eur-scientific-and-technical-research-reports/trends-eu-agricultural-land-within-2015-2030), 66% of this corresponding to croplands (including permanent crops) and 34% to grasslands. The relative frequency of each P rate category (with mean values differing in one unit, 1 kg P ha−1) was multiplied for cropland's and grassland's total surface to estimate the surface with a given P requirement. The sum of the P requirement for each category was assumed to be the total P demand for the build-up component in EU-28 including the United Kingdom.

To estimate P needs in croplands, it is necessary to take into account P export with crops. For the major crops (49) in the EU-28 in 2015 (https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Agricultural_production_-_crops), the P export was estimated by multiplying the exportable yield by its usual P concentration according to USDA data compiled by Delgado et al. (2016) and Helin and Weikard (2019). The estimate of grassland P exportation was made on the ground of the grassland surface in different climatic zones with different productivity according to the CORINE land cover database of the year 2000 (Tóth et al., 2014), assigning an average productivity per zone according to Smit et al. (2008), and considering an average P concentration in grass and fodder of 3 g kg−1 (Panagos et al., 2022).

2.4. Statistical analysis

The study of the effect of the factors 'land use' (cropland or grassland) and 'crop' on threshold values was first performed using the Kruskall-Wallis test to evaluate median differences instead of the general linear model procedure (GLM) using Statgraphics Centurion XVIII software (Stratgraphics Technologies, 2018). Although data of threshold values were normally distributed, a non-parametric test was preferred given the differences in the dispersion data for each category of crop and land use.

The relationship between threshold values and soil properties, rainfall, temperature and crop was studied using the GLM and with multiple regressions based on the least squares method when only quantitative independent variables were taken into account. In the case of qualitative variables, the performance of dummy variables (binary) is required for the application of the GLM. The dimension of the model, that is, the number of variables to be included, was defined using the Akaike information criterion (AIC; Akaike, 1974), and the accuracy of the model was checked by the Mallows Cp statistic (Gilmour, 1996). All the explicative variables in the regression model were significant according to the t statistic at $P < 0.05$ and were not correlated with each other. The goodness of the regression model was checked on the basis of the determination coefficient (R2) which provides an information on the total variance explained by the model, and consequently of its predictive power (Altman and Krzywinski, 2015) and the root mean square error (RMSE), which provides an absolute measure of the predictive accuracy of the model. Good models should provide high R2 and low RMSE. The mean absolute error (MAE), i.e., the mean of absolute values of the difference between predicted and actual values, was used as the estimate of the prediction error.

Predictive models were validated by leave-one-out cross-validation (LOOCV) using partial least squares (Wold, 1980). Leave-one-out is an iterative method that starts by using as a training set all the available observations except one, which is excluded for use as validation. The process is repeated as many times as there are available observations. This avoids the limitation of a non-extensive dataset (60 cases including soil pH and clay content), for selecting a training set and a validation set. With the cross-validation, R2 and predicted R2 of the model are compared to assess if there is overfitting in the model i.e., if predicted R2 are clearly lower than R2, the model fails to predict future observations reliably.

The root square mean error (RMSE) was used to estimate the confidence levels for the prediction of the observed values (prediction intervals). The upper confidence level for the prediction (relevant for defining a threshold value) at 90% can be estimated as the predicted value + 1.3 RMSE (1.3 = t value for a tailed distribution and $\alpha = 0.1$). The test to assess the significant differences between regressions was performed using the same software described above. To this end, a new regression with joint data of both regressions was performed with the introduction of a categorical variable. The interaction between the categorical variable and the explicative variable was evaluated to check the null hypothesis, i.e., no differences between the regression coefficients, by means of an analysis of variance.

3. Results

3.1. Olsen P-threshold value for fertilizer response in different crops

The soils in the studied cases showed a wide range of properties. For croplands, the pH ranged between 4.7 and 8.6 (n = 79), soil organic C from 3.2 to 83 g kg−1 (n = 59), clay content from 50 to 610 g kg−1 (sandy to clay textures, n = 60), annual rainfall from 263 to 1535 mm and average annual temperature from 4.6 to 26.9. For grasslands, the ranges were: pH 4.5–7.9, clay 182–580 g kg−1, soil organic C 15.3–553 g kg−1, and annual rainfall 668–1591 mm (Table S2).

In the 79 cropland cases finally included in the analysis, the P threshold values ranged between 3.2 and 32 mg kg−1 (Fig. 1). The lowest value corresponded to lowland rice, cultivated under flooding. The upper (Q3) and lower quartile (Q1) were 16 and 9 mg kg−1, respectively, which provides an idea of the range of more usual values. In the case of grasslands (n = 23), the threshold values varied in the range 5.3–36.1, with Q1 and Q3 of 12.4 and 19.4 mg kg−1, respectively.

The effect of agricultural use (croplands or grasslands) was not significant according to the Kruskall-Wallis test. The different crops had a significant effect on the Olsen P threshold values according to this test (Fig. 1; P = 0.034). Overall, tuber and root crops showed higher threshold values than cereals. The Q1-Q3 range in cereals was 8.1–17 mg kg−1, meanwhile that for potato and sugar beet was 17–25 mg kg−1. The average Olsen P for sugar beet and potato (20.3; n = 4) was higher than that of cereals (12.6; n = 67) or pulses (soybean, 8.4; n = 6), and industrial crops showed intermediate values (13.9; n = 2). When the analysis was performed excluding root and tuber crops, there was no significant effect of the crop on the Olsen P threshold values (not shown); however, most of the cases (67 of 79) corresponded to cereals. The average Olsen P threshold value for maize was influenced by two high values, while the median value was the lowest among cereals (Fig. 1).

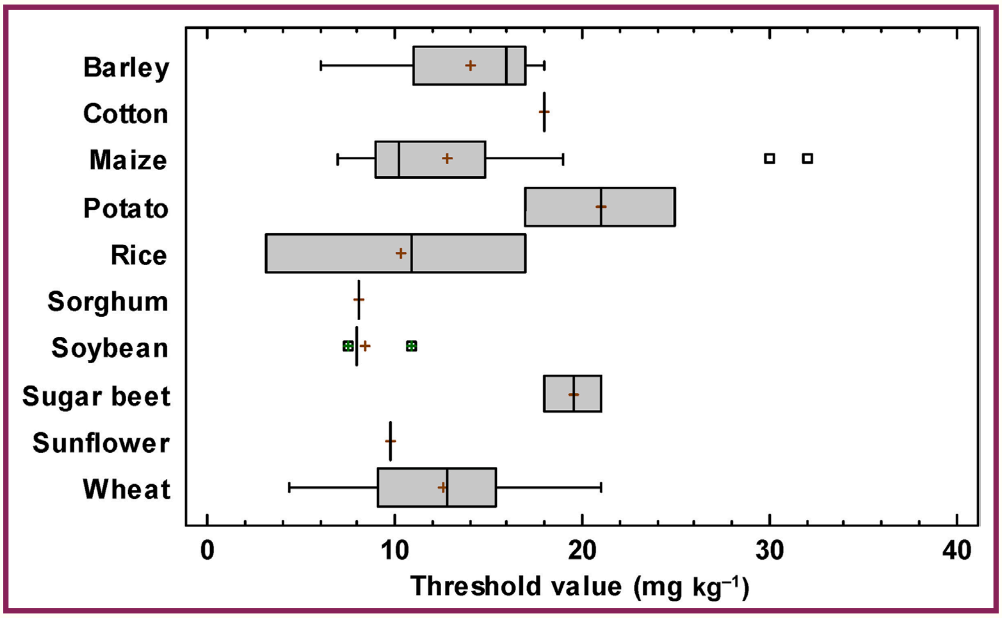

Fig. 1. Box and whisker plot of the Olsen P threshold values for P fertilizer response for different crops in croplands (n = 79). The effect of agricultural use on threshold values was not significant, and the effect of crop in croplands was significant according the Kruskal-Wallis non-parametric test (P = 0.034). In the case of rice, the threshold value is very low in the case of paddy soils (lowland rice). Excluding rice, Q1-Q3 values are in the range 9–25 mg kg−1.

3.2. Estimation of the Olsen P threshold values

In the data set that included the soil clay content (n = 60), the best model to predict the threshold values involved the soil clay content and pH and the annual rainfall, explaining 61% of the variance in the threshold values (Y = 51.5–0.011 Clay – 4.3 pH–0.008 Rainfall; Fig. 2). Predicted R2 in the LOOCV with the best combination of components was 0.55, slightly lower than the R2 of the model (0.61). Thus, there is no significant overfitting, and we can assume that the model can reliably predict future observation. When clay content and pH were the only explicative variables in the model, 49% of the variance in threshold values was explained with a mean absolute error of 3.4 mg kg−1 (Y = 43.7–0,016 Clay – 3,81 pH; Fig. 3).

This regression model was not significantly different from the previous work in pots of Recena et al. (2016). For the regression model, predicted R2 in the LOOCV was 0.42, and consequently it can be considered reasonable to predict future observations.

When crop was included in the GLM in addition to clay, pH, and rainfall, its effect was not significant. Organic C of the soil or the temperature did not have any predictive value for the Olsen P threshold values. In all cases, the models clearly worsened if grassland data were included. When GLM was performed only for grasslands, there was no significant relationship between Olsen P threshold values and any explicative variable mentioned above.

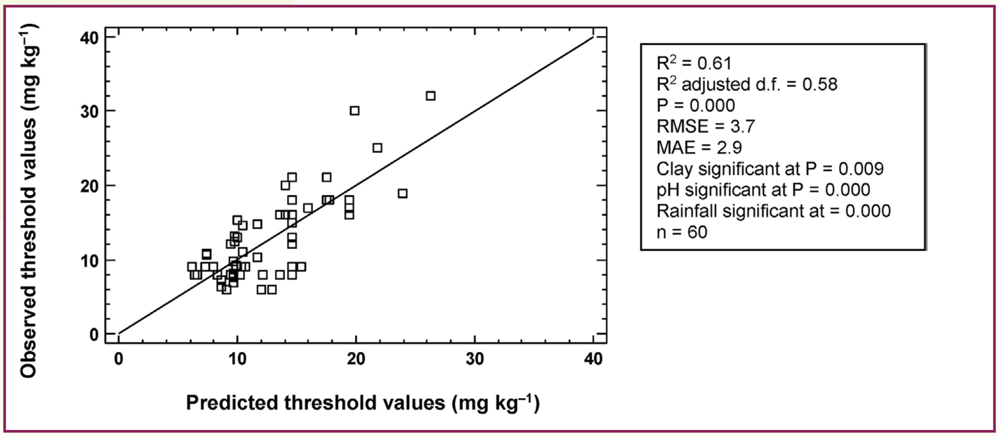

Fig. 2. Multiple regression for explaining the effect of soil clay content, pH and rainfall in croplands on Olsen P threshold values (Y = 51.5–0.011 Clay – 4.3 pH–0.008 Rainfall). Threshold values have a normal distribution according to the Kolmogorov-Smirnov test (P < 0.05). RMSE, root mean square error; MAE, mean absolute error.

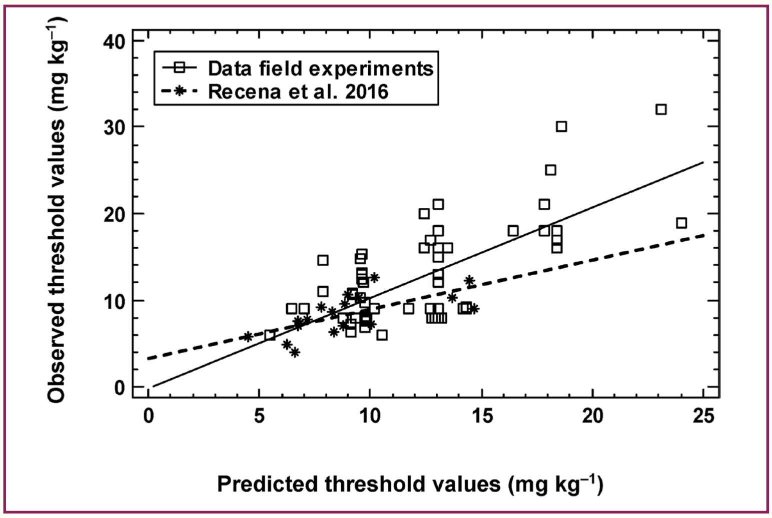

Fig. 3. Estimation of Olsen P threshold values for fertilizer response with the model for studied cases based on field experiments (solid line): Y = 43.7–0,016 Clay – 3,81 pH; R2 = 0.49; P = 0.000; n = 60) RMSE = 4.1; MAE = 3.4. Clay significant at P = 0.001, and pH significant at P = 0.000.

This model (intercept and slope) is not significantly different from that obtained by Recena et al. (2016) in a pot experiment: Y = 36–0.012 Clay – 3.75 pH; R2 = 0.81; P = 0.000 (n = 16) (dotted line).

RMSE, root mean square error; MAE, mean absolute error.

3.3. Status of phosphorus availability in European soils

With a conservative approach, the confidence levels for the prediction of the threshold values for crops were defined at 90% (Table 2). Thus, a low risk of having a real threshold value higher than that estimated with the model can be assumed. Under a sufficiency fertilization strategy, i.e., P fertilization only when soil Olsen P is less than the threshold value, this minimizes risks of P deficiency in crops. In the cases of grasslands, since there was no possible prediction based on soil or climatic properties, the upper quartile was taken as the threshold value under a conservative approach.

Approach	*Model (threshold values in mg kg^{-1})*
Croplands	
Conservative[a]	Y = 49–0.016 Clay – 3.81 pH
Minimal[b]	Y = 43.7–0.016 Clay – 3.81 pH
Graslands	
Conservative[c]	19.4
Minimal[d]	14.9

Table 2. Models for estimating Olsen P threshold values.

Clay in g kg^{-1}; pH in water or dilute electrolyte (1:10 $CaCl_2$).

[a] Estimated threshold values according to models in Fig. 4 are increased by 1.3 x RMSE in order to include the 90% confidence levels of the predictions.

[b] Estimate of the average values according to models in Fig. 4; in this case, it should be taken into account the risk of infra-estimation (the mean absolute error of the regression model is 3.4).

[c] Lower limit of the upper quartile of values of grassland cases (n = 23).

[d] Average value of all the grasslands cases.

On the European scale (Fig. 4), the estimated threshold values in croplands based on clay content and pH of soils increased from south to north and from east to west. This reflects the geographical distribution of both soil properties affecting threshold values for fertilizer response. When conservative approach estimates were applied to the LUCAS cropland soil dataset used in this study, only 27.8% of the soils were P-responsive (Olsen P to threshold value ratio <1), while 39.3% had Olsen P values greater than twice the threshold values (Fig. S1; Table S3). In the grasslands soil set, 42.7% of the soils were P-responsive and 29.8% showed Olsen P values higher than twice the threshold values (Fig. S2; Table S3). When the analysis was done by country, relevant differences were found in the ratios of Olsen P to the threshold value for croplands (Fig. 5, descriptive statistics in Table S3). Overall, Belgium and the Netherlands showed median values of the Olsen P to threshold value ratio of around 4. In Germany, these values were frequently around 3. On the other hand, the Olsen P values were frequently below threshold values (ratios <1) in Bulgaria, Greece, Lithuania, Romania and Portugal (Fig. 6). For grasslands, the situation was very similar, with Benelux countries showing median values of the Olsen P to threshold value ratio higher than 3 (Fig. 6). Overall, the lowest Olsen P values in soil relative to the threshold values were found in some Eastern and Mediterranean countries. Between crops, potato and sugar beet tended to be clearly overfertilized, with the lower quartile of the Olsen P to threshold value ratio well above 1 (Table S4). Between cereals, maize was the crop showing the highest Olsen P to threshold values ratios, also with the lower quartile above 1. Some horticultural crops (orange, strawberry) were also clearly overfertilized.

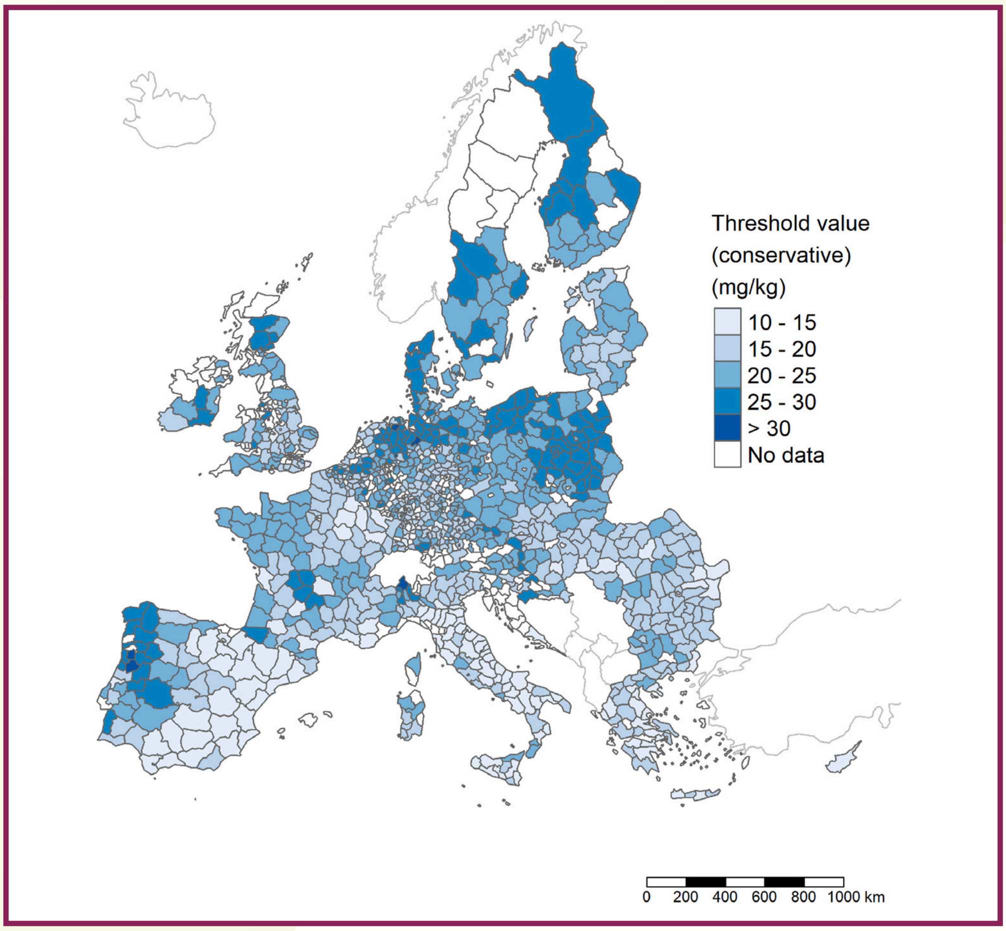

Fig. 4. Distribution of Olsen P threshold values for croplands in the European Union (EU-28 including United Kingdom). The figure represents median values by NUTS3 regions according to the conservative model for threshold value estimation based on soil clay content and pH proposed in Table 2.

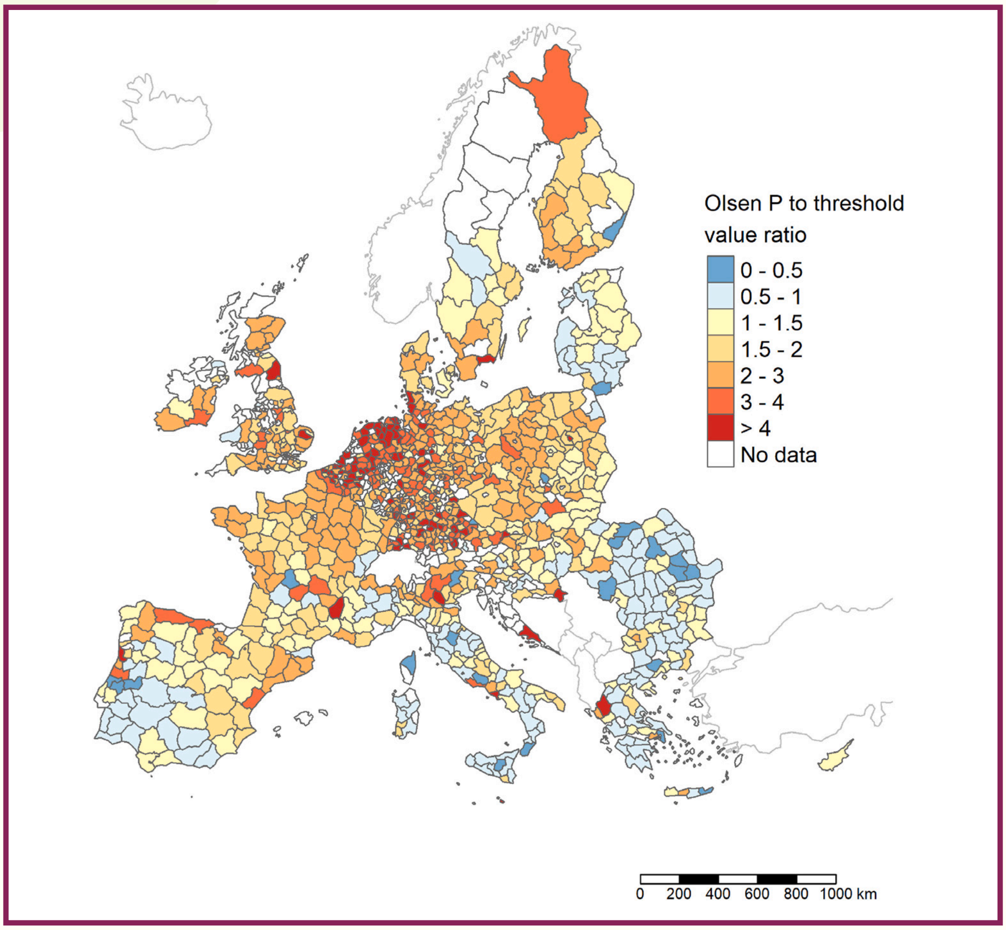

Fig. 5. Olsen P to threshold values ratio for croplands in the European Union (EU-28 including United Kingdom). The figure represents median values by NUTS3 regions according to threshold values estimated according to the conservative model based on soil clay content and pH (Table 2).

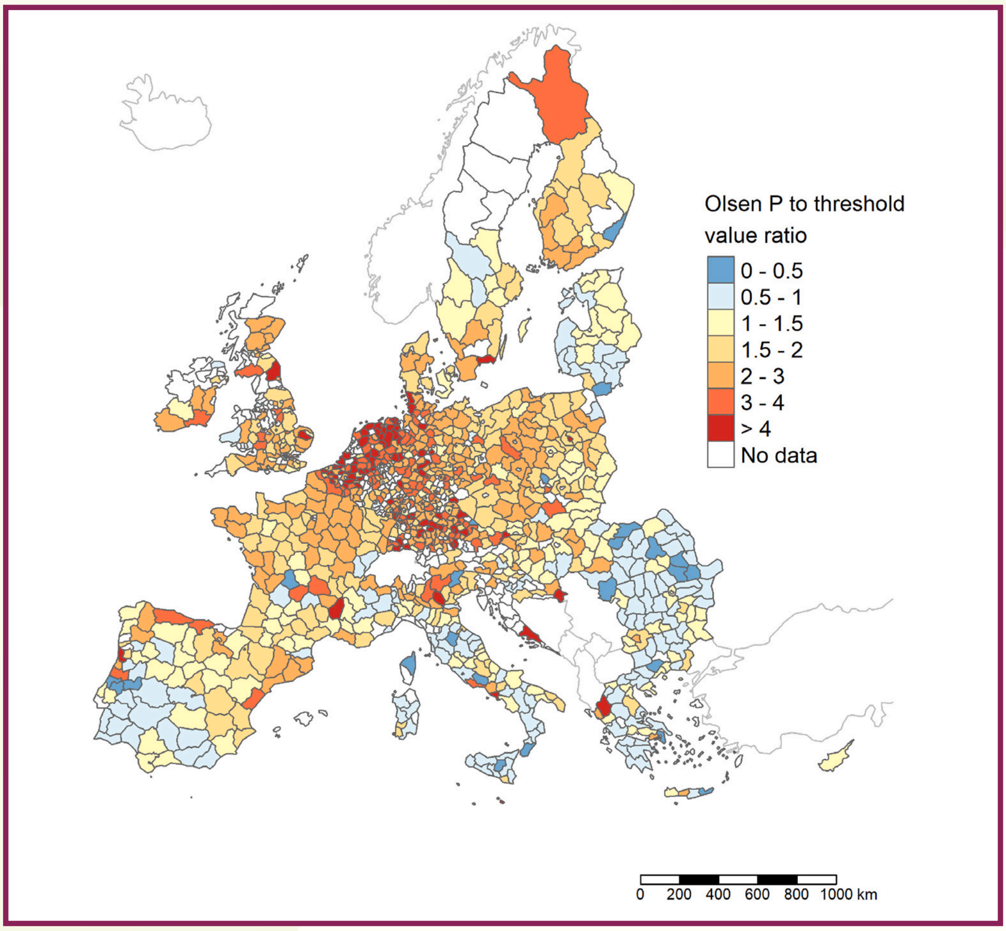

Fig. 6. Olsen P to threshold values ratio for grasslands in the European Union (EU-28 including United Kingdom). The figure represents median values by NUTS3 regions according to threshold values estimated according to the conservative model (Table 2).

3.4. Phosphorus fertilizer needs in Europe

The total demand for P in croplands in the EU was estimated according to the build-up and maintenance strategy, i.e., as the sum of the build-up component and the crop P exportation. With soil and land surface data for 2015, the build-up component was estimated at 760 and 378 Gg of P for croplands and grasslands, respectively (Tables S5 and S6). Except in the southwest of the Iberian peninsula, central and southern Italy, Greece, Bulgaria, and Romania, the build-up component of the fertilizer requirements was zero (Fig. 7). Therefore, in these regions with a zero build-up component, soil fertility is expected to be sustained under a build-up and maintenance strategy that supplies equivalent amounts of P to crop exportations. With a sufficiency strategy, agricultural production can be maintained for some time without the supply of P fertilizers. In the case of grasslands, most of the southern and eastern European regions require a significant supply of P as a build-up component of the total P fertilizer rate (Fig. 8). The estimated P export was 1228 Gg for 49 major crops in the EU-28 (Table S7) and 965 Gg in grasslands in 2015 (Table S8).

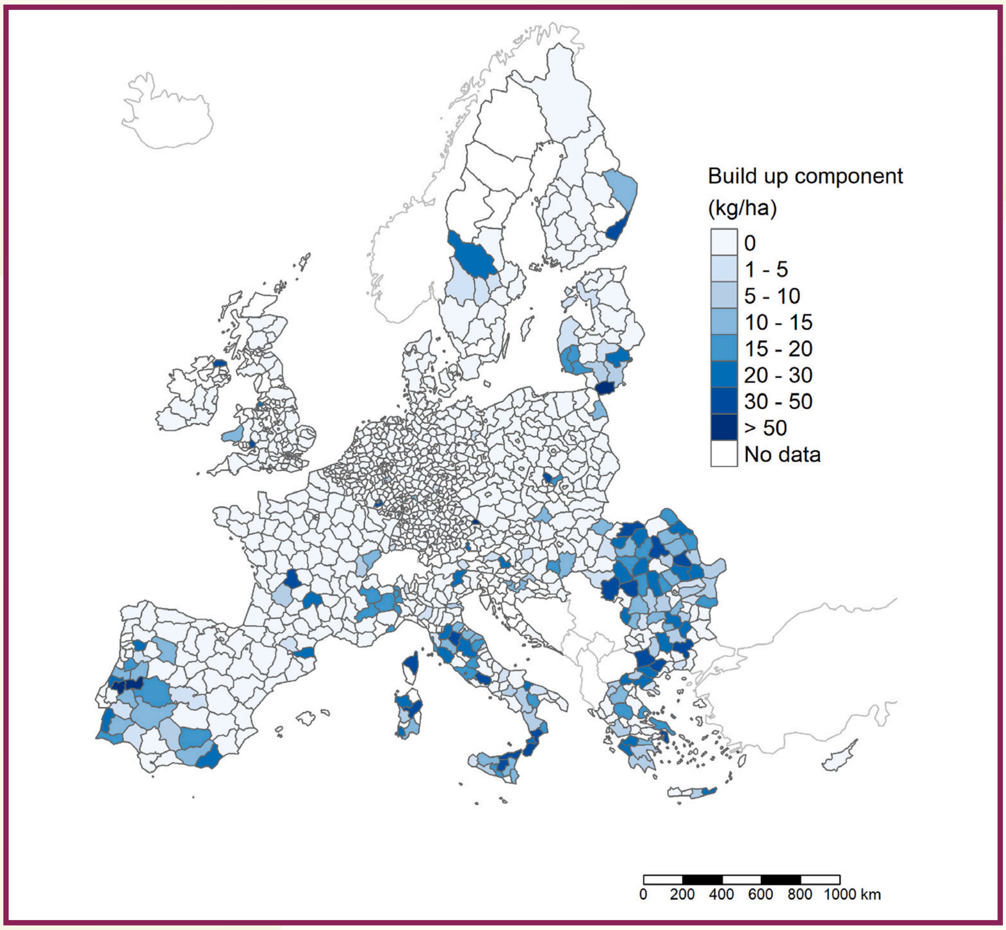

Fig. 7. Build up component of the fertilizer P rate in croplands according to the fertilizer strategies described in Table 1 in the NUTS3 regions of the European Union (EU-28 including United Kingdom). A build up component of zero implies that under an "Increase and maintenance strategy" the P fertilizer should compensate crop P exportations, and under a "Sufficiency strategy", no fertilization is required.

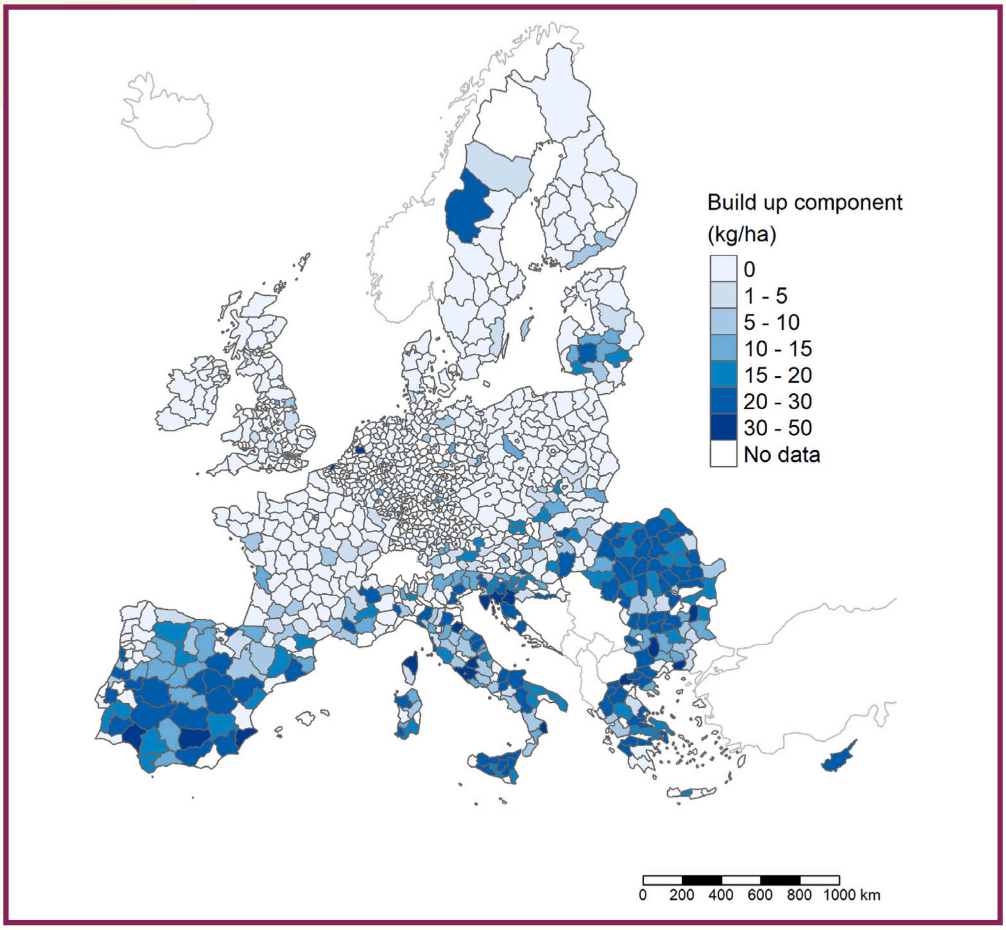

Fig. 8. Build up component of the fertilizer P rate in grasslands according to the fertilizer strategies described in Table 1 in the NUTS3 regions of the European Union (EU-28 including United Kingdom). A build up component of zero implies that under an "Increase and maintenance strategy" the P fertilizer should compensate crop P exportations, and under a "Sufficiency strategy", no fertilization is required.

4. Discussion

4.1. Identification of P-responsive sites

Environmental factors appeared to be more relevant than crops in explaining Olsen P threshold values. However, despite the high average value for root and tuber crops, the results were not fully conclusive, as the data set was clearly dominated by cereals. The Olsen P threshold values were reasonably predicted with a regression model that included clay, pH, and annual average rainfall as predictive variables. This model explained 61% of the variance in threshold values, with a very reasonable MAE (2.9). Thus, this verifies our hypothesis of estimating the Olsen P threshold value using routinely determined soil properties and climatic variables, but not based on crops. This also reveals that climatic factors affect threshold values, since there is a negative effect of rainfall on the estimates of the Olsen P threshold values. An increase in biomass production is expected under rainfed conditions with increased rainfall, which may imply an increase in the demand for P by crop. However, the reasons for this negative effect of rainfall may be attributed to the effect of the soil water content on the movement of P to the roots. Matar et al. (1992) described an increase in Olsen P threshold values with increased aridity in Mediterranean environments. This was explained because P in the soil solution mostly moves to the roots by diffusion, which is reduced when the soil is dry. In addition, a decrease in the soil water contents implies an increase in the ionic strength in the soil solution. This enhances P adsorption in soils when the pH is above a certain value (Bolan et al., 1986), affecting the equilibrium between the solid and water phases and decreasing the release of P from the sorbent surfaces. Thus, it seems that a more constant humidity in the soil improves the use of P by crops, reducing the threshold values for fertilizer response. This reveals the need to consider the climatic conditions in each growing season. Furthermore, increased aridity, as a consequence of climate change, would mean higher threshold values and less efficient use of P by crops. The extreme situation is lowland rice cultivation under flooding, where the reduction of P sorbent surfaces may explain very low threshold values (3.2 mg kg−1).

Almost half of the variance (49%) in the threshold values was explained if only clay content and pH were included in the model, with a MAE of 3.4. It should be noted that this model was not significantly different from that previously described by Recena et al. (2016) using a pot experiment growing wheat and sunflower. It can be assumed that with an accurate estimate of threshold values, Olsen P can be deemed a valid soil P test for acid soils.

The negative effect of clay content on Olsen P threshold values has been ascribed to the positive correlation usually found between clay content and P buffer capacity (Recena et al., 2016). The threshold value decreases with increased P buffer capacity (Ehlert et al., 2003; Delgado et al., 2010) since the soil can keep the P concentration more constant due to P desorption after P uptake by plants. Additionally, threshold values decrease with increased P sorption capacity, which is generally positively correlated with clay content (Recena et al., 2016). The negative effect of pH on Olsen P threshold values has been ascribed to its influence on soil P dynamics and its correlation with other soil properties such as the type of sorbent surface that affects P availability to plants (Delgado and Torrent, 1997). Thus, the use in the predictive model of soil properties related to its P buffer and sorption capacity seemed crucial to achieving reasonably accurate estimates of Olsen P threshold values.

The Olsen P threshold estimation model has uncertainties. The main one is likely the variability in the determination of Olsen P values between different laboratories as Jordan-Meille et al. (2012) described. Thus, accurate analytical protocols are also required for large-scale recommendations based on the Olsen P method. Another uncertainty is that the model takes into account crop type but not crop rotations. It is known that preceding crops can affect P availability to plants (Lukowiak et al., 2016), but this information was not always available in the dataset used for the model. Analysis of soil P status in Europe was carried out with the model based on soil clay and pH (Fig. 3) since it was not easy to find reliable and current information on average annual rainfall at all sampling points of the LUCAS project. Additionally, rainfall is the most changeable predictive factor, and annual variation can be significant in affecting crop response to soil P. This lack of precise information on rainfall also contributes to uncertainty in the model. However, the mechanistic support of the model seemed solid, since the results based on the literature review were fully consistent with the results obtained under the environmental controlled conditions described by Recena et al. (2016). Furthermore, cross-validation supported a reliable estimate of future observations.

4.2. Status of soil P in Europe

In general, we found a high general P level in a representative set of European soils, 72.2% of croplands and 57.3% of grasslands being not P-responsive taking the starting point in 2015. When analyzed by countries, the very high levels of Olsen P values compared with threshold values found in some countries of western and central Europe reflect the consequences of the balance of P fertilizers in European soils, with less overfertilization in grasslands than in croplands (Tóth et al., 2014; Van Dijk et al., 2016). The comparison between countries based on Olsen P values was done by Tóth et al. (2014) using the LUCAS project database (with the 2009 dataset). However, this comparison was made on the basis of absolute values and not on the Olsen P-to-threshold value ratio for each specific site. This may lead to a likely overestimation of high-P sites, since areas with high Olsen P values according to the LUCAS project database frequently correspond to soils with low clay content and pH (e.g., The Netherlands). In these soils, the threshold values for fertilizer response are assumed to be higher than in soils with a high pH and clay content. However, in soils from south and eastern Europe, with the lowest average Olsen P values, P-responsive sites may be overestimated since soils with high pH and clay content, thus with lower threshold values, are more frequent in these areas. However, in these latter cases the median of Olsen P to threshold value tended to be much lower than the mean (Table S3), indicating that the mean value is affected by a reduced number of very high values. Consequently, soils with an Olsen P-to-threshold value ratio lower than 1 are more frequent in the southern and eastern regions of the EU (Fig. 5, Fig. 6).

The highest Olsen P to threshold value ratio was observed in crops with high biomass yield and high P uptake: potato, sugar beet, and maize (Table S4). This means that farmers' perception of a high P uptake led to overfertilization of these crops. However, the average ratio of Olsen P to threshold value in potato and sugar beet seemed to be influenced by extremely low values, while that of maize seemed to be influenced by extremely high values. The latter seems to be the case for most crops. All of this revealed wide variations in the amount of P fertilizers applied to a given crop within the EU, leading to wide differences in the available P status of the soil.

4.3. Phosphorus fertilizer needs in Europe

Regions with a build-up component equal to zero (Fig. 7, Fig. 8) are those with the highest positive P balance (Tóth et al., 2014), frequently attributed to the application of high manure rates. The total estimated amount for the build-up component is not far from the annual P enrichment (positive balance of 924 Gg) of agricultural land in the EU estimated by Van Dijk et al. (2016). However, this current enrichment is not necessarily allocated to P-responsive sites. This reveals the need for a better allocation of the P resource on the continental scale to reduce the excessive enrichment of P in agricultural soils in some regions and consequently the environmental problems ascribed to this enrichment. Furthermore, a more precise allocation of P resources will increase agricultural productivity in P-responsive sites.

The annual demand for P to build up the P reserve until it reaches the threshold value in soils below it amounted to 1138 Gg of P for EU-28 in 2015 (croplands + grasslands). We estimated 1228 Gg of P export for main crops and 965 for grasslands in the EU-28, which is a total of 2193 Gg of P, in 2015. This roughly agrees with the estimate of P removal by crops and grasslands described by Panagos et al. (2022) for the EU-28 (including the UK) in 2016, and with Van Dijk et al. (2016), who estimated P export from agricultural land at 2300 Gg for the EU-27 in 2005. This means that for a build-up and maintenance strategy, the annual total P demand is around 3330 Gg (1138 of the build-up component + 2193 as maintenance component), roughly equivalent to the total P applied in 2005 as manure and mineral fertilizers according to Van Dijk et al. (2016) or in 2015 according to the European Commission (https://ec.europa.eu/info/sites/default/files/food-farming-fisheries/farming/documents/market-brief-fertilisers_june2019_en.pdf). This is the scenario with the highest P demand based on a P fertilization strategy to build up and maintain. The estimated total demand according to this strategy does not mean a decrease compared to the total P fertilizer applied to European agricultural soils. However, our proposal accounts for an increased allocation of resources to P-responsive sites based on the use of Olsen P. With time, the P enrichment of P-responsive sites will lead to a decrease in the demand for P fertilizer in Europe.

4.4. A circular economy approach to decreasing mineral P fertilizer demand in Europe

Returns to agricultural land from human consumption, food processing, and manure account for around 1900 Gg y−1 (Van Dijk et al., 2016). Losses in human food consumption, food and non-food processing were around 1070 Gg in 2005 (van Dijk et al., 2016). Thus, 2970 Gg of P y−1 can be recycled from agricultural systems, food processing and urban residues (wastewater and urban solid wastes) for using in agriculture. This would be enough to cover a large part of the P fertilization needs estimated above under the scenario with the highest demand based on a build-up and maintenance strategy. This means that mineral fertilizer needs would be reduced from around 1200 (https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Agri-environmental_indicator_-_mineral_fertiliser_consumption#Analysis_at_EU_level) to around 330 Gg y−1. However, this need will decrease in the future if the P resources are utilized in P responsive sites as mentioned above. Our estimate is a starting point defined in 2015 according to the available LUCAS dataset. The main constraint to achieve this circular economy-based strategy is the logistic requirement to use sources (biobased fertilizers) with low P concentration or the new knowledge required to concentrate P in these materials.

However, a circular economy approach in the use of P will have benefits that should be taken into account as offsets of the mentioned constraints. Valorising residues will contribute to solving their management problems. On the other hand, recycled P forms, in particular organic sources, can increase available P in soil more efficiently than soluble mineral fertilizers through an effect of organic matter blocking P adsorption sites and precipitation in soils (Delgado and Scalenghe, 2008) and may induce benefits on soil quality (Moreno et al., 2016).

5. Conclusions

Identification of P-responsive sites in EU-28 (including the UK) is possible using a simple model for the estimation of Olsen P threshold values involving soil properties routinely determined in soil analysis (clay and pH). This will allow for a better allocation of P resources and more accurate estimates of P fertilizer rates as a basis for sustainable fertilization schemes. This will lead to a decrease in P fertilizer needs in the future by increasing P levels in P-responsive sites while decreasing excessive enrichment in non-P-responsive sites and the associated environmental impact. The estimated demand for P in Europe based on this information indicated that it is possible to cover most of this demand (86%) by optimizing the recycling of P from food processing, manure, wastewater, and municipal solid waste. The proposed method for identifying P-responsive sites and the circular economy approach in the use of P will contribute to agricultural sustainability, food security, and environmental performance in the use of this resource.

Credit authorship contribution statement

Ramiro Recena: Conceptualization, Methodology, Formal analysis, Writing – original draft. Ana M. García-López: Methodology, Formal analysis. José M. Quintero: Conceptualization, Methodology. Annaliina Skyttä: Visualization, Formal analysis. Kari Ylivainio: Writing – review & editing, Conceptualization. Jakob Santner: Writing – original draft, Conceptualization. Else Buenemann: Writing – original draft, Conceptualization. Antonio Delgado: Conceptualization, Formal analysis, Writing – review & editing.

Declaration of competing interest

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

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Potential ammonia volatilization from 39 different novel biobased fertilizers on the European market – A laboratory study using 5 European soils

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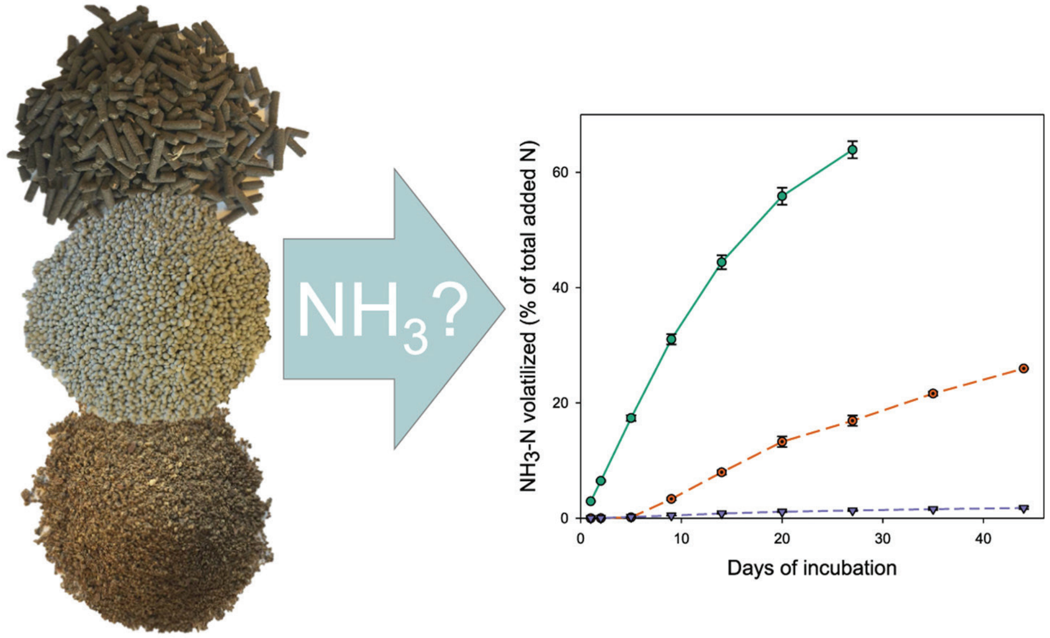
HIGHLIGHTS

- ***NH_3 volatilization potential from 39 EU marketed biobased fertilizers varied vastly.***
- ***Highest NH_3 volatilization potential from digestates.***
- ***Lowest NH_3 volatilization potential from composts and struvites.***
- ***Incorporation of biobased fertilizers reduced potential NH_3 volatilization.***
- ***Soil characteristics affected biobased fertilizers' potential NH_3 volatilization.***

ABSTRACT

Current political focus on promoting circular economy in the European Union drives great interest in developing and using more biobased fertilizers (BBFs, most often waste or residue-derived). Many studies have been published on environmental emissions, including ammonia (NH_3) volatilization from manures, but there have only been a few such studies on BBFs. Ammonia volatilization from agriculture poses a risk to the environment and human health, causing pollution in natural ecosystems when deposited and formation of fine particulate matter (PMx). Furthermore, NH_3 volatilization results in removal of plant-available N from agricultural systems, constituting an economic loss for farmers.

The aim of this laboratory study was to determine the potential NH_3 volatilization from 39 different BBFs commercially available on the European market. In addition, this study aimed to investigate the effect of incorporation, application rate, soil type, and soil moisture content on potential NH_3 volatilization in order to derive suggestions for the optimal field application conditions. Results showed a great variation between BBFs in potential NH_3 volatilization, both in terms of their temporal pattern of volatilization and amount of NH_3 volatilized. The potential NH_3 volatilization varied from 0% of applied total N (olive oil compost) to 64% of applied total N (manure and crop digestate) during a 27- or 44-day incubation period. Characteristics of BBFs (pH, NH_4^+-N, NO_3^--N, DM, C:N) and their interaction with time could explain 89% of the variation in accumulated potential NH_3 volatilization. Incorporation of BBFs into an acidic sandy soil effectively reduced potential NH_3 volatilization by 37%–96% compared to surface application of BBFs. Potential NH_3 volatilization was not significantly affected by differences in application rate or soil moisture content, but varied between five different soils (with different clay and organic matter content), with the highest NH_3 volatilization potential from the acidic sandy soil.



KEYWORDS

Ammonia volatilization

Biobased fertilizers

Incorporation

Surface application

Incubation

Soil type

1. Introduction

Biobased fertilizers (BBFs) can be defined as materials or products derived from biomaterials (plant, animal or microbial origin, often wastes, residues or side-streams from agriculture, industry or society) with a content of bioavailable plant nutrients suitable to serve as a fertilizer for crops. Producing and using BBFs is therefore a means to recycle otherwise potentially wasted nutrients. They can replace mineral fertilizers, lowering the environmental and climate impacts of mineral nitrogen (N) fertilizer production, and the environmental and resource depletion impacts of phosphorus (P) and potassium (K) mining and extraction.

Therefore, there is a lot of political interest in promoting waste- or residue-based BBFs in a circular economy context in the European Union (EU) (EC, 2015). A new EU Fertilizing Products Regulation (EU, 2019/1009) has been approved by the European Commission and will be implemented in the member states in the coming years. This is expected to lead to an increase in the use of novel BBFs, as the new fertilizer regulation will allow various BBFs to enter the free trade market for fertilizers, provided they comply with certain production and quality standards (Schoumans et al., 2019). The recent instability of mineral fertilizer markets, with rapidly fluctuating fertilizer prices (Baffes and Koh, 2021), will also increase interest in alternative and less energy market-sensitive nutrient sources.

However, knowledge about the N fertilizer effect and environmental impacts of the use of novel BBFs is currently very limited. An important aspect is ammonia (NH_3) volatilization, which is of growing environmental concern (Li et al., 2020). Globally, 80% of NH_3 volatilization is associated with human activities, mainly related to animal husbandry and the application of fertilizers (UNEP, 2019). Once volatilized, NH_3 reacts with acidic gasses which impacts the formation, transformation, and deposition of aerosols (Akiyama et al., 2004). Re-deposition of NH_3 may contribute directly or indirectly to soil acidification, eutrophication of aquatic environments, and biodiversity loss. Furthermore, NH_3 may be oxidized to nitrate (NO_3^-) and further transformed to the potent greenhouse gas N_2O through denitrification (Ferm, 1998). In addition to environmental concerns, secondary ultrafine particles in the atmosphere formed by NH_3 and other reactive compounds pose a significant human health risk (Sanz-Cobena et al., 2014). Moreover, NH_3 volatilization may also reduce the inorganic N content in the soil applied with BBFs, thereby causing decreases in yields, with consequential economic losses for the farmer (Kirchmann and Lundvall, 1993).

Theoretically, BBFs with a high pH and/or high ammonium (NH_4^+) and/or high uric acid content will be expected to have higher NH_3 volatilization potential compared to BBFs with a low pH and/or low NH_4^+ and/or low uric acid content (Jensen and Sommer, 2013; Sommer and Feilberg, 2013). However, BBFs with a low NH_4^+ content may contain a substantial pool of easily mineralizable organic N, which upon soil microbial decomposition of the BBF will become mineralized and provide NH_4^+-N, increasing the potential for NH_3 volatilization. Moreover, the physical form, e.g. pelletized, liquid or powder, may affect the NH_3 volatilization potential, as it affects the dissolution and diffusion of the NH_4^+ content of the BBF into the soil (Sommer et al., 2004). NH_3 may also be lost during the BBF production process, as observed e.g. during the composting (Usmani et al., 2020) and drying of anaerobic digestate (Awiszus et al., 2018).

Apart from the BBF properties, the soil type to which the BBF is applied may affect the NH_3 volatilization potential. In a study including 22 soils differing in properties, Duan and Xiao (2000) found NH_3 volatilization rates to be positively correlated with soil pH, $CaCO_3$, and salt content and negatively correlated with soil organic matter (SOM) content, cation exchange capacity (CEC), and clay content. In acidic soils, or soils with a low content of pH buffer components, NH_3 volatilization will rapidly decline (Sommer et al., 2004). Moreover, soil moisture may affect NH_3 volatilization potential, as the concentration of NH_4^+ content in solution is lower at higher soil moisture, which may lead to lower NH_3 volatilization (Haynes and Sherlock, 1986).

Previous studies on NH_3 volatilization from BBFs have focused on a limited variety and number of BBFs, including mainly manure (Akiyama et al., 2004; Bernal and Kirchmann, 1992; Mkhabela et al., 2006) and to some extent digestates (Nkoa, 2014; Verdi et al., 2019). Ammonia volatilization from both livestock and green manure has been shown to be generally higher compared to mineral N fertilizers (Ma et al., 2021). Therefore, studies on NH_3 volatilization from novel BBFs covering a wide range of source material as well as chemical and physical properties are strongly needed.

Thus, the overall objective of this study was to determine the potential NH_3 volatilization from the use of 39 different BBFs under variation of soil type and moisture conditions, as well as application rate and method, and to derive suggestions for the optimal application conditions under practical settings.

The following hypotheses were tested: i) Novel BBFs are expected to behave in the same way as more traditional BBFs, e.g. manure, where a high pH and/or high NH_4^+ content will lead to high NH_3 volatilization potentials; ii) Biobased fertilizers produced partly or fully from poultry manures are expected to have high NH_3 volatilization potentials, due to their high content of uric acid, rapidly hydrolyzing to NH_4+; iii) Application of BBFs to soils with a high pH will increase their NH_3 volatilization potential, whereas soils with a high organic matter (OM) content, high clay content, and/or high CEC will decrease potential NH_3 volatilization of BBFs; and iv) Incorporation of BBFs into soil or sand will decrease the potential NH_3 volatilization.

The method used in this study was developed as a standard test method for the EU H2020 LEX4BIO project. The method is meant to be used as an assessment of whether the BBF poses a risk of NH_3 loss and does not take into account varying environmental conditions that can affect the actual NH_3 emissions in the field. It allows estimation of the potential NH_3 loss from a BBF under conditions of constant removal of NH_3 and CO_2, creating a maximum gradient for both gasses because they interact in enhancing NH_3 volatilization (Husted et al., 1991). Due to the maximized gas gradients, these conditions simulate field conditions with high wind speeds and no vegetation cover. Moreover, to assess the NH_3 volatilization potential from the 39 BBFs independently from their interactions with the soil, they were also applied to pure sand, imitating the physical properties of soil, but lacking the chemical and biological characteristics that may affect NH_3 volatilization.

2. Materials and methods

2.1. Materials

2.1.1. Biobased fertilizers

39 BBFs, produced from various waste- and side streams of agricultural, urban or industrial origin, were included in this study. A novel BBF is here defined as a BBF produced by processes beyond simple biogas digestion of animal manures and simple composting. The processes involved in producing novel BBFs can e.g. be drying, pelletizing or mineral extraction. Of the BBFs included in this study, 90% are defined as novel BBFs, with GRF, HDG, OOC and SDG defined as non-novel BBFs. All BBFs were available on the European market or on regional/national markets at the time of writing. A description of raw materials and technologies used, along with product function categories (PFC) and component material categories (CMC) according to the new EU Fertilizing Products Regulation (EU, 2019/1009), is provided in Table 1. The CMCs refer to the processing of BBFs, e.g. compost and digestate and the input material, e.g. industry by-products. The PFCs are related to the main BBF functions; subcategories relate to whether it is liquid or solid and the amount of mineral and organic components it contains. An extensive review of all technologies and processes involved in producing BBFs is beyond the scope of this study and readers are referred to Meers et al. (2020).

Moreover, the BBFs in this study were also grouped based on more classical terms used in the literature (Table 1). Standard categories were digestate and compost. Meat and bone meal and other products from the meat industry were grouped together as animal by-products. Struvites and other BBFs derived from mineral extractions were grouped together as mineral precipitates. Potato fruit juice and other BBFs produced solely from plant materials were grouped together as plant-based BBFs. BBFs in a pelletized form produced from various materials were lumped in a group called “mixed”.

Before application to soil or sand, all BBFs were homogenized. For this purpose, non-fluid BBFs were carefully crushed using a mortar until they could pass through a 2-mm sieve. For BBFs with a high-fiber content, which could not be crushed using the mortar, fibers were cut with scissors and passed through a 2-mm sieve. Dry BBFs with particle sizes <2 mm and homogenous liquid BBFs were not further processed. Non-homogenous liquid and moist BBFs, e.g. digestates and composts, were homogenized using a blender for approximately 1 min. Comparisons of NH_3 volatilization potential from homogenized and non-homogenized BBFs are included in Appendix A, Fig. A1.

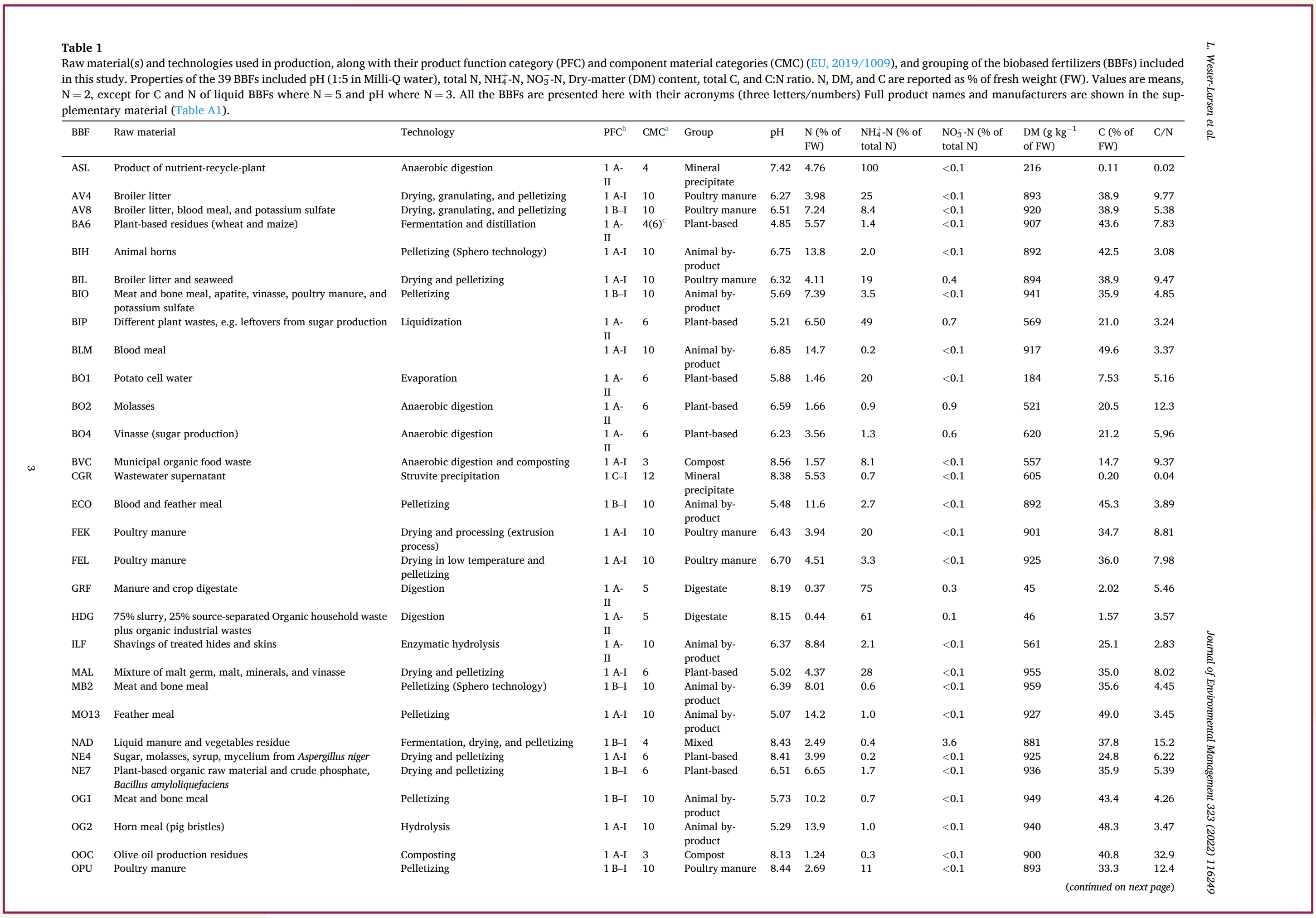


Table 1
Raw material(s) and technologies used in production, along with their product function category (PFC) and component material categories (CMC) (EU, 2019/1009), and grouping of the biobased fertilizers (BBFs) included in this study. Properties of the 39 BBFs included pH (1:5 in Milli-Q water), total N, NH$_4^+$-N, NO$_3^-$-N, Dry-matter (DM) content, total C, and C:N ratio. N, DM, and C are reported as % of fresh weight (FW). Values are means, N = 2, except for C and N of liquid BBFs where N = 5 and pH where N = 3. All the BBFs are presented here with their acronyms (three letters/numbers) Full product names and manufacturers are shown in the supplementary material (Table A1).

BBF	Raw material	Technology	PFC[b]	CMC[a]	Group	pH	N (% of FW)	NH$_4^+$-N (% of total N)	NO$_3^-$-N (% of total N)	DM (g kg^{-1} of FW)	C (% of FW)	C/N
ASL	Product of nutrient-recycle-plant	Anaerobic digestion	1 A-II	4	Mineral precipitate	7.42	4.76	100	<0.1	216	0.11	0.02
AV4	Broiler litter	Drying, granulating, and pelletizing	1 A-I	10	Poultry manure	6.27	3.98	25	<0.1	893	38.9	9.77
AV8	Broiler litter, blood meal, and potassium sulfate	Drying, granulating, and pelletizing	1 B–I	10	Poultry manure	6.51	7.24	8.4	<0.1	920	38.9	5.38
BA6	Plant-based residues (wheat and maize)	Fermentation and distillation	1 A-II	4(6)[c]	Plant-based	4.85	5.57	1.4	<0.1	907	43.6	7.83
BIH	Animal horns	Pelletizing (Sphero technology)	1 A-I	10	Animal by-product	6.75	13.8	2.0	<0.1	892	42.5	3.08
BIL	Broiler litter and seaweed	Drying and pelletizing	1 A-I	10	Poultry manure	6.32	4.11	19	0.4	894	38.9	9.47
BIO	Meat and bone meal, apatite, vinasse, poultry manure, and potassium sulfate	Pelletizing	1 B–I	10	Animal by-product	5.69	7.39	3.5	<0.1	941	35.9	4.85
BIP	Different plant wastes, e.g. leftovers from sugar production	Liquidization	1 A-II	6	Plant-based	5.21	6.50	49	0.7	569	21.0	3.24
BLM	Blood meal		1 A-I	10	Animal by-product	6.85	14.7	0.2	<0.1	917	49.6	3.37
BO1	Potato cell water	Evaporation	1 A-II	6	Plant-based	5.88	1.46	20	<0.1	184	7.53	5.16
BO2	Molasses	Anaerobic digestion	1 A-II	6	Plant-based	6.59	1.66	0.9	0.9	521	20.5	12.3
BO4	Vinasse (sugar production)	Anaerobic digestion	1 A-II	6	Plant-based	6.23	3.56	1.3	0.6	620	21.2	5.96
BVC	Municipal organic food waste	Anaerobic digestion and composting	1 A-I	3	Compost	8.56	1.57	8.1	<0.1	557	14.7	9.37
CGR	Wastewater supernatant	Struvite precipitation	1 C–I	12	Mineral precipitate	8.38	5.53	0.7	<0.1	605	0.20	0.04
ECO	Blood and feather meal	Pelletizing	1 B–I	10	Animal by-product	5.48	11.6	2.7	<0.1	892	45.3	3.89
FEK	Poultry manure	Drying and processing (extrusion process)	1 A-I	10	Poultry manure	6.43	3.94	20	<0.1	901	34.7	8.81
FEL	Poultry manure	Drying in low temperature and pelletizing	1 A-I	10	Poultry manure	6.70	4.51	3.3	<0.1	925	36.0	7.98
GRF	Manure and crop digestate	Digestion	1 A-II	5	Digestate	8.19	0.37	75	0.3	45	2.02	5.46
HDG	75% slurry, 25% source-separated Organic household waste plus organic industrial wastes	Digestion	1 A-II	5	Digestate	8.15	0.44	61	0.1	46	1.57	3.57
ILF	Shavings of treated hides and skins	Enzymatic hydrolysis	1 A-II	10	Animal by-product	6.37	8.84	2.1	<0.1	561	25.1	2.83
MAL	Mixture of malt germ, malt, minerals, and vinasse	Drying and pelletizing	1 A-I	6	Plant-based	5.02	4.37	28	<0.1	955	35.0	8.02
MB2	Meat and bone meal	Pelletizing (Sphero technology)	1 B–I	10	Animal by-product	6.39	8.01	0.6	<0.1	959	35.6	4.45
MO13	Feather meal	Pelletizing	1 A-I	10	Animal by-product	5.07	14.2	1.0	<0.1	927	49.0	3.45
NAD	Liquid manure and vegetables residue	Fermentation, drying, and pelletizing	1 B–I	4	Mixed	8.43	2.49	0.4	3.6	881	37.8	15.2
NE4	Sugar, molasses, syrup, mycelium from *Aspergillus niger*	Drying and pelletizing	1 A-I	6	Plant-based	8.41	3.99	0.2	<0.1	925	24.8	6.22
NE7	Plant-based organic raw material and crude phosphate, *Bacillus amyloliquefaciens*	Drying and pelletizing	1 B–I	6	Plant-based	6.51	6.65	1.7	<0.1	936	35.9	5.39
OG1	Meat and bone meal	Pelletizing	1 B–I	10	Animal by-product	5.73	10.2	0.7	<0.1	949	43.4	4.26
OG2	Horn meal (pig bristles)	Hydrolysis	1 A-I	10	Animal by-product	5.29	13.9	1.0	<0.1	940	48.3	3.47
OOC	Olive oil production residues	Composting	1 A-I	3	Compost	8.13	1.24	0.3	<0.1	900	40.8	32.9
OPU	Poultry manure	Pelletizing	1 B–I	10	Poultry manure	8.44	2.69	11	<0.1	893	33.3	12.4

(*continued on next page*)

a CMC 3: Compost, CMC 4: Fresh crop digestate, CMC 5: Digestate other than fresh crop digestate, CMC 6: Food industry by-products, CMC 10: Derived products within the meaning of Animal By-products Regulation, and CMC 12: Precipitated phosphate salts and derivates (EU, 2019/1009).

b PFC 1 A-I: Solid organic fertilizer: ≥ 15% organic C, PFC 1 A-II: Liquid organic fertilizer: ≥ 5% organic C, PFC 1 B–I: Solid organo-mineral fertilizer: ≥ 7.5% organic C, 1 B-II: Liquid organo-mineral fertilizer: ≥ 3% organic C, 1 C–I: Straight solid inorganic macronutrient fertilizer, and 1 C–I: Compound solid inorganic macronutrient fertilizer (EU, 2019/1009).

c For BBFs which belong to more than one CMC group, the secondary CMC group is included in brackets.

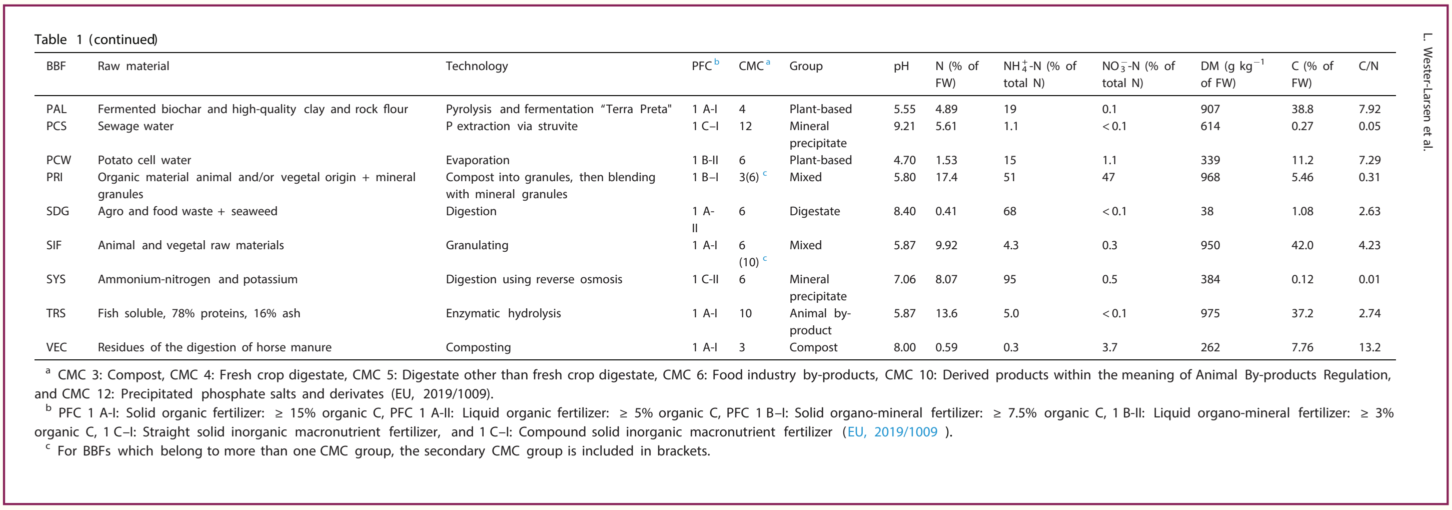


Table 1 (continued)

BBF	Raw material	Technology	PFC[b]	CMC[a]	Group	pH	N (% of FW)	NH$_4^+$-N (% of total N)	NO$_3^-$-N (% of total N)	DM (g kg^{-1} of FW)	C (% of FW)	C/N
PAL	Fermented biochar and high-quality clay and rock flour	Pyrolysis and fermentation “Terra Preta"	1 A-I	4	Plant-based	5.55	4.89	19	0.1	907	38.8	7.92
PCS	Sewage water	P extraction via struvite	1 C–I	12	Mineral precipitate	9.21	5.61	1.1	< 0.1	614	0.27	0.05
PCW	Potato cell water	Evaporation	1 B-II	6	Plant-based	4.70	1.53	15	1.1	339	11.2	7.29
PRI	Organic material animal and/or vegetal origin + mineral granules	Compost into granules, then blending with mineral granules	1 B–I	3(6)[c]	Mixed	5.80	17.4	51	47	968	5.46	0.31
SDG	Agro and food waste + seaweed	Digestion	1 A-II	6	Digestate	8.40	0.41	68	< 0.1	38	1.08	2.63
SIF	Animal and vegetal raw materials	Granulating	1 A-I	6 (10)[c]	Mixed	5.87	9.92	4.3	0.3	950	42.0	4.23
SYS	Ammonium-nitrogen and potassium	Digestion using reverse osmosis	1 C-II	6	Mineral precipitate	7.06	8.07	95	0.5	384	0.12	0.01
TRS	Fish soluble, 78% proteins, 16% ash	Enzymatic hydrolysis	1 A-I	10	Animal by-product	5.87	13.6	5.0	< 0.1	975	37.2	2.74
VEC	Residues of the digestion of horse manure	Composting	1 A-I	3	Compost	8.00	0.59	0.3	3.7	262	7.76	13.2

[a] CMC 3: Compost, CMC 4: Fresh crop digestate, CMC 5: Digestate other than fresh crop digestate, CMC 6: Food industry by-products, CMC 10: Derived products within the meaning of Animal By-products Regulation, and CMC 12: Precipitated phosphate salts and derivates (EU, 2019/1009).

[b] PFC 1 A-I: Solid organic fertilizer: ≥ 15% organic C, PFC 1 A-II: Liquid organic fertilizer: ≥ 5% organic C, PFC 1 B–I: Solid organo-mineral fertilizer: ≥ 7.5% organic C, 1 B-II: Liquid organo-mineral fertilizer: ≥ 3% organic C, 1 C–I: Straight solid inorganic macronutrient fertilizer, and 1 C–I: Compound solid inorganic macronutrient fertilizer (EU, 2019/1009).

[c] For BBFs which belong to more than one CMC group, the secondary CMC group is included in brackets.

a Total C and N was determined by Dumas combustion.

b CEC determined by the NH₄+ acetate method, quantifying NH₄+-N with flow injection analysis.

c Texture and OM content determined at Agrolab Sarstedt by sieving and sedimentation for texture and by Dumas combustion for total OM.

2.1.2. Soil and sand matrix

For the incubation experiments on potential NH_3 volatilization, either pure sand or different soils were used as the matrix to which the BBFs were added. The sand used was in the size range 0.4–0.9 mm, contained 0.2% OM, and had been washed with water (Dansand A/S, Brædstrup, Denmark). Five different soils were used in the different experimental runs. These soils were selected from the experimental field sites of the EU H2020 LEX4BIO project, representing some of the variation in soil types present in Europe (Table 2). The soil samples were collected from the top 0–30 cm. Acidic sandy soil was air-dried and sieved to 2 mm. Acidic clay soil, Alkaline loamy soil, Neutral loamy soil, and Alkaline clay soil were sieved to 4 mm and air-dried.

2.2. Incubation setup for determining potential ammonia volatilization

The experiment was performed using a static diffusion enclosure method, developed by modifying the procedures described by the following authors (Husted et al., 1991; Ndegwa et al., 2009; Mandal et al., 2016). The method is meant to be used as an assessment of whether the BBF poses a risk of NH_3 loss and does not take into account varying environmental conditions that can affect the actual NH3 emissions in the field. A detailed methods description is openly available online in ERDA, the repository of the University of Copenhagen: https://doi.org/10.17894/ucph.456e08b8-e902-49a5-a51c-9ecd65216df0.

One hundred g (oven dry weight) of air-dry sieved soil/sand was added to 120 mL plastic containers. The soil was compacted to 1.25 g cm −3 (Acidic sandy soil and Alkaline loamy soil), 1.11 g cm−3 (Neutral loamy soil and Alkaline clay soil), and 1 g cm−3 (Acidic clay soil). The sand was not compacted. Milli-Q water was added to each container with a pipette to adjust the water content to 60% of the soil's water-holding capacity (WHC, determined modified according to ISO 14238). For the sand, it was assessed that 20 mL of Milli-Q water was suitable for 100 g (dry weight) of sand. The moisture content of the air-dry soil/sand and the water content of the BBFs were subtracted from the amount of water to be added to ensure an equal moisture content in all setups. The containers with moist soil/sand were pre-incubated for 5 day at 15 °C in a dark incubator (Termaks, A/S Ninolab, Solrød, Denmark) before addition of the BBF.

To mimic areas of a field receiving high BBF applications on its soil surface, e.g. a strip of liquid digestate from a trailing hose or the area around a solid BBF pellet, 400 kg total-N ha−1, corresponding to 0.004 g total-N cm−2, was applied as the standard rate for all 39 BBFs in experiment 1 (Table 3). In a different trial, eight selected BBFs were either surface applied and distributed evenly on the soil/sand surface (standard application method) or they were applied and thoroughly incorporated by mixing into the soil/sand before addition of Milli-Q water (see Table 3, experiment 2). Furthermore, to test the implication of the application rate, selected BBFs were applied at both the standard rate (1* application rate), which corresponds to 720 mg N kg−1 soil; half the rate (½ * application rate), corresponding to 360 mg N kg−1 soil (200 kg BBF N ha−1); and double the rate (2* application rate), corresponding to 1440 mg N kg −1 soil (800 kg BBF N ha−1) (see Table 3, experiment 3). The effect of the soil type was tested with five different BBFs (see Table 3, experiment 4). Moreover, the effect of the soil moisture was tested with three BBFs (see Table 3, experiment 5).

Experiment	*No of BBFs*	*Soil/sand*	*BBF application*	*Water content (% of WHC)*	*BBF application rate (mg N kg−1 soil)*
1	39	Sand	Surface	60	720
2	8	Acidic sandy soil; Sand	Surface; Incorporated	60	720
3	3	Acidic sandy soil	Surface	60	360; 720; 1440
4	5	Acidic sandy soil; Acidic clay soil; Neutral loamy soil; Alkaline loamy soil; Alkaline clay soil	Surface	60	720
5	3	Acidic sandy soil	Surface	30; 60; 90	720

Three replicates of each treatment were included in all experimental runs. Three replicates of controls with only sand/soil and no fertilizer were also included, as well as two blank tests of the setup without any sand/soil or fertilizer. Both no-treatment controls and blanks generally had NH_3 concentrations below the detection limit and were therefore not accounted for. Moreover, a reference fertilizer of ammonium bicarbonate (NH_4HCO_3) dissolved in Milli-Q water was included in each experimental run. This was, firstly, to serve as a reference for maximum potential NH_3 loss (due to all N being present as NH_4^+ and bicarbonate promoting pH rise upon application) and, secondly, to allow comparisons between experimental runs.

Each 120 mL plastic container with soil/sand and applied BBF, surface area of 18 cm2, was incubated in a glass canning jar (0.75 L) with an airtight lid. A trap consisting of 5 mL 0.2 M sulfuric acid (H_2SO_4) in an open plastic container (26 mL airtight plastic container, Frisenette ApS, Knebel, Denmark) was placed in the canning jar. The amount and concentration of H_2SO_4 was calculated stoichiometrically so that the H_2SO_4 was able to trap the double amount of NH_3 that could potentially volatilize (Ndegwa et al., 2009). The surface area of the acid in the acid trap was 7 cm2. In a pre-trial, the efficiency of the acid trap was tested with NH_4HCO_3 added to sand. The result showed that 82% of the N added as NH_4HCO_3 was recovered in the acid trap during an experimental period of 44 days (Fig. 1). This is within the range of previously reported NH_3 recovery values of 73–103% in laboratory setups (Woodward et al., 2011) and indicates that the setup did not have any significant leakage. The trap collected after the last trap exchange in the test trial with NH_4HCO_3 contained NH_3 and, thus, NH_3 was still volatilizing at the end of the trial period. If the experimental period had been extended, the recovery percentage would likely have approached 100%.

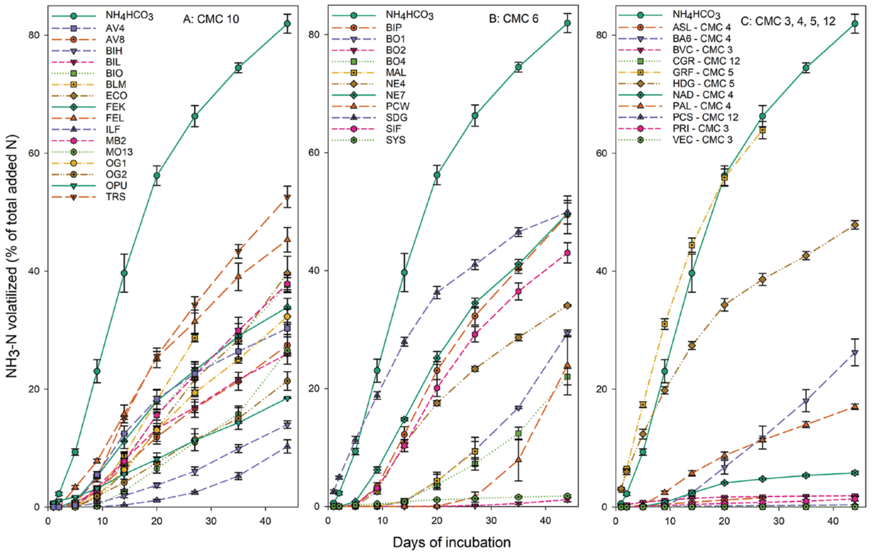


Fig. 1. Mean accumulated NH_3–N volatilized (% of total added N) ± standard error during 44 (a few with only 27) days of incubation from 38 different biobased fertilizers and a reference of NH4HCO3. A) BBFs from CMC 10 (Animal by-products). B) BBFs from CMC 6 (Food industry by-products). C) BBFs from CMC 3, 4, 5, and 12 (Composts, crop digestate, other digestates, salts & derivates respectively). All BBFs were surface applied on sand at an application rate of 0.72 g N kg−1 DW soil. N = 3.

A base trap consisting of 10 mL of 1 M sodium hydroxide (NaOH) in a plastic shot glass was additionally inserted in the canning jar to trap any CO_2 evolved during the incubation. Furthermore, a plastic shot glass containing 10 mL of deionized water was placed in the canning jar to maintain high humidity and prevent desiccation of the BBF and soil sample over time.

Canning jars were placed in a dark incubator (Termaks, A/S Ninolab, Solrød, Denmark) set to 15 °C to reflect a mean European air temperature.

2.3. Trap exchange and quantification of NH_3

The H2SO₄ and NaOH traps were exchanged 1, 2, 5, 9, 14, 20, and 27 days after the start of the experiment at the same time of day ±30 min. For the experimental run with all BBFs surface-applied to sand (Experiment 1 Table 3), two additional sampling times (35 and 44 days after the start) were applied. However, four of the 39 BBFs (MAL, BLM, ASL, and GRF) were included in a different experiment which only ran for 27 days. The base traps with NaOH were replaced, but not analyzed for CO_2 content.

The acid traps with H_2SO_4 were stored at ambient temperature with air-tight lids for a maximum of two weeks until analysis of the NH_4^+-N content. The stability of the NH_4^+ content in the traps was assessed to be at least three weeks by analyzing the NH_4^+-N in the same traps at different time points. The NH_3 trapped in the H_2SO_4 was quantified by analyzing the NH_4^+-N content in the traps using flow injection analysis (FIAstar 5000 flow injection analyzer (Foss Analytical, Hillerød, Denmark)). The lowest detected concentration was 0.0045 mg NH_4^+-N L−1. This method of quantifying NH_3 was tested against the titration method (see Fig. A2).

2.4. Analysis of soil and BBFs

At the end of each experimental run, all samples of soil/sand with BBFs applied were mixed thoroughly and a subsample of five g was collected to determine the pH value. The pH was determined on the last day of the experiment (day 27 or day 44) as 1:5 in Milli-Q water.

Dry matter (DM) of solid BBFs was determined at 105 °C by TGA701 (Leco) and that of liquid BBFs by drying in a ventilated oven (105 °C) until the weight did not change. The total C and N of BBFs was determined by the Dumas dry combustion method (Trumac or CHN628, Leco). The water-soluble NH_4^+-N and NO_3^--N of the BBFs were analyzed in 1:60 water extracts with a continuous flow analyzer (Skalar San ++ System). All analyses of BBFs were carried out on their original dry matter content.

2.5. Statistics

All illustrations were made in SigmaPlot 14.00 (Systat Software, Inc.). All statistical analyses were performed in R version 4.0.2 (R Core Team). A minimum significance level of $p < 0.05$ was applied for all tests. Data were visually assessed with diagnostic plots to check the homogeneity of variance and data were square-root transformed for all statistical analyses due to heterogeneity of variance.

The analyses were performed on the accumulated NH_3–N volatilized as a percentage of total added N for all days. The repeated measurements of accumulated NH_3 volatilization of each sample were accounted for by setting the sampling day as a repeated variable. This transformation was applied for all statistical analyses. All analyses were performed using linear mixed models and pairwise comparisons of least square means. R2 values and correlation coefficients were retrieved from the linear mixed models. A quadratic term of measurement day was included in the linear mixed models to account for non-linearity. Moreover, the sample number was always included as a random effect. BBF was included as a random effect for experiment 1 (Table 3) and for the correlation coefficients and R2 value for experiment 4 (Table 3), but not for the remaining analyses, as these were performed separately for each BBF treatment. See table A2 for further information on statistics.

3. Results

3.1. BBF properties

The properties of the 39 BBFs varied substantially (Table 1). The greatest variations were found in NH_4^+-N content and dry matter (DM) content.

3.2. Experiment 1: potential NH3 volatilization from all BBFs

The 39 BBFs surface applied to sand varied greatly in terms of accumulated potential NH_3 volatilized at the end of the incubation period (Fig. 1). However, all the BBFs showed some potential NH_3 volatilization during the incubation period, except for OOC (data not shown), where volatilization was below the detection limit on all days. Moreover, the temporal pattern of potential NH_3 volatilization during the incubation period differed between BBFs. Some BBFs had a high initial potential NH_3 volatilization and had concave shaped curves of accumulated potential NH_3 volatilization. For other BBFs, however, the initial potential NH_3 volatilization was very low and increased towards the end of the incubation period, resulting in convex curves of accumulated potential NH_3 volatilization.

Among the six CMCs, the accumulated NH_3 volatilization on day 27 was lowest for BBFs in CMC 12, followed by CMC 3 < 4 < 6 < 10 < 5. Among the six PFCs, the accumulated NH3 volatilization on day 27 was lowest for BBFs in PFC 1 A-II, followed by 1 C–I < 1 C-II < 1 B-II < 1 A-I < 1 B–I < 1 A-II. Among the seven BBF groups, the accumulated NH_3 volatilization on day 27 was lowest for Compost followed by Mineral precipitate < Mixed < Plant based < Animal by-products < Poultry manure < Digestate.

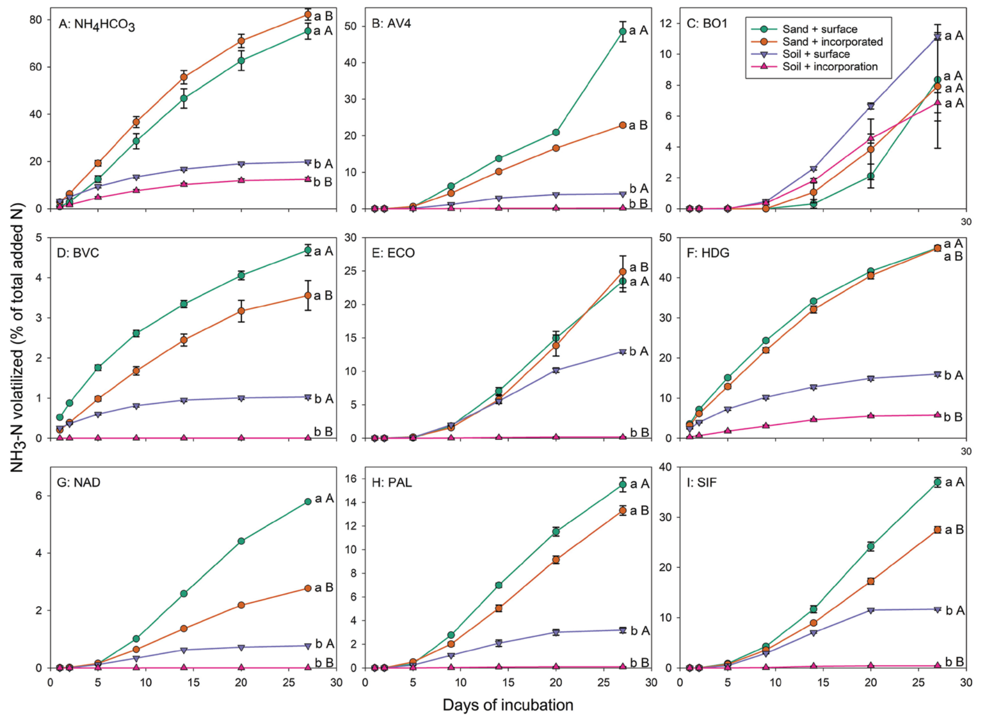


Fig. 2. Mean accumulated NH_3–N volatilized (% of total added N) ± standard error during 27 days of incubation from biobased fertilizers (B–I) and a reference of NH_4HCO_3 (A) surface applied or incorporated into soil or sand. Application rate of 0.72 g N kg−1 DW soil and a soil moisture content at 60% of WHC. Note different scales on vertical axes. N = 3. Lower case letters indicate significant different NH_3 volatilization potential between sand and soil within each BBF, Capital letters indicate significant different NH_3 volatilization potential between incorporation and surface application within each BBF.

Based on the number of significant differences between categories/groups in the three different categorizations included, CMCs and PFCs were not as good at predicting accumulated potential NH_3 volatilization compared to the groups based on traditional categorizations (Table A3).

A linear mixed model including BBF properties (pH, NH_4^+-N, NO_3^--N, DM, C:N) and their interaction with time explained 89% of the variation in accumulated potential NH_3 volatilization during the experimental period of 44 days. Potential NH_3 volatilization was positively correlated with pHMilli-Q water (0.312) and NH_4^+-N content (0.013) and negatively correlated with NO_3^--N content (−0.007), DM content (−0.01), and C:N ratio (−0.002).

3.3. Experiment 2: soil vs. sand and BBF application technique

The potential NH_3 volatilization was significantly lower for soil (Acidic sandy soil) compared to sand for the NH_4HCO_3 reference and all BBFs, except BO_1 ($P < 0.0001$) (Fig. 2). Moreover, potential NH_3 volatilization was significantly lower for incorporation compared to surface application for all BBFs ($P < 0.0001$), except BO_1 (Fig. 2). For the digestate HDG, the NH_3 volatilization after one day was reduced by 88% as a result of incorporation into soil relative to surface application. For the remaining BBFs, no noteworthy NH_3 had volatilized during the first day of incorporation. Looking at the accumulated NH_3 volatilization after 27 days of incubation, incorporation into soil reduced NH_3 volatilization by 37% and 64% for the NH_4HCO_3 reference and HDG respectively compared to surface application on soil. For AV4, SIF, PAL, ECO, NAD, and BVC, incorporation reduced NH_3 volatilization by more than 96%.

3.4. Experiment 3: BBF application rate

For the NH_4HCO_3 reference and AV4 (Fig. 3 A + B), the accumulated NH_3 volatilized was approximately doubled at the end of the incubation (day 27) when doubling the application rate. For ECO and HDG (Fig. 3 C + D), the differences between application rates were smaller, but showed a similar trend. Therefore, the potential NH_3 volatilized did not generally increase linearly with an increasing application rate. However, there were no overall significant differences between the three application rates. Only ½ the application rate was significantly different from both 1 and 2 times the application rate for AV4 and the NH_4HCO_3 reference (Fig. 3 A and B).

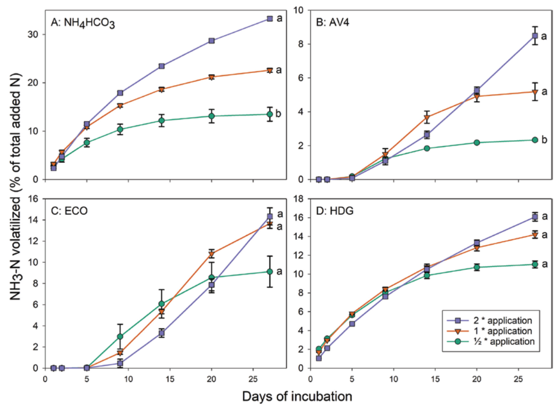


Fig. 3. Mean accumulated NH_3–N volatilized (% of total added N) ± standard error during 27 days of incubation from biobased fertilizers and a reference of NH_4HCO_3 surface applied to soil (Acidic sandy soil) at application rates of ½: 0.36 g N kg−1 DW soil, 1: 0.72 g N kg−1 DW soil, and 2: 1.44 g N kg−1 DW soil. Soil moisture content at 60% of WHC. Note different scales on vertical axes. Letters indicate significant different NH_3 volatilization potential between application rates within each BBF.

3.5. Experiment 4: effect of soil type

The accumulated potential NH_3 volatilization was significantly higher for Acidic sandy soil for all BBFs and the NH_4HCO_3 reference at the end of the incubation period compared to Acidic clay soil, Neutral loamy soil, and Alkaline clay soil (Fig. 4). The accumulated potential NH_3 volatilization was lowest for Acidic clay soil and Alkaline clay soil.

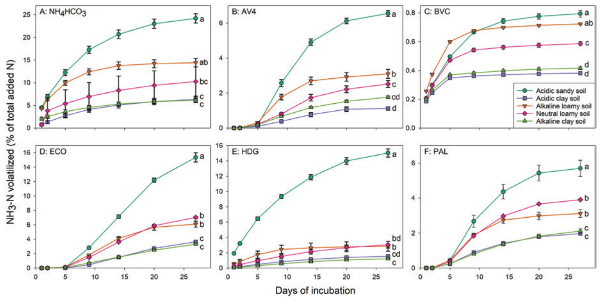


Fig. 4. Mean accumulated NH_3–N volatilized (% of total added N) ± standard error during 27 days of incubation from biobased fertilizers (B–F) and a reference of NH_4HCO_3 (A) surface applied to five different soils (Acidic sandy soil, Acidic clay soil, Alkaline loamy soil, Neutral loamy soil, and Alkaline clay soil). Application rate of 0.72 g N kg−1 DW soil and a soil moisture content at 60% of WHC. Note different scales on vertical axes. Letters indicate significant different potential NH_3 volatilization between soils within each BBF. N = 3, except for D: ECO on day 20 for Alkaline loamy soil where N = 2 and B: AV4 on day 27 for Acidic clay soil where N = 2.

In a linear mixed model, soil characteristics (pH $CaCl_2$, OM, and clay content) and their interactions with time explained 88% of the variation in potential NH_3 volatilization for all days, all five soils and all BBFs + NH_4HCO_3 reference. Accumulated potential NH_3 volatilization was negatively correlated with pHCaCl2 (−0.15), OM (−0.13), and clay content (−0.002).

3.6. Experiment 5: effect of soil moisture

No clear pattern across BBFs was observed for the differences in soil moisture (WHC levels) (Fig. 5). There were no marked differences in NH3 volatilization between WHC levels for ECO and HDG. For AV4, 90% WHC resulted in the highest volatilization and 30% WHC in the lowest; whereas, the opposite was true for the NH_4HCO_3 reference.

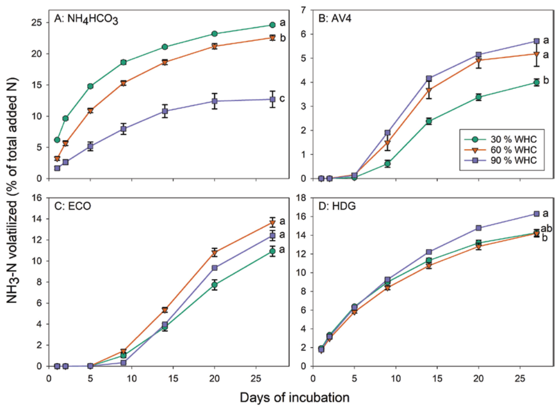


Fig. 5. Mean accumulated NH_3–N volatilized (% of total added N) ± standard error during 27 days of incubation from biobased fertilizers and a reference of NH_4HCO_3 surface applied to soil (Acidic sandy soil); soil moisture content was at 30%, 60% or 90% of WHC. Application rate of 0.72 g N kg−1 DW soil, except for D: HDG 30% WHC with an application rate of 0.48 g N kg−1 DW soil. Note different scales on vertical axes. N = 3.

4. Discussion

4.1. Potential NH_3 volatilization from biobased fertilizers

The great variability in the quantity and temporal pattern of potential NH_3 volatilization from the 39 BBFs included in this study (Experiment 1) highlights the importance of accounting for the fertilizer type when predicting NH_3 volatilization upon application.

4.1.1. Temporal pattern in NH_3 volatilization

The Michaelis-Menten or Monod type equation has often been used to describe NH_3 volatilization from soil upon application of slurry (Monaco et al., 2012). Liao et al. (2019) observed high initial NH_3 volatilization during the first 2–3 days from digestates applied to soil using a dynamic flow-through setup. After the initial days, NH_3 volatilization was very low. Thus, the pattern of NH_3 volatilization followed a concave/Michaelis-Menten type equation. The findings of Liao et al. (2019) are in agreement with this study regarding the three digestates SDG, GRF, and HDG (Fig. 1). However, for the majority of BBFs, the pattern of potential NH_3 volatilized followed a convex shape in the initial period of 20 days, where a lag phase in the potential NH_3 volatilization was observed (Fig. 1). This is in agreement with the findings of Erwiha et al. (2020), who also found convex shaped curves of accumulated NH_3 volatilization during the initial 2–3 weeks after application of blood meal and feather meal on a fine clay loam in a field trial in Colorado, USA. This convex curve of NH_3 volatilization potential could indicate that NH_3 volatilization from the majority of BBFs is controlled by the rate of BBF N mineralization.

However, this was not measured in the present study. Another explanation for this delay in NH_3 volatilization, resulting in convex shaped curves, could be an increase in pH during the experimental period, which was not measured in the present study; pH was only measured, after thoroughly mixing the sand with BBF applied, at the end of the incubation. At the end of the incubation period (day 27/44) nearly all samples with BBFs surface applied to sand had a pH above 7 (Table A4). Only SYS had a pH below 7 (6.7) and only three treatments (ASL, MAL, and SYS) had a pH below the no treatment control of pH 7.9. Thus, pH was not the factor limiting NH_3 volatilization at this last stage, where close to all NH_4^+-N could potentially volatilize as NH_3. However, earlier in the incubation period, low pH might have limited NH_3 volatilization.

4.1.2. BBF properties' ability to predict NH_3 volatilization potential

89% of the variation in accumulated NH3 volatilization potential could be explained by initial BBF properties (pH, NH_4^+-N, NO_3^--N, DM, and C:N) and their interaction with time. The ammonium-N content and pH of the BBFs showed a weak positive correlation with potential NH_3 volatilization on the first day. This confirms the hypothesis that BBFs with a high NH_4+-N content and/or high pH will have a high NH_3 volatilization potential.

4.1.3. Digestates

Generally, digestates with animal manure and slurry as source material have a higher NH_3 volatilization potential upon application in the field compared to non-digested animal manure and slurry (Moeller and Stinner, 2009; Nkoa, 2014). In this study, the three digestates (HDG, SDG, and GRF) (Table 1) were also the BBFs with the highest NH_3 volatilization potential. Rabiger et al. (2020) found NH_3 volatilization of 7.6–18.3% of total applied N from digestate applied at five different sites in Germany, using a standardized dynamic closed chamber method. The results of NH_3 volatilization from digestates surface applied to sand in this study were higher (39–64% of applied N). However, the results of Rabiger et al. (2020) are comparable, although slightly higher, compared to the results in this study on NH_3 volatilization potential from the digestate HDG surface applied to five different soils (1.2–15% of applied N).

4.1.4. Poultry manure containing BBFs

This study included six BBFs containing poultry manure or poultry litter (Table 1). In a previous laboratory incubation study, using a sandy loam soil, NH_3 volatilization from application of poultry manure was found to range from 3.2% to 6.1% of applied N (Akiyama et al., 2004). For AV4 surface applied to the Acidic sandy soil, accumulated NH_3 volatilization on day 27 was only 4.1% of applied N, which is comparable to the results of Akiyama et al. (2004). The hypothesis that BBFs produced from poultry manure would have a high NH_3 volatilization potential can neither be completely confirmed nor completely rejected, as the poultry manure BBFs were the group with the second highest accumulated NH_3 volatilization potential after digestates, but very similar to the animal by-product BBFs (see Fig. A4). The comparatively low NH_3 volatilization potential may be due to the production process of the BBFs containing poultry manure, since this typically includes a drying step and thereby already promotes a potential NH_3 loss during production. Lockyer et al. (1989) found lower NH_3 volatilization of air-dried poultry manure (6.5% of applied N) compared to poultry slurry (45.5% of applied N). The air-dried poultry manure contained 30% NH_4^+-N of total N compared to 55% NH_4^+-N of total N for the poultry slurry (Lockyer et al., 1989).

Moreover, Lockyer et al. (1989) found a high initial NH_3 volatilization from poultry, pig, and cattle manure and slurry, with 80% or more of the NH_3 volatilization occurring within the first 48 h after application. This rapid initial NH_3 volatilization was not observed for the poultry manure containing BBFs included in this study, which all had a delayed response in NH_3 volatilization (Fig. 1). This might be explained by a lower average concentration of 15% NH_4^+-N of total N in the poultry manure containing BBFs compared to the air-dried poultry manure in Lockyer et al. (1989). Marshall et al. (1998) conducted a study using broiler litter with similar average NH_4^+-N of total N, 14%, as in this study. Comparable to the observations of this study, Marshall et al. (1998) observed a delayed response in NH_3 volatilization with a sharp increase in the NH_3 volatilization rate 1–3 days after broiler litter application in a field study, using the micrometeorological method.

4.1.5. Animal by-product BBFs

This study included nine BBFs containing animal by-products (Table 1). Accumulated NH_3 volatilization on day 27 from these BBFs surface applied to sand ranged from 6.1% to 34.3% of applied N and was generally in the upper range of NH_3 volatilization potential from all BBFs (see Fig. A4). However, the animal by-products containing BBFs was the group with the lowest NH_4^+-N content with 2% NH_4^+-N of total N. Thus, the relatively high accumulated NH_3 volatilization could not be explained by a high NH_4^+-N content. Therefore, a rapid mineralization of N and subsequent volatilization of the NH_4^+-N likely explains the relatively high NH_3 volatilization. Erwiha et al. (2020) conducted a field experiment on a fine clay loam soil using a semi-static chamber and found NH_3 volatilization of 25% and 32.1% of applied N for blood meal and feather meal respectively.

The NH_3 volatilization potential from animal by-product derived BBFs in this study is thus comparable, although lower than that found by Erwiha et al. (2020) especially considering that BBFs were applied to sand in this study and to a fine clay loam in the study conducted by Erwiha et al. (2020).

4.2. Implication of BBF application technique and rate

4.2.1. Application technique

The incorporation of all BBFs reduced potential NH_3 volatilization significantly, except for BO_1 (Experiment 2, Fig. 2). This is in agreement with numerous previous studies conducted on other BBFs in both field and laboratory trials (Svensson, 1994; Nyord et al., 2012; Feilberg and Sommer, 2013; Herr et al., 2019; Liao et al., 2019; Rocha et al., 2019; Maris et al., 2020).

For the digestate HDG, which was the only BBF with a substantial NH_3 volatilization potential during the first day that was tested for the effect of incorporation, the incorporation reduced the potential NH_3 volatilization markedly by 88% during the first day. Thus, incorporation was an effective way of preventing initial NH_3 volatilization. Looking at the accumulated NH_3 volatilization for the 27-day period for HDG, it was overall reduced by 64% though, showing that some NH_3 still volatilized. From these results, it was concluded that incorporation is an effective way to reduce NH_3 volatilization from BBFs, as is also often assumed for more commonly studied BBFs, e.g. manure. Thus, this confirms the hypothesis that incorporation reduces the potential NH_3 volatilization from BBFs.

4.2.2. Application rate

Although a tendency towards a non-linear increase in potential NH_3 volatilization was visually observed for AV_4, HDG, and the NH_4HCO_3 reference, it was not clearly significant (Experiment 3, Fig. 3). This is in agreement with results from a study conducted by Erwiha et al. (2020), who found no clear response of NH_3 volatilization to the BBF application rate of blood meal, feather meal, fish emulsion, and cyano-fertilizer applied on a fine clay loam in a field trial in Colorado, USA. This suggests that the overall trends found in this study are valid over a wider range of application rates than those tested here.

4.3. Effect of soil type and soil moisture

4.3.1. Soil properties

Soil characteristics and their interaction with time explained 88% of the variation in accumulated potential NH_3 volatilization from BBFs applied to different soils (Experiment 4. Fig. 4). Potential NH_3 volatilization was found to negatively correlate with soil $pHCaCl_2$ and soil OM. Moreover, a very weak negative correlation was found between potential NH_3 volatilization and soil clay content. The negative correlation observed between soil pH and potential NH_3 volatilization is the opposite of what was expected. This is likely attributed to the fact that the soils expected to have a high NH_3 volatilization due to their alkaline pH also had a high content of clay, which sorbs NH_4^+. Even though Alkaline clay soil had the highest pH, Acidic clay soil and Alkaline clay soil overall had the lowest NH_3 volatilization potentials. Alkaline clay soil had, though, by far the highest CEC and clay content, which must have counteracted the effect of the high pH on the potential NH_3 volatilization. However, the hypothesis that high OM and high clay content decrease the potential NH_3 volatilization can be confirmed.

The results of this study indicate that it is important to consider the potential interactions of soil characteristics that impact NH_3 volatilization when assessing the impact of the soil on potential NH_3 volatilization. This viewpoint is in agreement with Zhenghu and Honglang (2000), who stress that no single soil property alone can explain NH_3 volatilization. However, it should be emphasized that only five soils were included in this study. Thus, results on the impact of the soil type are not comprehensive, as only a small fraction of variation in soil types was considered here. Despite the incomplete set of soil types included in this study, the effect of the soil type was consistent between BBFs, with the same soils resulting in the highest and lowest NH_3 volatilization potentials, although the magnitude of the difference between soils differed between the different BBFs.

4.3.2. Soil moisture

Mkhabela et al. (2006) found that NH_3 volatilization increased with increasing water filled pore space (WFPS) (50, 70, and 90% WFPS) from hog slurry applied to a fine loam soil in a laboratory study. However, this was not the case for all BBFs in this study. Only AV_4 and partly HDG showed a tendency to increase NH_3 volatilization with increasing soil moisture level (Experiment 5, Fig. 5). This study's' finding that there is no clear relationship between NH_3 volatilization potential and soil moisture level is, however, in agreement with other previous studies conducted by Akiyama et al. (2004) and Liao et al. (2019). Liao et al. (2019) found soil moisture to have relatively little impact on NH_3 volatilization, using a dynamic flow-through setup. Akiyama et al. (2004) found no significant effect of different WFPS (40, 60, and 80%) levels on NH_3 volatilization on a sandy loam soil, using a flow-through chamber technique.

5. Conclusions

The 39 novel BBFs surface applied to sand varied immensely in potential NH_3 volatilization during the 27-day incubation period. CMC and PFC grouping systems for BBFs could not adequately explain the differences in potential NH_3 volatilization from BBFs. However, a grouping of BBFs based on more traditional concepts was markedly better in explaining differences in potential NH_3 volatilization. The highest accumulated NH_3 volatilization potential was found for digestates (48% of applied N volatilized) while the lowest was found for composts and struvites (<1% of applied N volatilized). Poultry manure, animal by-products, plant-based, and mixed source BBFs had intermediate accumulated NH_3 volatilization potentials in a similar range (12%–20% of applied N). The temporal pattern of potential NH_3 volatilization also varied greatly between BBFs, with most BBFs showing a delayed response in NH_3 volatilization.

The initial BBF characteristics measured in this study and their interaction with time explained 89% of the variation in accumulated potential NH_3 volatilization from the 39 novel BBFs surface applied to sand. Potential NH_3 volatilization was affected significantly by soil type, with highest NH_3 volatilization potential for the sandy soil (acidic) and lowest for the two clayey soils (acidic and alkaline). The incorporation of BBFs in soil could effectively reduce potential NH_3 volatilization. However, when incorporation is not an option, e.g. when applying BBFs in growing crops, NH_3 volatilization may pose a significant risk of yield loss and environmental impact for certain BBFs. It should be emphasized that under field conditions where crops will take up some of the NH_4+, and the gas gradient of NH_3 and CO_2 might be less steep, NH_3 volatilization might not be as severe as in this laboratory incubation where conditions favoring NH_3 volatilization were applied.

Author contribution

Lærke Wester-Larsen: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Resources; Validation; Visualization; Roles/Writing - original draft; Writing – review & editing. Dorette Sophie Müller-Stöver: Conceptualization; Methodology; Resources; Supervision; Writing – review & editing. Tapio Salo: Data curation; Formal analysis; Methodology; Resources; Validation; Writing – review & editing. Lars Stoumann Jensen: Conceptualization; Funding acquisition; Methodology; Project administration; Resources; Supervision; Writing – review & editing.

Declaration of competing interest

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

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Optimising bio-based fertilisers in agriculture

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