Assessing the environmental benefit of a new fertilizer based on activated biochar applied to cereal crops

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Abstract

This study analyzes the environmental benefits that a nitrogen fertilizer based on activated biochar has in comparison to other traditional fertilizers (urea, ammonium nitrate (AN), ammonium sulfate (AS) and di-ammonium phosphate (DAP)). With this aim, activated biochar was generated from residual biomass (barley straw) through physical activation and the resulting biochar was combined with mineral fertilizer to synthethise the fertilizer. This new product was subjected to environmental assessment by means of two different approaches, Life Cycle Assessment (LCA) and nitrogen footprint procedure, both of which considered standard conditions typical of Mediterranean climate and wheat and corn as the fertilized crops. Emission factors of traditional fertilizers were obtained from internally developed models, which were in turn based on real data from literature. As for emission factors of the new product, they were calculated basing on experimental results. Fertilizer impacts in terms of acidification, eutrophication and climate change were estimated, thus revealing a great performance of activated biochar over other fertilizers in terms of reactive nitrogen (Nr), reaching a maximum saving rate of 63% in the amount of Nr released by volatilization and leaching. In addition, this work offers a methodology

for environmental analysis of fertilizers and provides useful quantitative indicators for the environmental benefit and the saving of reactive nitrogen, which could contribute to the development of new commercial low N-emissions fertilizers.

Keywords: nitrogen fertilizer, activated biochar, LCA, reactive nitrogen

1. Introduction

One of the main environmental challenges that society must face today is the serious alteration of the natural cycle of Nitrogen (N) as a consequence of the high content of reactive nitrogen (Nr) released to the environment. This effect is largely due to nitrogen fertilization, which is undoubtedly one of the greatest achievements of modern society but also a source of environmental damage. Intensification of agricultural production is the result of significant growth population over the last century. One of the environmental threats associated with this intensification is the impact of mineral nitrogen fertilizers [1.].

In the agricultural sector, Nr has always been a limiting nutrient, since optimal levels of both biological N fixation and Nr recycling are required to increase production. Plants are able to directly assimilate Nr in the form of nitrates (NO_3^-) and ammonium (NH_4^+) [2.], which may be present in the soil as a result of natural mineral deposits, artificial fertilizers, animal manure, organic matter decomposition or atmospheric deposition. In agriculture, a large part of the fertilizers nitrogen is released to the environment. This Nr excess either enters into the hydrological system through leaching, flow and groundwater runoff, or else it is emitted to the atmosphere. Once released, the Nr moves through the natural ecosystem (biota) and the physical environment, changing forms and flowing through the soil, water and air, and thus triggering several undesired consequences [3.]. This is known as the nitrogen cascade first described by Galloway, which is based on the fact that the geographical extent of the Nr effects increases over time. Thus the effects of the Nr in the short term are mainly local or regional, while their different forms (for example, NH_3, NO_x, NO_3) can have a variety of specific effects. However, the same Nr atom can cause over time multiple effects on the atmosphere, terrestrial ecosystems, freshwater and marine systems, as well as in human health [4.].

Sustainable agriculture requires the use of appropriate fertilizers that favor the reduction of these emissions to the environment. In this context, biochar soil treatment is a reported strategy in the mitigation of nitrogen emissions in agricultural sector [5.] to improve soil fertility [6.] and agricultural N-cycle [7.], which encourages its use as a fertilizer. According to several bibliographic sources biochar amendments may provide environmental benefits such as carbon sequestration, reduction of nitrate leaching [8.] and reduction in N_2O flux in treatments containing biochar [9.]. Some studies states that the combined application of biochar and nitrogen fertilizer benefits nitrogen retention towards near-root areas [10.] as well as grain yield, nitrogen uptake and soil carbon content [11.].

Moreover, the microcrystalline structure created during the activation process of biochar from carbonaceous materials confers it an excellent adsorption capacity, which offers a further advantage in its use as a complement to nitrogen as it enables it to capture a variety of chemical species through chemical or physical processes [12.]. There are numerous studies that prove its positive effect on agricultural soils by improving crop yields [13.],[14.],[15.],[6.], reducing N_2O [16.],[17.] and NH_3 emissions [5.] and nitrate leaching [18.],[19.].

The double-fold objective of the present study is to determine the environmental benefit produced by application of a biochar-based fertilizer as opposed to traditional fertilizers, as well as to quantify the achieved reduction of reactive nitrogen losses through volatilization and leaching.

To this end, a biochar-based fertilizer was synthesized from activated biochar of barley straw and its benefits were analyzed for a particular case study.

Environmental analysis are usually based on LCA methodology which has become a very common approach for identifying, quantifying and evaluating the potential environmental impacts of production processes or products [1.]. Defined in the standard ISO 14040 [1.], this method consists in of gathering and evaluating input and output data for its production or use and assessing its potential effects on the environment during its life cycle [20.]. According to the guidelines described by the norm, the system boundaries of the case study can comprise raw materials procurements, production, utilization and final storage [21.].

Previously published LCA assessments on agricultural field, have focused on the environmental impacts of different types of fertilizers. For example, Hasler et al. [22.] compared complex, bulk blend and single nutrient fertilizers in order to analyze their environmental impact along their whole supply chain. Martinez-Blanco et al. [23.] compared compost and mineral fertilizer in a tomato Mediterranean production under open-field and standard greenhouse systems. Similarly, Romero-Gámez et al. [24.] analyzed two different green bean cropping systems when different mineral fertilizers were applied with the aim of improving the cultivation techniques, equipment, and structures.

As for biochar assessment from a LCA point of view, previous research works have been focused on the comparative evaluation of different schemes of biochar production using different feedstocks [25.],[26.],[27.],[28.]. Other studies [29.] used the LCA analysis to evaluate possibilities of neutralizing global warming impacts in crop production using biochar produced from side flows and buffer-zone biomass. Also, the study performed by Qian et al. [30.] demonstrated that compound organic/inorganic fertilizers with biochar from different feedstocks as N blinder reduced GHGs emission in rice paddy fields. Nevertheless, none of the previous works focused on the study of the fertilizer during its application to the field. In contrast, this is considered a key stage in the analysis, given the importance of N-emissions losses through volatilization and leaching in the field application of the fertilizer, because their impacts may substantially differ among different fertilizers and are strongly influenced by the soil edaphic conditions, climate conditions and crop management.

Among those impacts associated to mineral fertilizers, a difference must be made between industrial production impacts and those produced during their application in agroecosystems. In order to highlight the environmental effects of using the fertilizer in the field and compare the level of impact of different products, this work takes into account only the effects of the application stage. In addition to this, LCA analysis usually involves the use of estimated indexes derived from inputs and outputs data that comprise a multitude of parameters, giving rise to qualitative indicators that offer interesting information on environmental risks but that do not inform about the specific losses of reactive nitrogen. In contrast, other studies focused on determining volatilization and leaching nitrogen loses [31.]-[59.]. Among these, the first one are based on field studies, while leaching ones are based on simplified models of nitrogen and water balances, since they basically depend on soil-related and climate-related parameters. Apart from that, no detailed studies were found that analyzed global losses considering both processes in a systematic way. In this sense, the environmental analysis carried out in this work maintains the ease and usability of indicators while offering rigorous, quantitative information of the main reactive nitrogen losses from the perspective of nitrogen footprint [60.]. In addition, the methodology makes use of characteristic emission factors based on statistical analysis and on field measurements, according to the basic parameters that govern volatilization and leaching processes.

The final results of the environmental analysis showed the ability of the biochar-based fertilizer to save reactive nitrogen when it is applied to different cereal crops. The aim of the present study was to provide a consolidated background for evaluating the sustainability of a new fertilizer product based on activated biochar applied to conventional agro-ecosystems.

2. Materials and methods

2.1. Biochar-based fertilizer

Biochar is the solid carbonaceous residue resulting from thermal conversion of biomass in an oxygen-limited environment, typically through gasification or pyrolysis. There is a huge range of potential feedstocks for biochar production, among which those based on lignocellulosic waste were the most interesting from an environmental point of view [25.]. Like activated carbon, biochar has multiple applications as an adsorption material, and this capacity can be enhanced when biochar is activated [61.]. In this work, activated biochar was produced and used as matrix for the fertilizer production.

Barley straw was the precursor material selected for the production of activated biochar. Barley is the crop with the largest territorial base in Spain (~ 2.5 million hectares, 19% of the total cultivated area) and with distribution throughout the entire territory [62.]. In addition, it is one of the main products contributing to world’s diet. Apart from the use of grain, straw is also used in animal feed and bedding as an inert vegetable cover in woody crops and for other energy uses. However, several studies estimate an availability coefficient for these secondary uses that varies between 85 and 50%, which means that between 15-50% of the residual biomass is not used. According to data on barley production and estimations on waste end use, between 2 and 6 Mt of the residual barley straw remains unused.

Moreover, barley shows good characteristics for biochar production such as low ash and high volatile content, similar to those materials previously used as precursors in physical activation processes [63.][64.][65.].

The physical activation method was carried out in two stages, carbonization at 500ºC and activation at 800ºC using carbon dioxide as activating agent. The text experimental rig is basically consists of an externally heated quartz tubular reactor. Table 1 summarizes the main properties of the activated biochar used in this study: ultimate analysis (CHNS Thermo Flash 1112 analyzer), mineral matter composition (ICP-OES Thermo Elemental IRIS Intrepid) and N_2 adsorption tests results (ASAP 2020 Micromeritics gas sorption analyzer) specifying BET surface area (S_{BET}), micropore surface area (S_{micro}), total pore (V_T) and micropore volume (V_{micro}). More details on the process conditions and the physical-chemical characterization of the resulting activated biochar can be found in our previous works [66.].

Ultimate analysis % wt (dry basis)	**C**	**H**	**N**	**S**	**O**	**Ash**
	51.88	0. 50	1.98	0. 17	10.29	35.18
Mineral content mg/g	**Al**	**Ca**	**Cu**	**Fe**	**K**	**Mg**
	2.121	21.65	0.023	1.021	75.05	6.313
	Mn	**Na**	**P**	**S**	**Ti**	**Zn**
	0.164	1.021	3.697	1.788	0.109	0.081
N_2 adsorption isotherm at 77 K	**S_{BET} (m^2/g)**	**S_{micro} (m^2/g)**	**V_T (cm^3/g)**	**V_{micro} (cm^3/g)**		
	789	778	0.3495	0.3268		

Table 1. Ultimate analysis (dry basis), mineral content (ICP-OES) and physisorption test results of activated biochar.

The next stage in the fertilizer production process is the complex reaction of macro (N, P, K) and micro-nutrients (Ca, Mg, Zn, K, NH_4^+) with the produced biochar. In order to achieve this, different active principles are mechanically mixed with the biochar and then dried and conditioned (grinding and sieving).

In order to analyze the potential benefit derived from applying biochar-based fertilizer to cereal crops, its environmental impact was compared to that of four fertilizers (urea, ammonium sulfate (AS), ammonium nitrate (AN) and diammonium phosphate (DAP)), traditionally used in the Spanish agricultural sector [67.]. Crop management is defined by the concentration and appearance forms of nutrient elements, which implies: fertilizer doses, application moments and how they should be incorporated. Table 2 shows the nitrogen content of each fertilizer and the N-form.

Fertilizer	Nitrogen source			
	Total N (%)	Ammonia N (%)	Nitric N (%)	Ureic N (%)
Urea	46	--	--	46
Ammonium sulfate (AS)	21	21	--	--
Ammonium nitrate (AN)	33,5-34,5	16,7-17,2	16,7-17,2	--
Diammonium phosphate (DAP)	18	18	--	--
Biochar-based Fertilizer	1,48	--	--	1,48

Table 2. Nitrogen type and concentration in selected fertilizers.

2.2. Methodology

The global objective of the study is to create an evaluation procedure that determines the environmental benefit offered by the use of a biochar-based fertilizer over traditional products, which can be accomplished through the saving of Nr. With this aim, the work carries out a theoretical analysis supported by experimental results and bibliographic data analysis.

The methodology starts from predictive models developed from experimental and bibliographic data regarding volatilization and leaching losses. These models result in specific emissions factors which indicate the kilograms of substance (nitrate, ammonia and nitrous oxide) per kg of nitrogen added. After that, LCA indicators are defined and calculated according to the emissions inventory. This inventory also informs of the rate of Nr saving achieved by each fertilizer, which allows classifying fertilizers according to their environmental benefit.

The methodology also relies on several instruments originally defined in sectors such as environmental management or risks analysis [68.][69.]. Based on these, a tool was developed to classify traditional fertilizers according to their impact on the environment, as well as to objectively quantify the environmental benefit achieved by the new biochar-based fertilizer.

The outline of the environmental analysis is shown in figure 1:

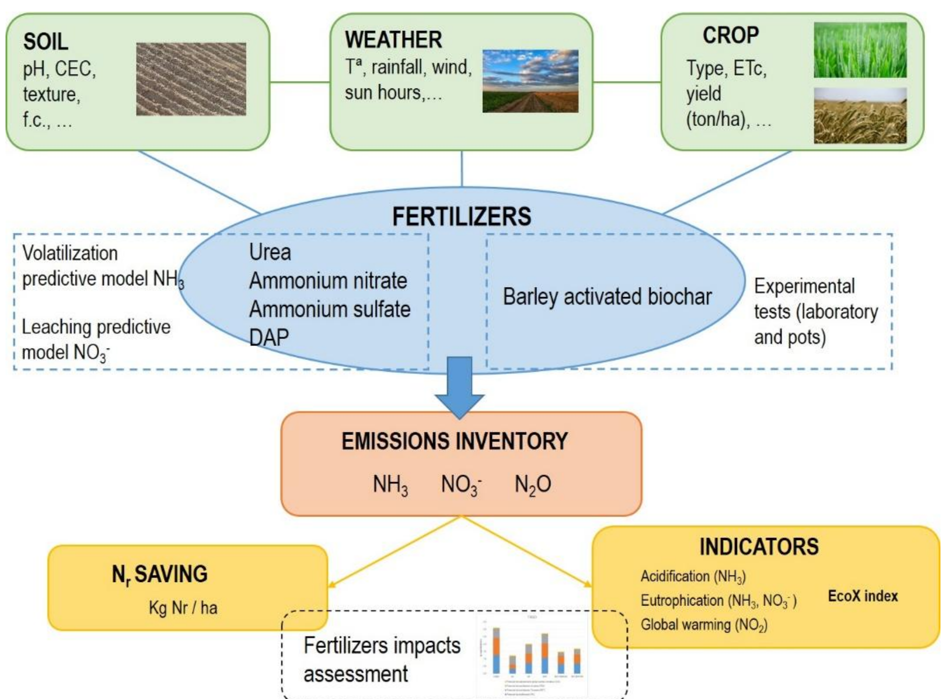


Figure 1. Layout of the environmental analysis.

The analysis begins requires input data referring to soil, climate and crop. Then, internally developed predictive models make use of input data to estimate the emission factors of both volatilization and leaching of nitrogen compounds for four of the most used traditional fertilizers. In contrast, for biochar-based fertilizer, these factors are obtained experimentally. The next step consists in determining the emissions inventory for each fertilizer by defining the amount of emitted nitrogen expressed in kg of compound per crop hectare. Environmental indicators of acidification, eutrophication (terrestrial and aquatic) and global warming are calculated from the inventory and lead to a final classification of the fertilizers in terms of their impact level. EcoX index is also determined [76.] to aggregate all the indicators in a single value, thus allowing a global comparison of the total environmental impact. Finally, the total amount of reactive nitrogen contained in the nitrogen emissions is calculated for each fertilizer in the case study.

2.2.1. Description of boundary conditions

Most of the nitrogen applied through fertilization is lost as a result of volatilization in the form of gaseous ammonia (NH_3) or nitrous oxide (N_2O), as well as of leaching processes in the form of nitrate (NO_3^-). These losses are controlled by edaphic, climatic and crop management factors which in turn depend on fertilizer and crop types and it is therefore essential to determine how all these factors affect the rate of nitrogen losses. With this aim, predictive models require data on the edaphic conditions of greater influence (temperature, pH, field capacity, nitrogen content and cation-exchange capacity (CEC)), on climate conditions (temperature, precipitation, wind, humidity, sun hours) and finally, on crop management (crop type, expected yield, evapotranspiration rate, irrigation needs and fertilization rate).

In order to compare the reduction in nitrogen losses as well as the global environmental indicators between biochar-based and traditional fertilizers, the predictive models developed in this work were applied to two of the more widespread and traditional crops in the region of Aragon (Spain), wheat and corn. Typical fertilizer doses for these crops were estimated in the present study as 150 kg N/ha and 300 kg N/ha, respectively, according to fertilization studies and regional agricultural practice [67.]. Other relevant parameters regarding crop yields, nitrogen uptake, irrigation needs and sowing time per hectare (ha) are shown table 3.

Crops properties:			
	WHEAT	CORN	
Expected production	2	9	ton/ha
Planting month	October	May	
Dose *	150	300	kg N/ha
Uptake N	60	198	kg N/ha

** according to expected yield*

Table 3. Crops management

Local weather conditions (Aragón, Spain) were collected from regional weather stations during the period 2014-2018. Mean values of temperature, rainfall, humidity, wind and sun were used for estimations and input data model. A characteristic *sandy clay loam* soil in the region was selected, considered the properties shown in Table 4.

Soil properties:		
Bulk density	1,35	g/cm^3

Field capacity	0,34	kg H_2O/kg_{soil}
Texture	*Sandy clay loam*	
Initial content of N	50	kg N/ha
pH	8,5	
Cation Exchange capacity (CEC)	12,1	meq/100g

Table 4. Soil properties

2.2.2. Estimation of nitrogen losses related to each fertilizer. Emission factors

Volatilization and leaching are the main processes involving nitrogen loses in agricultural sector. Volatilization losses produced when applying mineral fertilizers are due to different chemical, physical and biological processes and their magnitude depends on environmental, edaphic and crops management factors. These losses are produced fundamentally in the form of NH_3 and N_2O.

NH_3 emissions are the most important in fertilization processes, accounting for nearly 90% of the global emissions related to agriculture [70.]. They show important variation in the N-form but also they also are dependent on the climatic conditions and soil properties.

These factors and the specific fertilizer characteristics may significantly affect the amount of losses due to volatilization under certain conditions. In order to determine the volatilization losses associated to each fertilizer, a detailed statistical data study was performed, based on an extensive revision of bibliographic data [31.]-[59.]. The analysis uses volatilization data from experimental on-field trials with traditional fertilizers (urea, AS, AN and DAP), and it is based on variance analysis of relevant factors, such as soil pH, temperature, cation exchange capacity (CEC), CO_3 content, clay content, organic material content, nitrogen fertilizer dose and sampling time, and their interactions. As a result, soil pH, temperature and CEC have been identified as the most critical target variables for the volatilization process in the soil-plant-atmosphere system. Finally, based on a multiple regression linear model different expressions were obtained to quantify volatilization losses according to target variables.

In the regression model, the percentage of volatilized ammonia is expressed as a linear function of the objective variables pH, temperature, CEC and time.

$$\%NH3 = \beta1 + \beta2(pH) + \beta3(T) + \beta4(CEC) + \beta5(t) + \varepsilon$$

where β1, β2, β3, β4, β5 are the regression coefficients that quantify the relationship between the outcome variable and each independent variable, and ε is the random error term, which accounts for the influence of other variables not considered in the model. Determination of the regression coefficients was performed by minimizing the mean squared error (MSE). Table 5 presents the regression equations for ammonia losses due to volatilization of each fertilizer.

	Urea
f (pH, T, CEC)	$\%NH_3$= -66.77+3.98(pH)+1.81(T)+0.68(CEC)
	AS
f (pH, T, CEC)	$\%NH_3$= -29.674+3.127(pH)+0.211(T)+0.761(CEC)
	AN
f (pH, T, CEC)	$\%NH_3$= -7.359+1.052(pH)+0.107(T)+0.102(CEC)
	DAP
f (pH, T, CEC)	$\%NH_3$= -36.16+4.14(pH)+0.54(T)+0.49(CEC)

Table 5. Volatile ammonia prediction equations based on fertilizer type and variables involved in the process.

In order to know the reduction on ammonia volatilization when biochar was added to the soil, an experimental test campaign was conducted by analyzing different mixtures of biochar and soil before and after adding urea. The percentage of biochar used was 2% and the urea added was about 5.12 g. Soluble carbon and nitrogen were measured several times during a 7-day period. The most relevant results were obtained for nitrogen content after 7 days, which shows a significant ammonium retention when the mixture contains biochar, compared to that obtained in the soil sample (without biochar). This results in a reduction of the NH_3 released of about half in the case of soil-biochar mixtures. There is therefore a retention of ammonium from urea, preventing its transformation in NH_3 and its loss by volatilization. Results show that the ammonia volatilization in a soil fertilized with Urea is reduced in a 49.95% by adding 2% of biochar from barley straw.

N_2O emissions are produced after NH_3 volatilization and they come from nitrification and denitrification processes. Around 80% of the N_2O emissions due to agriculture are related to the use of mineral and organic fertilizers [70.]. Several interactions between soil and climate related factors and other parameters determined by crop management influence the N_2O emissions. However, its contribution to the reactive nitrogen losses is much lower than that of NH_3. In addition, bibliographic data are not enough to develop a suitable statistical analysis. In order to include its contribution to the model, the N_2O emission factor was adopted from Bouwman (1995) [71.] who proposed the following expression from field experiments with mineral and organic fertilizers.

$$N_2O[kg\ N_2O - N \cdot ha^{-1}] = 0.0125 \cdot N\ applied^{a}[kg\ N \cdot ha^{-1}]$$

[a] *the amount of N applied is corrected by eliminating the NH_3 emissions since they occur before those of N_2O.*

As for nitrogen leaching losses, these are directly related to deep drainage processes and depend on local environmental factors [72.]. The key parameters involved in those processes are related to soil and weather, but the net effect also depends on the result of the nitrogen balance in the agricultural system. Field capacity in effective rooting zone [70.] is the fundamental parameter to calculate the leaching rate. It describes the soil capacity to absorb water in the roots zone and it varies depending on the texture and soil type. Experimental *on field* investigations focused on leaching processes are scarce and most of the published studies in the literature are based on predictive models instead of direct measurements. Following a similar methodology, a simulation model was here developed in order to estimate the nitrate losses through leaching associated to each traditional fertilizer when applied to wheat and corn crops under particular conditions (climatic, edaphic and crop management).

The developed leaching model accounts for the nitrogen transformations and interactions within the agro-system cycle, where atmosphere and aquifers were considered as upper and lower limit, respectively. Likewise, water dynamics is taken into account, through a balance of nitrogen and water in the system, in order determine the nitrates that will leave the system by leaching. The most important factors that determine the nitrate and water balance are related to crop type, weather and crop management (evapotranspiration rate, effective precipitation, irrigation needs among others)[73.]. The proposed model involves several key variables: nitrogen input (N) expressed as kg N/ha, drainage water % (D), soil pH (pH), soil temperature (º C) (T), and field capacity % (f.c). Finally, following a similar methodology to that developed for volatilization losses, different model simulations were run for the particular conditions of the study and a multiple regression model was accordingly developed giving rise to the following expressions:

Urea

Wheat	$NO_{3\_leached}= 1{,}047+5{,}62(10^{-5})N+0{,}052D-0{,}017pH-0{,}007T-0{,}27f.c$
Corn	$NO_{3\_leached} = 0{,}95+2{,}03(10^{-4})N+0{,}010D-0{,}015pH-0{,}007T-0{,}037f.c$

AS

Wheat	$NO_{3\_leached}= 1{,}021+5{,}618(10^{-5})N+0{,}051D-0{,}027pH-0{,}002T-0{,}270f.c$

Corn	$NO_{3\_leached} = 0{,}917+2{,}208(10^{-3})N+0{,}009D-0{,}025pH-0{,}002T-0{,}037f.c$
	AN
Wheat	$NO_{3\_leached}= 0{,}915+5{,}618(10^{-5})N+0{,}054D-0{,}009pH-0{,}001T-0{,}285f.c$
Corn	$NO_{3\_leached} = 0{,}811+2{,}85(10^{-4})N+0{,}007D-0{,}009pH-9{,}266(10^{-4})T-0{,}030f.c$
	DAP
Wheat	$NO_{3\_leached}= 1{,}098+5{,}618(10^{-5})N+0{,}050D-0{,}034pH-0{,}005T-0{,}265f.c$
Corn	$NO_{3\_leached} = 0{,}998+1{,}782(10^{-4})N+0{,}011D-0{,}031pH-0{,}004T-0{,}040f.c$

Table 6. Multiple linear regression equations for the calculation of nitrate leached in wheat and corn crops according to fertilizer type.

Again, in order to determine the reduction on nitrates leaching when biochar was added to soil, an experimental leaching test campaign was conducted. Pot experiments with the selected crops, corn and wheat were performed to compare the extent of leaching. In this case, 70% of soil was mixed with 30% of the biochar-based fertilizer. Experiments were conducted during 4 weeks approximately, performing periodic irrigation and collecting and analyzing the leached samples. After this period the resulting plants were collected and measured in order to obtain different growth parameters. Results showed a reduction in nitrogen leaching from 37% to 14% compared to another traditional fertilizer (urea). A 7% of increase in the N uptake by the crop was also observed, which in practice resulted in a substantial improvement of the biometric parameters of the plant (efficiency of the use of radiation, root growth rate, growth rate of the aerial part and CO_2 fixation).

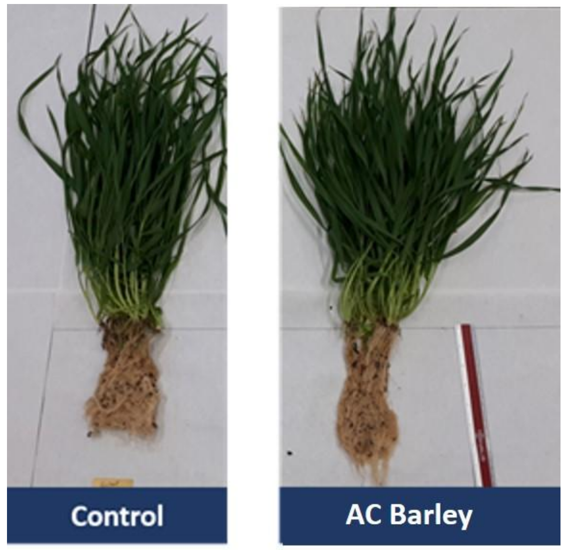


Figure 2. Plant growth comparison from pot trials of wheat (fertilization with control (urea) and biochar-based fertilizer).

After developing and validating the volatilization and leaching models, these were applied to the determination of the emission factors of ammonia and nitrate leaching for the four traditional fertilizers. In the case of biochar-based fertilizer, factors were in turn obtained from the experimental tests.

An emission factor is a representative value that relates the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant [74.]. In this work, emission factors express the amount (in kilograms) of nitrogen in form of nitrate, ammonia or nitrous oxide emitted per kg of nitrogen applied through fertilization. It can also be expressed as percentage of the total amount of nitrogen applied. According to this, emission factors of urea, AS, AN, and DAP are derived from expressions on table 5 and 6 using boundary conditions as input data. Table 7 shows the calculated emission factors of each fertilizer.

		UREA	AN	AS	DAP	BB FERT.
NH_3 volatilization factor:						
----	kg $N\text{-}NH_3$/kg N applied	0,2059	0,0549	0,1139	0,1849	0,0849
N_2O volatilization factor						
----	Kg N_2O/kg N applied	0,0099	0,0118	0,0111	0,0102	0,0114
NO_3 leaching factor:						
WHEAT	kg $N\text{-}NO_3$/kg N applied	0,4077	0,4884	0,4569	0,4189	0,1384
CORN	kg $N\text{-}NO_3$/kg N applied	0,5511	0,6647	0,6203	0,5669	0,1445

Table 7. Emission factors.

2.2.3. Quantification of environmental benefit

An environmental analysis of data from predictive models and experimental tests was carried out within the framework of risk analysis and footprint approach.

2.2.3.1. Indicators description based on LCA impact categories

Life Cycle Assessment (LCA) is a systematic process to identify and quantify the environmental burdens associated with a product (or service) during its life cycle. The final objective is to evaluate the environmental impacts derived from them and to define the measures or improvements throughout the cycle. One of the fundamental steps on LCA is the characterization of impacts according to different categories. It consists in transforming the collected data into impact category or damage category indicators [75.] [1.]. LCA has been used in agriculture to evaluate how existing products, including fertilizers, interact with their environment [1.].

Based on these categories, several environmental indicators were selected to represent the environmental impact related to nitrogen losses.

Acidification. This impact is defined as the loss of the neutralizing capacity of soil and water, as a consequence of the return to the earth's surface, in the form of acids, of the oxides of sulfur and nitrogen released into the atmosphere [68.]. The acidification process takes place as a result of the NH_3, NOx and SO_2 emissions. SO_2 and NOx are mainly originated from combustion processes whereas NH_3 is due to animal husbandry and volatilization during application of ammonia-containing fertilizers [76.]. In the present study the substance considered for acidification impact is NH_3. Acidification potential (AP) is expressed in kg equivalents of SO_2 per ha (equation 1).

$$AP = m_{NH_3} * AF_{NH_3} \tag{1}$$

Where m_{NH_3} is the NH_3 mass expressed in kg NH_3/ha, and AF_{NH_3} is the NH_3 characterization factor, which represents the potential of a single emission to contribute to the respective impact category, considering deposition patterns and susceptibility to acidification determined for the Spanish region [78.].

Eutrophication. This impact accounts for terrestrial and aquatic eutrophication impacts. Since both the dynamics of the process and the species involved are different for both mechanisms, independent potential impacts were defined for each contribution. [76.].

Terrestrial eutrophication potential (TEP) was defined to account for the most relevant contributors to atmospheric deposition, NOx and NH_3 [77.], being ammonia the only substance taking part in the case study. A regionalized characterization factor developed by Huijbregts [78.], considering atmospheric pathways, deposition patterns and eutrophication effects of NH_3

emissions, was selected and used to calculate the potential. According to equation 2, TEP is expressed in kg equivalents of NOx.

$$TEP = m_{NH_3} * EF_{NH_3} \tag{2}$$

Where m_{NH_3} in the mass of NH_3 emission expressed in kg NH_3/ha, and EF_{NH_3} the characterization factor for terrestrial eutrophication impact corresponding to Spain, and expressed in kg NOx-equivalents/kg NH_3 emitted (see table 9).

Aquatic eutrophication potential (AEP), in addition to the atmospheric deposition of NH_3 considered in the previous category, must include the contribution of NO_3^- that reaches water bodies as a consequence of leaching processes. Both contributions are considered in equation 3 and the potential impact is expressed in kg equivalents of PO_4/ha. Atmospheric deposition on marine ecosystems caused by airborne NH_3 emissions is difficult to estimate and fate factors considering regional aspects are needed. Regionalized fate factor developed by Huijbregts et al.[79.] for aquatic eutrophication sub-category was used (table 9) to this end. For the estimation of NO_3^- leaching losses from soil to groundwater a reduction factor must be assumed since denitrification process is produced on the way from groundwater to surface water and finally the sea [76.]. According to Potting et al.[80.] this factor was set on 30%.

$$AEP = \left(m_{NH_3} \cdot FF_{NH_3,Spain} \cdot EF_{NH_3}\right) + \left(m_{NO3} \cdot RF_{NO3} \cdot EF_{NO3}\right) \tag{3}$$

Where m_{NH_3} is the mass corresponding to NH_3 emission, expressed in kg NH_3/ha, $FF_{NH_3,Spain}$ is the fate factor for NH_3 airborne emissions corresponding to Spain, EF_{NH_3} and EF_{NO3} are the eutrophication factors for NH_3 and NO_3^- (kg eq. PO_4/kg). Finally RF_{NO3} is the reduction factor for nitrate immission to surface water.

Climate change. This category, also defined as global warming potential, express the contribution of greenhouse gas emissions from agricultural production systems [76.]. The contribution to this potential corresponds to N_2O emissions produced during the fertilizer application. According to this, in this study the expression used for the climate change potential was:

$$CCP = m_{N_2O} * GWP_{N_2O} \tag{4}$$

Where m_{N_2O} is the N_2O expressed in kg N_2O/ha, and GWP_{N_2O} is the global warming potential of N_2O.

Table 8 shows all the specific factors applied to the calculation of each potential risk linked to the involved substance.

Characterization factors applied:				
Substance	**Potential risk**	**Value**	**Units**	**Reference**
ammonia (NH_3)	Acidification (AF)	0,27	eq. kg SO_2	[78.]
ammonia (NH_3)	Aquatic eutrophication (AEF)	0,35	eq. kg PO_4	[76.]
ammonia (NH_3)	Terrestrial eutrophication (TEF)	2,00	eq. kg NO_x	[78.]
ammonium ion (NO_3^-)	Aquatic eutrophication (AEF)	0,10	eq. kg PO_4	[76.]
nitrous oxide (N_2O)	Climate change (CCP)	298	eq. kg CO_2	[81.]

Table 8. Characterization factors.

In order to globally compare the environmental risk of each fertilizer, the obtained results from indicators are subject to a normalization and weighting process, making it possible to obtain a global index that collects all the burdens. On the one hand, normalization process converts the characterization results into neutral global units, dividing each one by a normalization factor. Through these factors, the contribution degree of each impact category on the local environmental problem is represented.

$$N_i = \frac{I_i}{NV_i} \tag{5}$$

Where N_i is the normalization result for impact category i, I_i is the indicator value for impact category I, and NV_i is an indicator value according to a reference situation (e.g. per person in Europe), all of these considering the functional unit (1 ha).

Impact category	**NV**	**WF**	**Units**
Climate change	9730	1,06	eq. kg CO_2
Acidification	47,7	1,34	eq. kg SO_2
Aquatic eutrophication	8,56	1,36	eq. kg PO_4
Terrestrial eutrophication	60,7	1,26	eq. kg NO_x

Table 9. Normalization values (NV) and weighting factors (WF) for the several impact categories in Europe [76.].

On the other hand weighting factors represent the contribution of each impact category. The standardized "distance-to-target" principle [76.] was considered for their calculation, comparing the current level of an environmental effect in a certain region and time, with the target level of that same effect. The ratio between both values provides the weighting factor for that environmental effect.

Finally, an aggregated environmental indicator, EcoX index, was defined in order to compare and categorize all the fertilizers based on their global environmental impact. This index is the result of adding all the normalized values of each impact category (N_i) multiplied by their corresponding weight factor (WF_i) and accounts for all the previous indicators in a single global value (equation 6).

$$EcoX = \sum N_i \cdot WF_i \tag{6}$$

2.2.3.2. Reactive nitrogen and N Footprint approach

Nitrogen footprint (NF) was introduced to express the total amount of reactive nitrogen lost to the environment as a consequence of human activity [60.]. Nevertheless the NF concept is very recent and few nitrogen footprint models have been developed, being the N-calculator tool developed by Leach et al (2012) the most extensively known [82.]. Based on this model, reactive nitrogen losses linked to fertilizer application were calculated. To express the contribution of each compound on the total Nr, it is necessary to determine the N that is contained in the molecule and multiply it by the total amount of emitted substance. For the case of nitrogen emissions from fertilizer application the following expression determines the total amount of reactive nitrogen.

$$N_r = \frac{M(N)}{M(NH_3)} \cdot m(NH_3) + \frac{M(N_2)}{M(N_2O)} \cdot m(N_2O) + \frac{M(N)}{M(NO_3^-)} \cdot m(NO_3^-) \tag{7}$$

Where $M(N)$ is the molar mass of nitrogen and $M(NH_3)$ is the total molar mass of ammonia molecule, and thus for the rest of nitrogen compounds, respectively.

3. Results and discussion

3.1. Fertilizers emissions inventory and impact results

Table 10 gathers all the nitrogen emissions resulting from each fertilizer application on the selected crops, considering the emission factors presented on section 2.2.2. The kilograms of N in form of ammonia, nitrate and nitrous oxide per hectare are the basis for the environmental analysis. Potential risks are calculated according to equations (1) to (4) and results are gathered in table 11. Potential values are normalized and weighted by applying the equations (5) and (6), thus presenting the environmental impact in terms of global risk.

Fertilizer	WHEAT (150 kg N/ha)			CORN (300 kg N/ha)		
	kg NH_3/ha	kg NO_3^-/ha	kg N_2O /ha	kg NH_3/ha	kg NO_3^-/ha	kg N_2O /ha
Urea	30,88	61,16	1,49	61,76	165,34	2,98
DAP	27,74	62,84	1,53	55,48	170,06	3,06
AS	17,08	68,53	1,66	34,16	186,09	3,32
AN	8,24	73,26	1,77	16,47	199,40	3,54
BB Fert.	12,74	20,76	1,72	25,47	43,35	3,43

Table 10. Nitrogen emissions inventory from application of mineral fertilizers to wheat and corn crops under particular conditions.

Fertilizer	WHEAT				CORN			
	AP (eq. kg SO_2)	AEP (eq. kg PO_4)	TEP (eq. kg NOx)	CCP (eq. kg CO_2)	AP (eq. kg SO_2)	AEP (eq. kg PO_4)	TEP (eq. kg NOx)	CCP (eq. kg CO_2)
Urea	8,34	3,56	61,76	443,73	16,67	8,42	123,51	887,45
DAP	7,49	3,44	55,48	455,42	14,98	8,21	110,96	910,85
AS	4,61	3,01	34,16	495,13	9,22	7,50	68,32	990,26

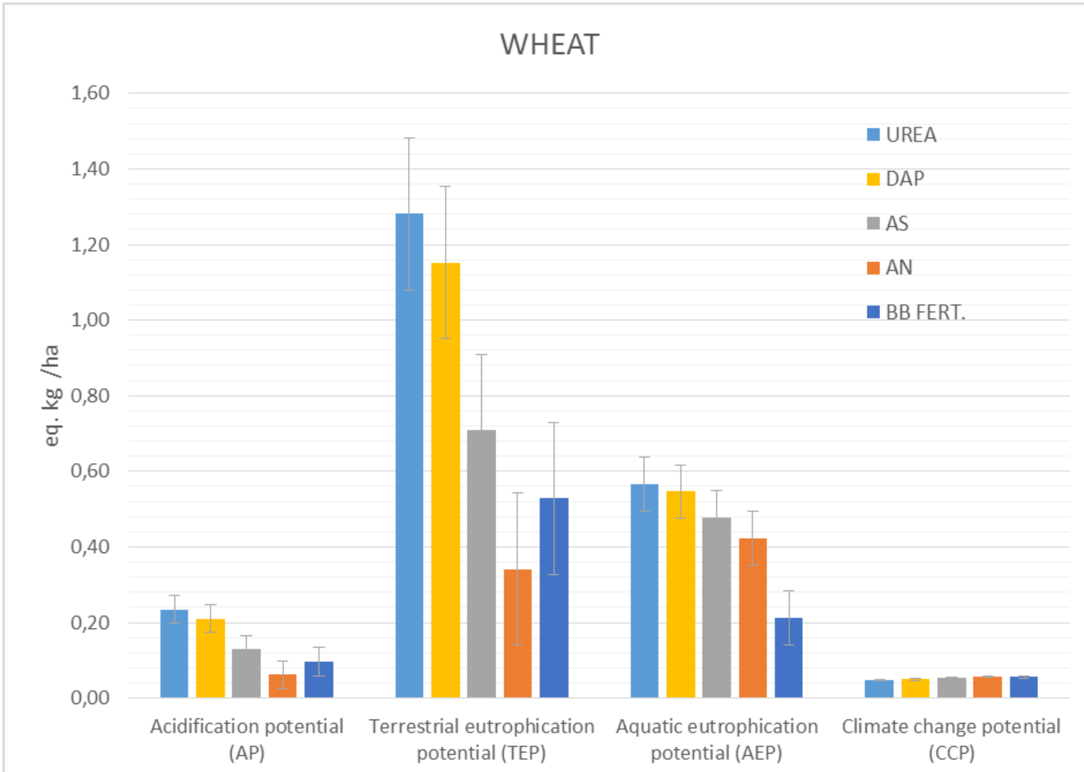
AN	2,22	2,66	16,47	528,07	4,45	6,90	32,94	1056,15
BB Fert.	3,44	1,34	25,47	511,30	6,88	2,73	50,95	1022,61

Table 11. Quantification of the environmental risk potential (due to acidification, eutrophication and climate change) of the selected fertilizers.

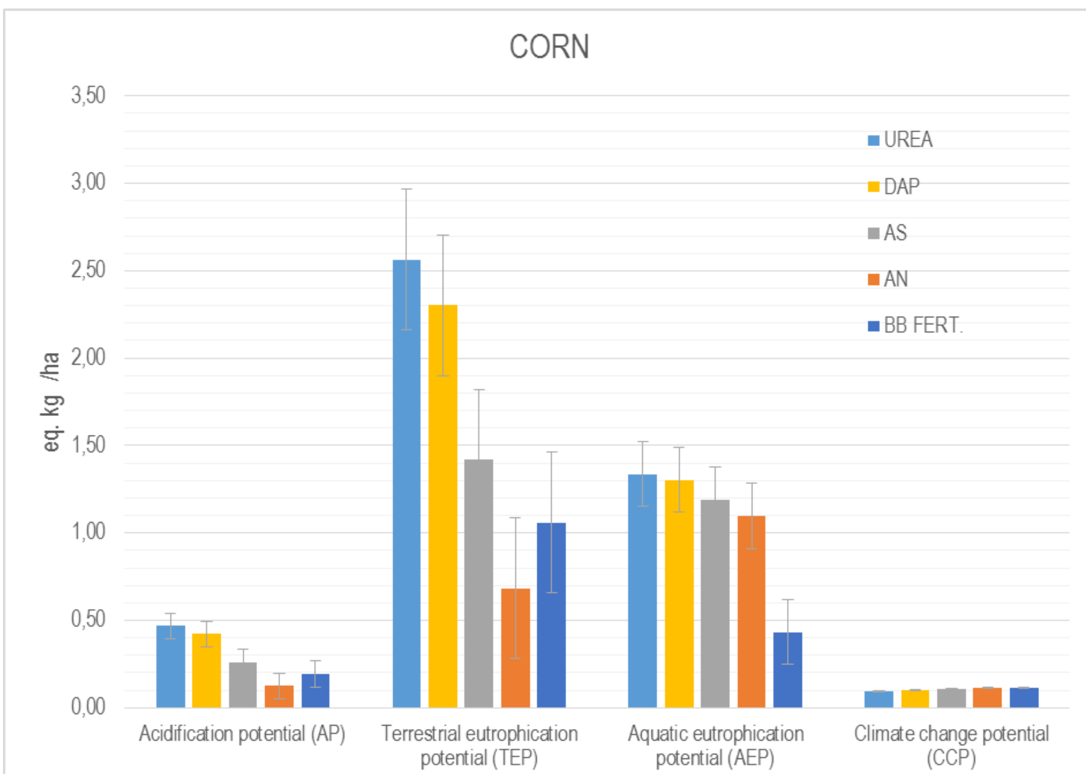
Fertilizer	WHEAT				CORN			
	AP	AEP	TEP	CCP	AP	AEP	TEP	CCP
Urea	0,23	0,57	1,28	0,05	0,47	1,34	2,56	0,10
DAP	0,21	0,55	1,15	0,05	0,42	1,30	2,30	0,10
AS	0,13	0,48	0,71	0,05	0,26	1,19	1,42	0,11
AN	0,06	0,42	0,34	0,06	0,12	1,10	0,68	0,12
BB Fert.	0,10	0,21	0,53	0,06	0,19	0,43	1,06	0,11

Table 12. Potential risks of the selected fertilizers after normalization and weighting processes (eq. kg /ha).

The results yielded by indicators inform about the level of impact of each fertilizer.



a)



b)

Figure 3. Environmental indicators results for selected fertilizers applied to a) wheat crops, and b) corn crops.

As Figure 3 shows, a wide variability was detected between potential risks, among which terrestrial and aquatic eutrophication risks were identified as the most significant. Also different fertilizers were found to have widely different potential for environmental damage, among which urea and DAP had the highest. AN shows the lowest risk in acidification and TE potentials thanks to its low emission of NH_3. The reason is that AN combines the advantages of containing nitric nitrogen, of immediate availability, and ammonium nitrogen, with a longer action since it must undergo the nitrification process. Nevertheless, its contribution of NO_3^- is significant and that penalizes its global environmental impact.

Regarding to aquatic eutrophication risk, the achieved reduction in the case of the biochar-based fertilizer is 69% with respect to urea and 63% with respect to AN which means that more than half of the nitrate losses produced by leaching are avoided. As for climate change potential, all fertilizers show similar results, all of which contribute only to a small extent to the global calculation, because N_2O emissions are much lower than the other considered pollutants. In general, it can be stated that the most important risk in nitrogen fertilization is eutrophication, not only linked to nitrate leaching (aquatic eutrophication) but mostly because of the NH_3 emissions that contribute to the undesired increased in biomass production on terrestrial vegetation (terrestrial eutrophication).

Although NO_3^- (in kg of N/ha) emissions level is higher for traditional fertilizers, the aquatic eutrophication potential is lower than TEP for the most of the cases. This is explained by the fact that the environmental damage caused by the acidifying effect of ammonia is comparatively greater than the impact of nitrates on aquatic ecosystems.

Acid deposition of NH_3 emissions depends on deposition patterns and the potential damage of acidifying emissions in the local natural ecosystems. In this work, acidification risk was found to be of little significance compared to eutrophication, because of it depends on the sensitivity of the receiving area in terms of buffer capacity of soils and water or $CaCO_3$ content [73.]. For instance, 1 Kg of NH_3 released in Spain results in only 0.27 kg SO_2 equivalents when the same emission released in Norway has an acidification potential of 6 kg SO_2 equivalents [78.]. For this reason, this capacity of assuming acid deposits makes the potential risk less relevant in the considered region.

The contribution of each process into the impact categories is shown in Figure 4 for the case of Urea in wheat crop. Whereas impact associated to AP, TEP is entirely (100%) due to NH_3 volatilization, CCP is only linked to N_2O emissions. In contrast, aquatic eutrophication (AEP) depends on both NH_3 volatilization and NO_3 leaching processes and their contributions vary substantially for each fertilizer. For mineral fertilizers, the contribution of NH_3 volatilization is always lower than NO_3 leaching, whereas with the biochar-based fertilizer the contribution of nitrate leaching is less important than ammonia volatilization (Figure 5).

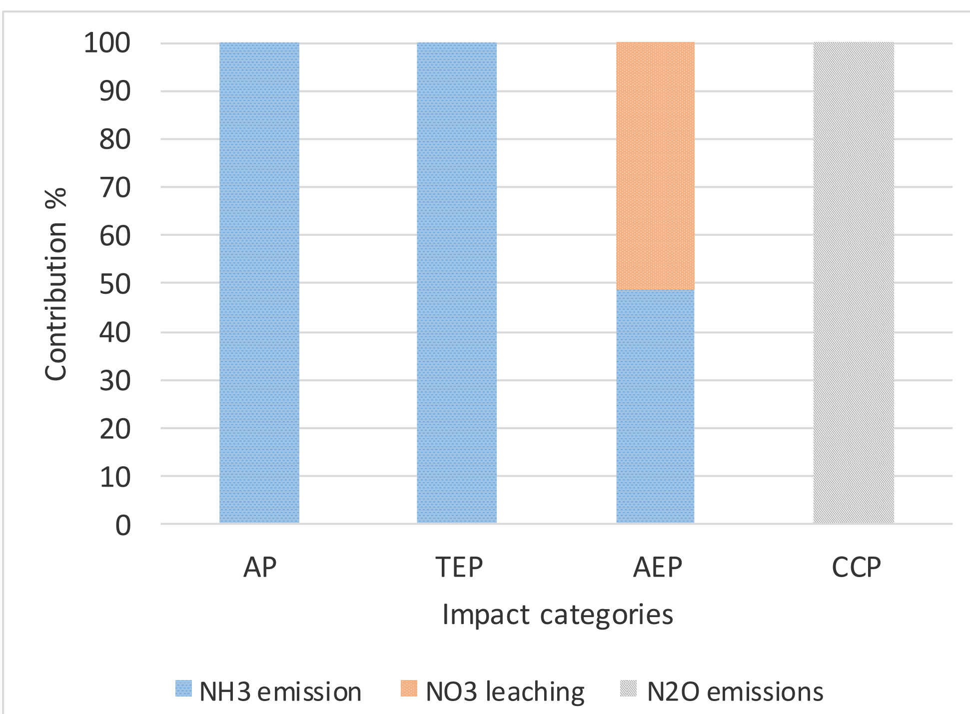
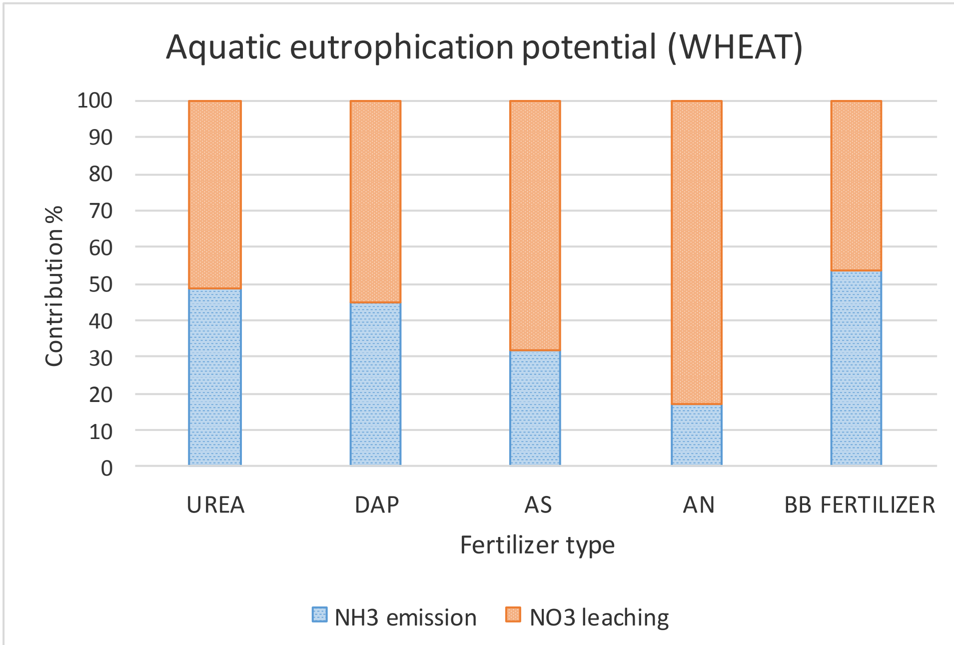
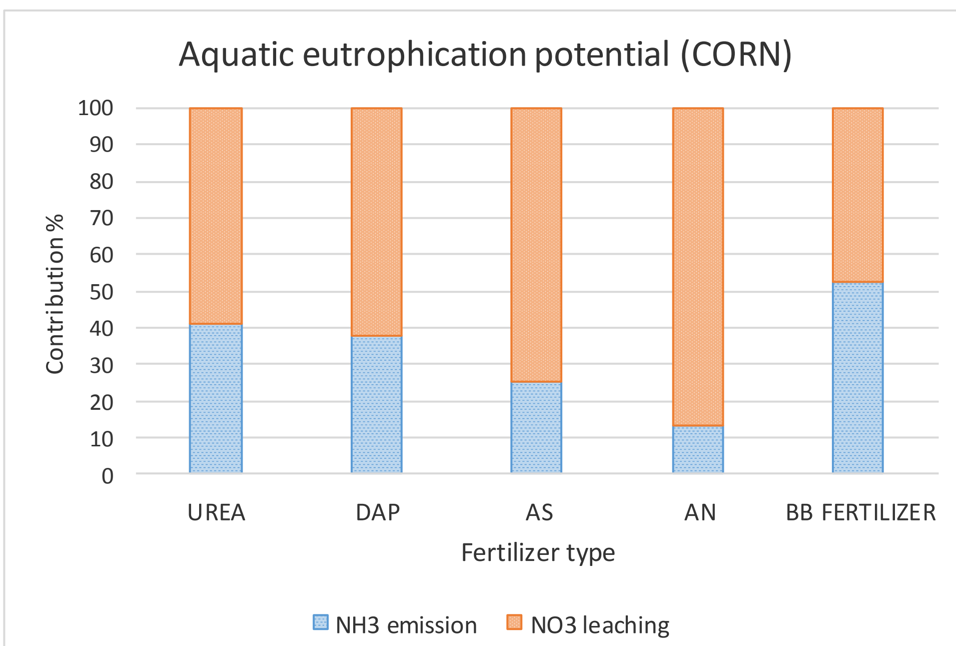


Figure 4. Contribution of each process into the impact categories corresponding to Urea fertilizer applied to a wheat crop.



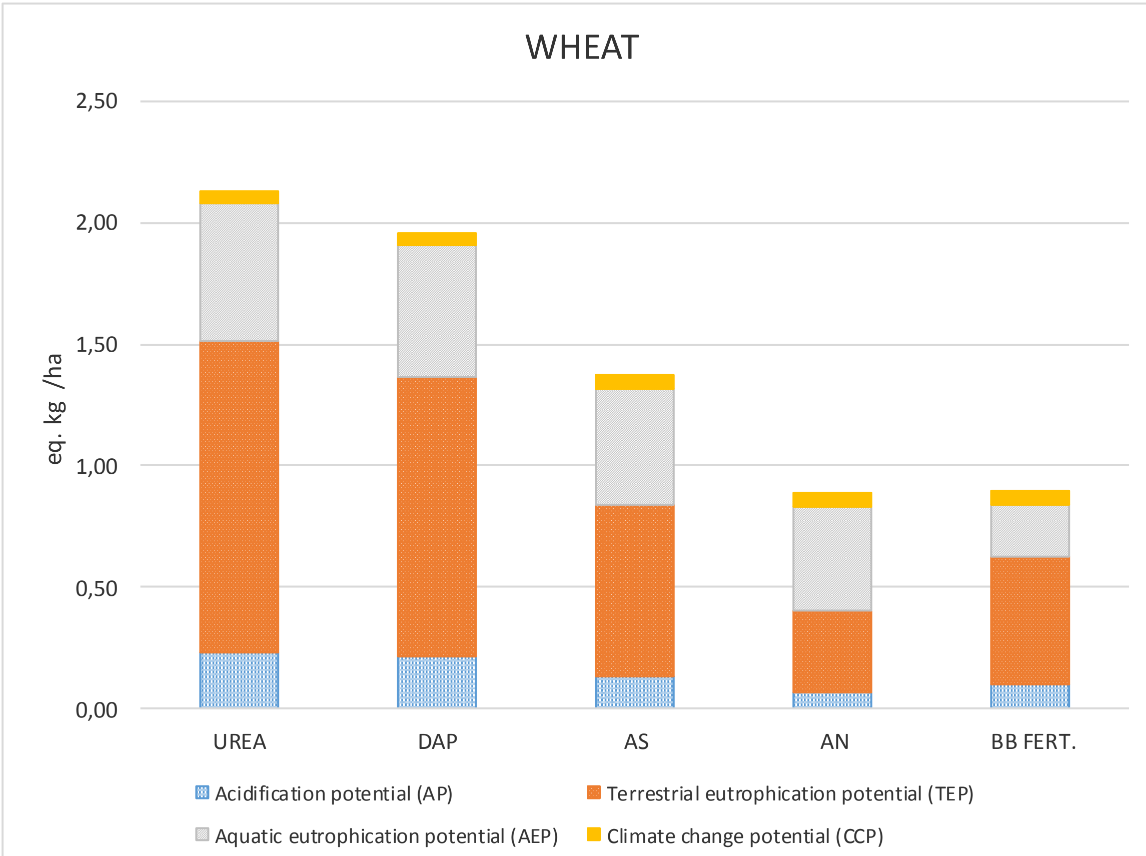
a)



b)

Figure 5. Contribution of NH_3 volatilization and NO_3 leaching processes into the AEP impact category for each fertilizer applied to a) wheat and b) corn crops.

a)


WHEAT
2,50
2,00
1,50
1,00
0,50
0,00
eq. kg /ha
UREA
DAP
AS
AN
BB FERT.
Acidification potential (AP)
Terrestrial eutrophication potential (TEP)
Aquatic eutrophication potential (AEP)
Climate change potential (CCP)

b)

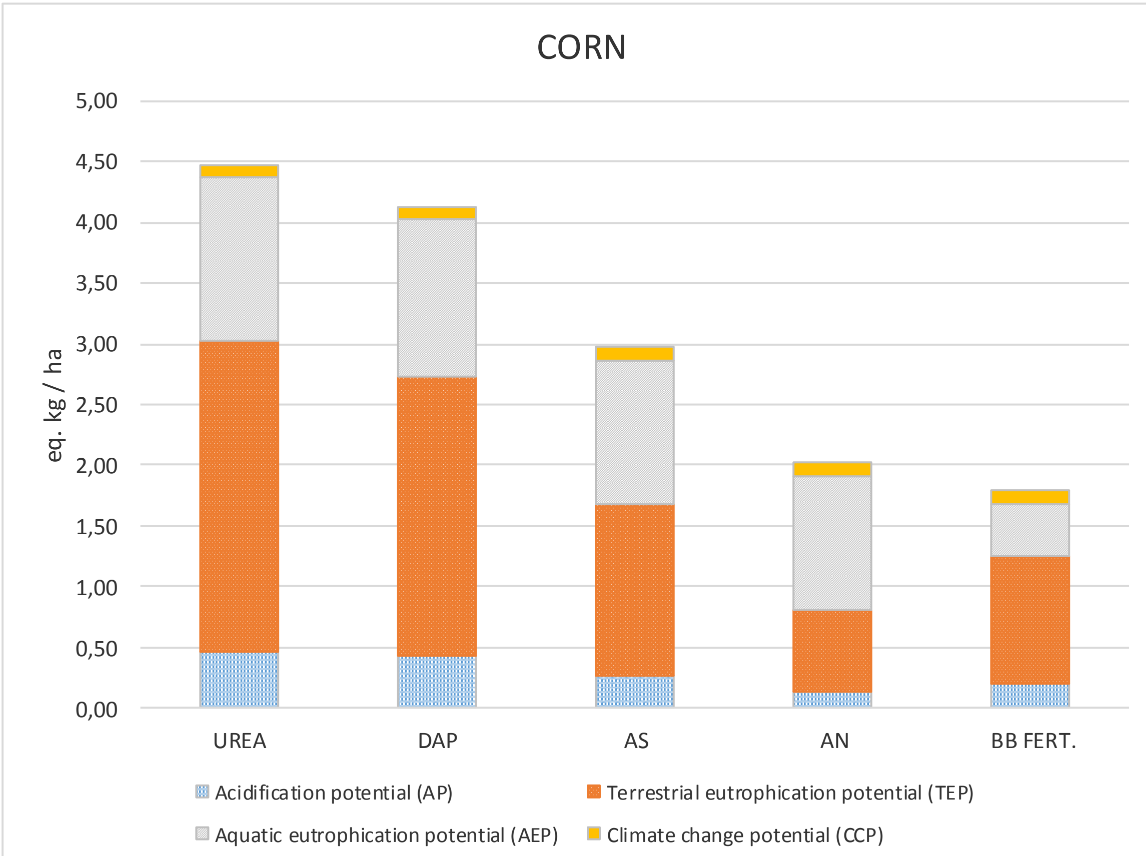


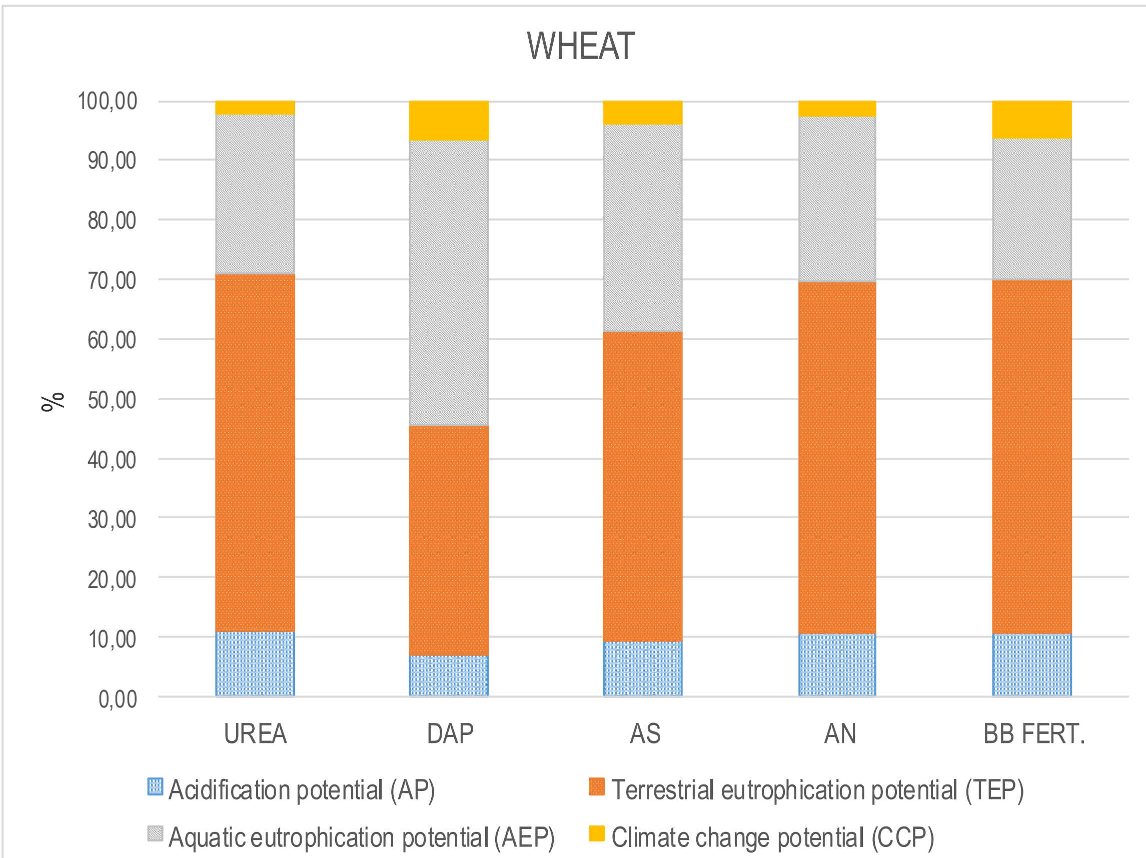
Figure 6. Impacts aggregation for each fertilizer in a) wheat crop, b) corn crop.

Figure 6 shows the aggregated values of all environmental risks derived from the application of each fertilizer, indicating the distribution of pollution potentials. The highest value corresponds to Urea (for both crops) and the lowest to the biochar-based fertilizer. The reduction of global environmental damage achieved with biochar-based fertilizer is between 58% (vs urea on wheat crop) and 11% (vs AN on corn crop) compared to traditional fertilizers.

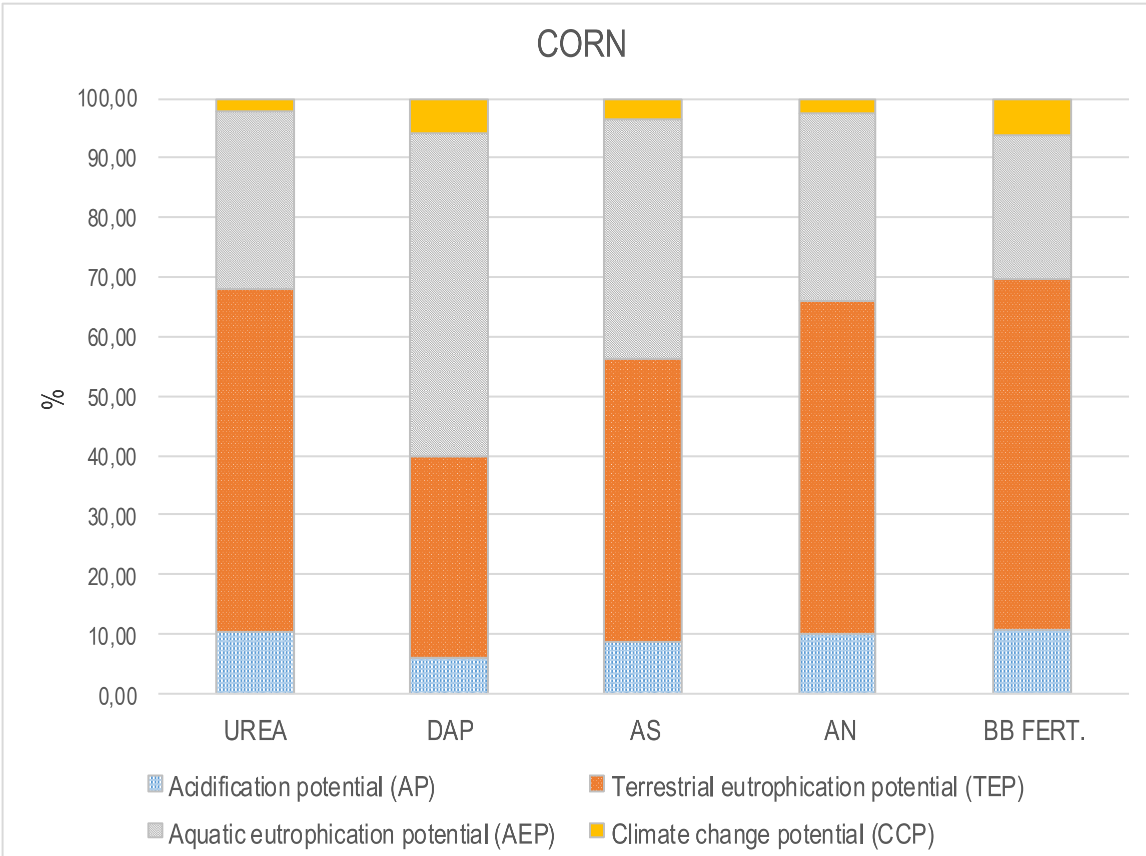
Distribution of risks in the case of urea, DAP, AS and biochar-based fertilizer shows the prevalence of terrestrial and aquatic eutrophication potential (both representing more than 80% of the total risks in all cases), while for AN the most important risk is the aquatic eutrophication potential (55% for wheat and 58% for corn).

Figures 7a and b show the contribution analysis of impacts in the application case of the analyzed fertilizer products. Terrestrial eutrophication potential presents the largest contribution for all fertilizers except for DAP for which the most important influence is aquatic eutrophication.

a)



501 b)



502

503 Figure 7. Contribution analysis of different impacts according to each fertilizer type for a) wheat and b) corn
504 crops.

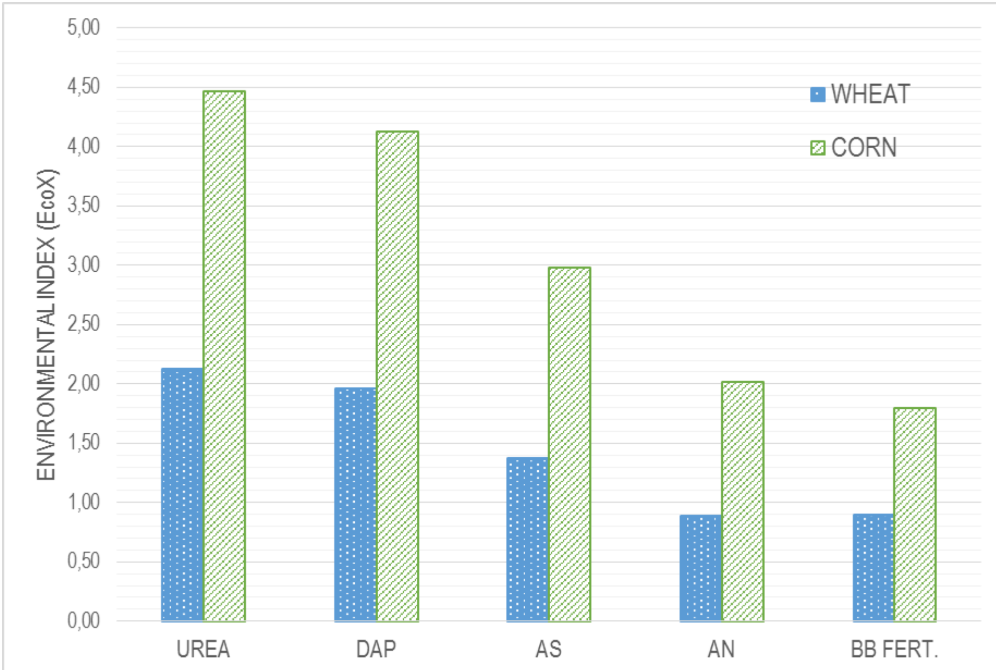


Figure 8. Aggregated environmental indicator values (EcoX) per hectare from selected fertilizers applied to wheat and corn crops.

EcoX indicator (Figure 8) shows global results that allow categorizing fertilizers according to their global risk. In this sense, urea represents the highest environmental risk fertilizer for the two studied crops. However, according to this indicator AN and biochar-based fertilizer involve a similar risk for the wheat crop while the biochar-based fertilizer shows a better environmental behavior for the corn crop when a greater amount of fertilizer is used.

3.2. Reactive nitrogen saving

The analysis of Nr saving shows a substantial reduction in the amount of nitrogen released to the environment for both crops when the biochar-based fertilizer is used. This is due to the difference in the nitrogen percentage of each molecule (NH_3, NO_3^- or N_2O). This result penalizes traditional fertilizers compared to new one which achieves a reduction of up to 63% in the Nr content (when compared to Urea for a corn crop).

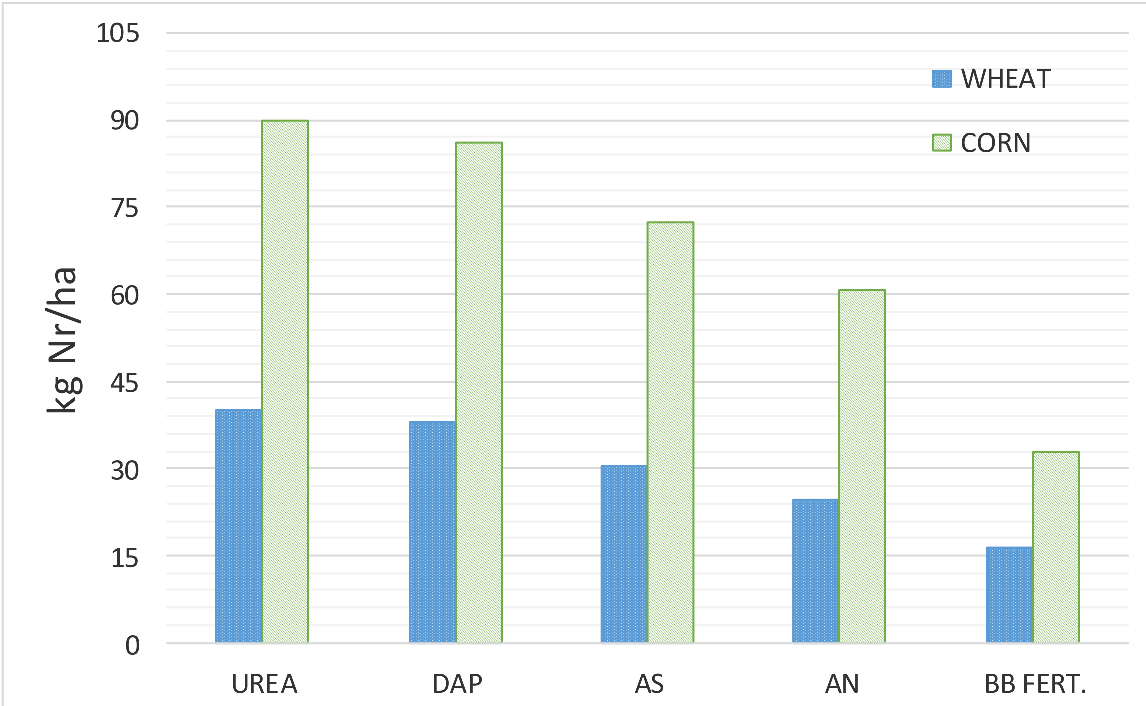


Figure 9. Reactive nitrogen released according to fertilizer type and crop (kg Nr / ha).

Figure 9 shows the total amount of reactive nitrogen released as a result of the application of each fertilizer. For the present case study and considering both crops, the biochar-based fertilizer is the product with the least nitrogen losses, 16,27 kg Nr/ha for wheat and 32,95 kg Nr/ha for corn. The highest degree of N_r savings is achieved with respect to urea, reaching almost 60% for wheat and 63% for corn. The results for Nr savings are shown in Table 13, which clearly show that the new fertilizer consistently achieves greater savings than the traditional ones for both crops.

	% Nr saving (wheat crop)	% Nr saving (corn crop)
Urea	59,52	63,42
AN	33,46	45,84
AS	46,83	54,40
DAP	57,19	61,70

Table 13. N_r relative saving of biochar-based fertilizer vs traditional fertilizers.

4. Conclusions

A new methodology for the environmental analysis of nitrogen fertilizers was developed and implemented in this work basing on the calculation of reactive nitrogen saving, and it was used to compare the potential risks associated to the application of different nitrogen fertilizers. The proposed methodology was based on the life cycle analysis approach and the nitrogen footprint tool, both developed in the agricultural field. By means of potential impact indicators, different traditional mineral fertilizers and a biochar-based fertilizer were classified according to their environmental risk. The study was developed considering local conditions and using predictive models of volatilization and leaching based on bibliographic and experimental data.

From the obtained results, it can be concluded that:

- The proposed methodology is adequate for the assessment of the environmental risks involved in the application of nitrogen fertilizers in agricultural practices. Its use allows to characterize different types of fertilizer products according to their specific environmental risks.

- The methodology enables determining to which extent the substitution of traditional fertilizers for the biochar-based fertilizer has a better performance in environmental terms.

- The application of this methodology to study the fertilization of two extensive cereal crops under autochthonous conditions successfully assessed the environmental performance of four different traditional fertilizers (urea, ammonium nitrate, ammonium sulphate and di-ammonium phosphate) and a new biochar-based product. In order to do this, internally developed predictive models were used to estimate nitrogen emissions derived from the use of the traditional fertilizers, whereas experimental data was used to determine the value of emission factors for the case of a biochar-based fertilizer.

- Whereas aquatic eutrophication is the main risk associated to ammonium nitrate, for the other three traditional fertilizers terrestrial eutrophication potential was identified as the most relevant environmental damage. .

- The analysis of reactive nitrogen savings provides a new tool for assessing the environmental benefit of a fertilizer. In this case, reactive nitrogen released by the application of the same amount of nitrogen was analyzed in the form of different chemical products was studied for all the considered fertilizers, which proved the biochar-based product to have the best environmental performance among them (63,42% saving of mineral nitrogen against urea).

As a result, it may me concluded that the use of biochar as fertilizer additive is a promising low-cost alternative for the reduction of nitrogen contamination through nitrate leaching in agricultural practice.

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