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## Agricultural valorization of organic residues: Operational tool for determining the nitrogen mineral fertilizer equivalent

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#### ABSTRACT

Organic residues from agriculture and waste and wastewater treatment can be used as organic fertilizers or soil amendments due to their nutrient and organic matter contents. In order to replace mineral fertilizers by organic residues at equivalent nutrient and fertilizer values, the mineral fertilizer equivalent (MFE) of the organic residue must be known. A simple Excel-tool was developed that allowed determination of the nitrogen MFE of organic residues based on their nitrogen content and composition, and nitrogen emissions from field application of the organic residue. Nitrogen field emissions were estimated using simple models and average climate and soil conditions. A global sensitivity analysis revealed that the application method, determining the extent of incorporation into the soil, contributed 66% to the variability of the calculated nitrogen MFE for application of raw pig slurry.

Keywords: agricultural valorization, organic residues, mineral fertilizer equivalent, sensitivity, substitution

#### 1. Introduction

Many organic residues from agriculture as well as waste and wastewater treatment are suitable for an agricultural valorization as organic fertilizer or soil amendment due to their nutrient and organic matter contents. Application of organic fertilizers can replace the use of mineral fertilizers resulting in a financial advantage for the farmer. Furthermore, if organic residues are applied instead of mineral fertilizers and not in addition to, nitrogen (N) and phosphorus (P) emissions will be reduced due to decreased N and P application to farmland. Organic fertilizers have, however, a lower fertilizing value than mineral fertilizers, because nitrogen is present in both mineral and organic forms. Organic nitrogen is only plant available after mineralization by soil microorganisms. For replacing mineral fertilizers by organic residues at equivalent nutrient and fertilizer values, the mineral fertilizer equivalent (MFE) of the organic residues must be known. So far, MFE values reported in literature were typically used when manures or sewage sludge were substituted for mineral fertilizers in life cycle assessment (LCA) studies (e.g. Bayo et al. 2012; De Vries et al. 2012; Johansson et al. 2008; Linderholm et al. 2012) (see Hélias and Brockmann (2014) for a review). Although simple methods for estimating the MFE of organic residues from their composition have been reported (Delin et al. 2012; Water Environment Federation 2005), they have not yet been applied in LCA studies. A decision support tool (MANNER-NPK) for determination of plant available nitrogen from manure has been developed by Nicholson et al. (2013). The decision support tool was designed for the use by farmers to calculate for a specific manure application the plant available nitrogen for the year of application and the following year. Quantification of the plant available nitrogen was based on organic nitrogen mineralization curves and a sophisticated calculation of nitrogen losses considering site specific climate (e.g. temperature, rainfall, wind speed) and soil conditions (e.g. moisture, temperature) (Nicholson et al. 2013).

The aim of this study was to develop a simple Excel-tool designated for the use in LCA studies that allows for determining the nitrogen MFE of organic residues. The nitrogen MFE is calculated based on the nitrogen content and composition of the organic residue, and nitrogen emissions from field application of the organic residues, which are estimated for average climate and soil conditions.

#### 2. Methods

#### 2.1. Nitrogen MFE calculation

We based the nitrogen MFE calculation on the plant available nitrogen (PAN) calculation presented by the Water Environment Federation (2005) for biosolids. But in contrast to Water Environment Federation (2005), we take into account all nitrogen emissions from field application of the residue instead of only  $NH_3$  emissions. In

general, the nitrogen MFE calculation is based on the nitrogen content and composition of the residue (ammonium-N, nitrate-N, organic nitrogen), a mineralization rate for organic nitrogen, and estimated nitrogen emissions from field application of the organic residue (Eq. 1).

$$PAN = N_{org} \cdot k_{min} + NH_4 \cdot N + NO_3 \cdot N - N_{emissions}$$
Eq. 1

where  $N_{org}$  is the organic nitrogen content of the fertilizer/amendment [kg Norg/kg N<sub>tot</sub>], *NH*<sub>4</sub>-*N* is the ammonium nitrogen content [kg NH<sub>4</sub>-N/kg N<sub>tot</sub>], *NO*<sub>3</sub>-*N* is the nitrate nitrogen content [kg NO<sub>3</sub>-N/kg N<sub>tot</sub>],  $k_{min}$  is the organic nitrogen mineralization rate factor [-], and  $N_{emissions}$  is the sum of all nitrogen emissions from fertilizer application (NH<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, N<sub>2</sub>O and NO<sub>x</sub>) [kg N/kg N<sub>applied</sub>]. Organic nitrogen mineralization rate factors for different organic residues are given in Table 1. Nitrogen emissions from fertilizer application are calculated with equations given in section 2.2.

Table 1. Organic	mineralization	rate factors	for different	organic residues.
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Mineralization rate factors					
Organic residue	Year of application	Long-term	Source		
Dairy cattle or other livestock					
Lagoon water (< 1% DM)	0.40	0.77	Sullivan (2008)		
Thin slurry (1 to 5% DM)	0.40	0.77	Sullivan (2008)		
Thick slurry (5 to 10% DM)	0.30	0.67	Sullivan (2008)		
Solid (> 10% DM)	0.30	0.67	Sullivan (2008)		
Separated dairy solids or horse manure <sup>a</sup>	0.10	0.35	Sullivan (2008)		
Compost	0.10	0.35	Sullivan (2008)		
Solid poultry (> 10% DM)	0.50	0.87	Sullivan (2008)		
Activated sludge (biosolids)	0.40	0.75	Water Environment Federation (2005)		
Supernatant <sup>b</sup>	0.40	0.75	Water Environment Federation (2005)		

<sup>a</sup> dairy solids from a mechanical separator.

<sup>b</sup> from activated sludge processes.

#### 2.2. Calculating nitrogen emissions from field application

Ammonia emissions from field application of organic fertilizers and amendments were calculated with the AGRAMMON model (Nemecek and Schnetzer 2012), which takes into account application method, time of incorporation after application, and weather conditions during application, among others.

$$NH_3 - N = TAN \cdot (EF + c_{app}) \cdot c_x$$
 Eq. 2

where  $NH_3$ -N is the emission of ammonia [kg NH<sub>3</sub>-N], *TAN* is the total ammonium nitrogen [kg N], *EF* is the emission factor [%TAN/100],  $c_{app}$  is a correction factor influencing the emission factor (applies only for liquid manure; [-]), and  $c_x$  is a correction factor taking into account impacts of application method and time [-]. Correction factors were taken from Agrammon Group (2013b). Emission factors for a range of organic residues are given in Table 2.

Table 2. Ammonia emission factors for different organic residues

Organic residue	Emission factor [%TAN]	Source	
Cattle manure, liquid	50	Agrammon Group (2013b)	
Cattle manure, solid	80	Agrammon Group (2013b)	
Pig manure, liquid	35	Agrammon Group (2013b)	
Pig manure, solid	60	Agrammon Group (2013b)	
Poultry manure, liquid and solid	40	Agrammon Group (2013b)	
Horse, sheep, goat manure	70	Agrammon Group (2013b)	
Compost, solid digestate	80	Agrammon Group (2013b)	
Liquid digestate	60	Agrammon Group (2013a)	
Activated sludge (biosolids)	50	Water Environment Federation (2005)	
Supernatant <sup>a</sup>	50	assumed to be the same as for biosolids	

<sup>a</sup> from activated sludge processes.

Nitrate emissions were estimated with the Smaling (1993) model, proposed by Roy et al. (2003), because the model enables to discriminate between nitrate emissions originating from organic residue application and background nitrate emissions from soil organic matter nitrogen.

$$\begin{aligned} NO_3 - N &= (N_{min,soil} + N_{fert}) \cdot (0.021 \cdot P_{prec+irr} - 3.9)/100, & \text{for } c < 35\% & \text{Eq. 3} \\ NO_3 - N &= (N_{min,soil} + N_{fert}) \cdot (0.014 \cdot P_{prec+irr} + 0.71)/100, & \text{for } 35\% < c < 55\% & \text{Eq. 4} \\ NO_3 - N &= (N_{min,soil} + N_{fert}) \cdot (0.0071 \cdot P_{prec+irr} + 5.4)/100, & \text{for } c > 55\% & \text{Eq. 5} \end{aligned}$$

 $NO_3$ -N is the amount of N leached to groundwater [kg N],  $N_{min,soil}$  is the amount of mineralized N in the upper 20 cm of the soil [kg N],  $N_{fert}$  is the amount of N applied with organic residues [kg N],  $P_{prec+irr}$  is the sum of precipitation and irrigation [mm/year], and c is the clay content of the soil [%]. To obtain only nitrate emissions directly related to organic residue application,  $N_{min,soil}$  was set to zero.

Nitrous oxide emissions were calculated with the IPCC method (IPCC 2006) following the equation given in Nemecek and Schnetzer (2012).

$$N_2 O = 44/28 \cdot \left(0.01 \cdot \left(N_{fert} + N_{cr}\right) + 0.01 \cdot NH_3 - N + 0.0075 \cdot NO_3 - N\right)$$
 Eq. 6

where  $N_2O$  is the emission of nitrous oxide [kg N<sub>2</sub>O],  $N_{cr}$  is the nitrogen contained in crop residues [kg N], and  $NH_3$ -N and  $NO_3$ -N are the ammonia and nitrate emissions calculated with equations given above.

Nitrogen oxide emissions were estimated according to Nemecek and Schnetzer (2012) based on nitrous oxide emissions.  $NO_x$  and  $N_2O$  are given in kg NO<sub>x</sub> and kg N<sub>2</sub>O, respectively.

$$NO_x = 0.21 \cdot N_2 O$$
 Eq. 7

#### 2.3. Determination of mean soil and climate conditions

Estimation of nitrate emissions from organic residue application required information on annual precipitation and irrigation, as well as on the clay content of the soil. Mean climate and soil conditions have been determined for five European countries: Denmark, France, Germany, The Netherlands, and Poland (Table 3).

	Precipitation (mm/year)		Agricultural surface area with			
Country		Irrigation <sup>a</sup> (mm/year)	clay content < 35%	clay content 35-55%	clay content > 55%	
Denmark	718 <sup>b</sup>	1.7 <sup>d</sup>	100.0% <sup>i</sup>	0.0% <sup>i</sup>	0.0% <sup>i</sup>	
France	700 <sup>b</sup>	15.0 <sup>e</sup>	93.3% <sup>j</sup>	6.7% <sup>j</sup>	0.0% <sup>j</sup>	
Germany	757 <sup>b</sup>	1.6 <sup>f</sup>	100.0% <sup>k</sup>	0.0% <sup>k</sup>	0.0% <sup>k</sup>	
Netherlands	854 <sup>b</sup>	7.4 <sup>g</sup>	92.5% <sup>1</sup>	$7.5\%^{1}$	$0.0\%^{1}$	
Poland	595°	0.6 <sup>h</sup>	99.0% <sup>m</sup>	1.0% <sup>m</sup>	0.0% <sup>m</sup>	

Table 3. Mean soil and climate conditions used.

<sup>a</sup> Irrigation per total agricultural surface area.

<sup>b</sup> ECA&D (2013)

<sup>c</sup> The Word Bank (2011)

<sup>d</sup> Eurostat (2013) and Statistics Denmark (2014)

<sup>e</sup> Commissariat Général au Développement Durable (2012) and Agreste (2013)

<sup>f</sup> Statistisches Bundesamt (2010) and Statistisches Bundesamt (2012)

<sup>g</sup> CBS et al. (2013) and Eurostat (2014)

<sup>h</sup> Central Statistical Office (2011)

<sup>i</sup> Adhikari et al. (2013)

<sup>j</sup> GIS Sol (2013)

<sup>k</sup> Düwel et al. (2007) and Bundesanstalt für Geowissenschaften und Rohstoffe (2007)

<sup>1</sup> WUR-Alterra (2006)

<sup>m</sup> FAO (2003)

#### 2.4. Sensitivity analysis

We carried out a global sensitivity analysis to evaluate the impact of different parameters on the calculated nitrogen MFE value of a selected organic residue (raw pig slurry). Parameters included in the analysis and their ranges and discrete values, respectively, are given in Table 4. Based on the clay contents of agricultural soils in the five European countries considered (see Table 3), it was assumed that agricultural soils do not have a clay content > 55%. The variance-based extended Fourier amplitude sensitivity test (extended FAST) was applied, which allows for estimating the contribution of individual input parameters to the variance of the output variable (Saltelli et al. 2000). First-order sensitivity indices ( $S_i$ ) provide the fractional contribution of individual parameters to the variance of the output. Total sensitivity indices ( $S_{Ti}$ ) estimate the contribution of individual parameters including interaction effects between parameters, and are defined as the sum of sensitivity indices involving parameter *i*. Sample generation and calculation of sensitivity indices was carried out using Simlab 2.2 (European Commission and IPSC 2004).

Parameter	Symbol	Values/range	Distribution	Source
Application method (correction factor)	CMethod	0.2; 0.3; 0.5; 0.7; 1.0	Discrete	Agrammon Group (2013b)
Season of application (correction factor)	CSeason	0.95; 1.00; 1.15	Discrete	Agrammon Group (2013b)
Daytime of application (correction factor)	CDaytime	0.8; 1.0	Discrete	Agrammon Group (2013b)
Application on unseasonably warm day (correction factor)	CWarm_day	0.96; 0.98; 1.00; 1.05	Discrete	Agrammon Group (2013b)
NH <sub>3</sub> emission factor (for raw pig slurry)	EF	0.35-0.75	Uniform	this study
Mineralization rate factor for organic ni- trogen	$\mathbf{k}_{\min}$	0.4-0.8	Uniform	this study (first-year vs. long- term mineralization rate)
Annual precipitation and irrigation [mm/year]	P <sub>prec+irr</sub>	600-850	Uniform	this study
Agricultural surface area with clay content < 35%	clay1	0-1	Uniform	this study
Agricultural surface are with clay content 35-55%	clay2	1-clay1	Relation	this study

Table 4. Parameter values and ranges used in the global sensitivity analysis

#### 3. Results

The developed Excel-tool requires as input information on nitrogen content and composition of the organic residue, type/nature of organic residue, application method and time of field application, and geographical location (for climate and soil conditions). First, field emissions of NH<sub>3</sub>, NO<sub>3</sub>, N<sub>2</sub>O and NO<sub>x</sub> during organic residue application are calculated. Then, the nitrogen MFE for the first year and for the long-term are calculated. Figure 1 shows nitrogen MFEs calculated for field application of raw pig slurry with 4 kg N<sub>tot</sub>/m<sup>3</sup>, 2.5 kg NH<sub>4</sub>-N/m<sup>3</sup>, 1.5 kg N<sub>org</sub>/m<sup>3</sup>, different application methods and different geographical locations. Nitrogen MFEs calculated for Danish and French climate and soil conditions were very similar. Total annual precipitation and irrigation differed only slightly (5 mm/year) between Denmark and France, but in contrast to Denmark, 6.7% of the French agricultural surface area had a clay content between 35 and 55% (Table 3). The lowest nitrogen MFEs were calculated for Dutch soil and climate conditions, while the highest MFEs were obtained for Poland. Poland had the lowest annual precipitation and irrigation, whereas the Netherlands had the highest annual precipitation and irrigation. For the same application method, the MFE increased by about 30% when the long-term mineralization rate factor for organic nitrogen was used instead of the mineralization rate factor for the year of application. For the same mineralization rate factor, nitrogen MFEs increased for application methods that allowed for better incorporation of the applied fertilizer into the soil, because burying the applied organic residue decreases NH<sub>3</sub> volatilization.

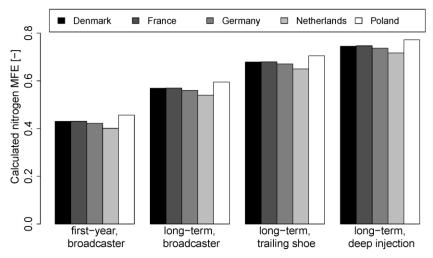


Figure 1. Calculated nitrogen MFE values for different application methods and geographical locations

Nitrogen MFE values calculated for the same application method did not vary much between the selected countries. The variations were mainly due to differences in annual precipitation and irrigation, as the soil types (clay content) were very similar for the different countries. To evaluate the impact of more extreme soil and climate conditions not covered by the selected countries, the clay content of the soil was assumed to be either <35%, between 35% and 55%, or >55%, and the annual precipitation and irrigation was assumed to be 250, 500, 750 or 1000 mm/year. First-year nitrogen MFE values calculated for broadcaster application and different soil and climate conditions are given in Figure 2. Nitrogen MFE values differed most for varying annual precipitation and irrigation decreased with increasing clay content of the soil. Independent of the clay content of the soil, nitrogen MFE values were higher for lower precipitation and irrigation due to lower nitrogen emissions. For low annual precipitation and irrigation (250 mm/year), nitrogen MFE values were higher for low clay contents, while for high annual precipitation and irrigation (1000 mm/year), nitrogen MFE values were higher for higher clay contents.

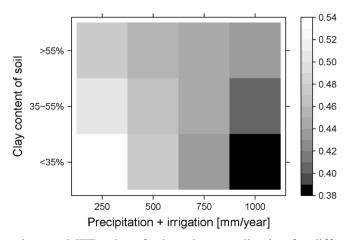


Figure 2. Calculated first-year nitrogen MFE values for broadcast application for different clay contents of soil and different annual precipitation + irrigation.

Calculated nitrogen MFEs presented above showed that application method, mineralization rate factor for organic nitrogen, amount of annual precipitation and irrigation, and clay content of the soil affected the calculated nitrogen MFEs. In order to quantify the impact of the different parameters on the variance of the MFE, a global sensitivity analysis using the extended FAST method was carried out. Figure 3 a) shows the large variability in the nitrogen MFE as a result of the variability in the model parameters. The contribution of individual parameters to the variance of the nitrogen MFE is presented in Figure 3 b). The type of application method chosen had

clearly the largest impact on the calculated MFE followed by the NH<sub>3</sub> emission factor (*EF*) and the mineralization rate for organic carbon ( $k_{min}$ ). The variability in the application method contributed 66.4% to the uncertainty in the calculated MFE based on the first-order sensitivity index and 73.1% based on the total sensitivity index. Contributions of the NH<sub>3</sub> emission factor and the mineralization rate factor for organic nitrogen to the variance of the MFE were very similar with 10.3% and 11.1% (first-order sensitivity index), respectively. All other parameters had only a minor impact (< 5%) on the calculated MFE.

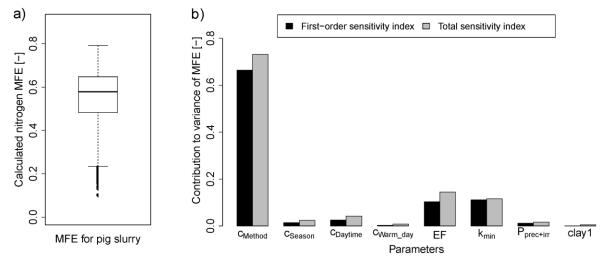


Figure 3. Uncertainty and sensitivity analysis results: a) Box-Whisker plot of the calculated nitrogen MFEs for raw pig slurry. The boundaries of the box mark the 25<sup>th</sup> and 75<sup>th</sup> percentile, and the line within the box marks the median. Whiskers above and below the box indicate the furthest points that are within 1.5 times the interquartile range (box length) from the end of the box; b) Contribution of the individual parameters to the variance of the calculated nitrogen MFE based on the first-order and total sensitivity indices calculated with the extended FAST method.

#### 4. Discussion

The developed Excel-tool was based on simple models describing emissions from field application of organic residues. The model for estimating NH<sub>3</sub> volatilization losses accounted only indirectly for climate conditions through different correction factors. In contrast, Nicholson et al. (2013) considered in their decision support tool the impact of soil moisture content, wind speed, land use, and rainfall after spreading on the volatilization of NH<sub>3</sub>. But it is difficult to say how much climatic conditions influence NH<sub>3</sub> emissions. Webb et al. (2012) showed that the measuring method and the incorporation of manure (vs. no incorporation) had significant effects on NH<sub>3</sub> emissions. The latter agrees with our results from the sensitivity analysis. When fixing the application method (or the extent of fertilizer incorporation) to broadcaster application without incorporation, the variability in the ammonia emission factor had the largest impact (55%) on the variance of the nitrogen MFE (data not shown). Thus, reducing the variability of the ammonia emission factor by determining, for example, a standard measurement method for ammonia field emissions, would significantly decrease the variability in the estimated nitrogen MFE.

In the calculation of the nitrogen MFE, we did not differentiate between different soil types when applying organic nitrogen mineralization rates. Shah et al. (2013) observed, however, that mineralization rates of organic nitrogen from organic residues vary widely with soil types. But the sensitivity analysis carried out in this study showed that the variation of the mineralization rate factor for organic nitrogen in the range of 0.4-0.8 contributed only 11% to the variation in the nitrogen MFE. Even for a fixed application method (broadcaster application), the contribution of  $k_{min}$  to the variance of the nitrogen MFE increased only slightly to 16% (data not shown). As a consequence, reducing the variability in  $k_{min}$  by considering the soil type would result only in a minor decrease in the variability of the nitrogen MFE. Thus, the simplification of not differentiating between soils considered to be acceptable.

Our goal was to develop a tool that is easy to apply and does not require many inputs. We think that using simple models and average climate and soil conditions for estimating the nitrogen MFE is reasonable for LCA studies, because LCA studies are often based on a regional or national level. Nonetheless, applying site specific soil and climate conditions and mineralization rates for organic nitrogen may reduce the uncertainty of the calculated nitrogen MFE for a specific case.

#### 5. Conclusion

An Excel-tool was developed that allows for fast and easy determination of the nitrogen MFE of organic residues valorized as organic fertilizers or soil amendments. The nitrogen MFE is needed for calculating the amount of substituted mineral fertilizers. The tool also calculated nitrogen field emissions from organic residue application. The nitrogen MFE was estimated using simple models and average climate and soil conditions for estimation of nitrogen field emissions. A global sensitivity analysis using the extended FAST method was used to quantify the contribution of individual parameters to the uncertainty in the calculated nitrogen MFE. For the case of raw pig slurry application, the type of application method selected (determining the extent of incorporation into the soil) contributed most (66.4%) to the variability of the nitrogen MFE, followed by the NH<sub>3</sub> emission factor and the mineralization rate for organic carbon. It is, therefore, essential to determine the nitrogen MFE for a specific application method to reduce the uncertainty in the calculated nitrogen MFE and with it the uncertainty in the amount of replaced mineral fertilizers. The Excel-tool is available from the authors upon request.

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