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Bio-Char II: Production, Characterization and Applications

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Comparative analysis of low nitrogen emissions fertilizers based on activated carbon from residual materials

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Bio-Char II: Production, Characterization and Applications

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COMPARATIVE ANALYSIS OF LOW NITROGEN EMISSIONS FERTILIZERS BASED ON ACTIVATED CARBON FROM RESIDUAL MATERIALS

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GOBIERNO DE ESPAÑA MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

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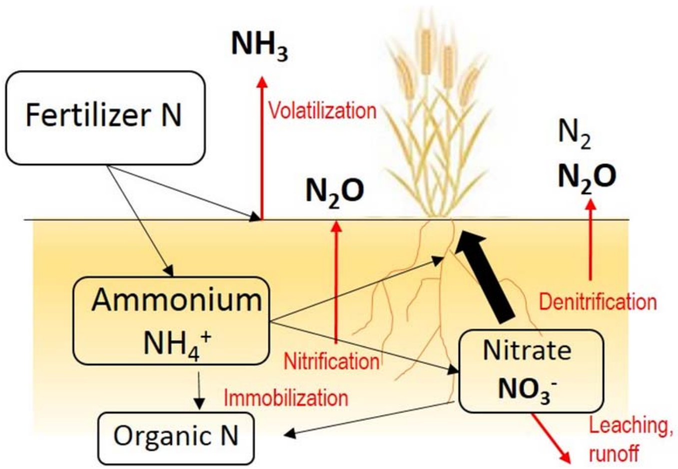
1. INTRODUCTION

Alteration of the agricultural nitrogen cycle due to mineral fertilizers supply, involves an increase of farmers costs and serious problems of **contamination of aquifers**, **depletion of soil fertility**, or **acidification,** which finally conducts to a **threat to environmental health**.



Agricultural nitrogen cycle

Nitrate (NO_3^-) leaching and **ammonia (NH_3) volatilization** are the main pathways of nitrogen loss in agriculture.

Nitrous oxide (N_2O) emissions are due to denitrification and nitrification processes and they are comparatively lower.

Emission rates are variable due to **soil type**, **climatic conditions** and **agricultural management** practices.

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1. INTRODUCTION

- **Innovation** in agricultural management systems is needed to fulfill the future demands while minimizing environmental impacts (*Kurt et al., 2012*).
- **Mineral fertilizers** will be still fundamental to support population growth but new environmental friendly fertilizers must be investigated to reduce **nitrogen losses** and **associated impacts**.
- One suggested solution has been to incorporate **biochar** as soil amendment since its effects on nitrogen retention and soil fertility are well known (*Haidel et al., 2018*; *Yu et al., 2018; Chan et al., 2007*)
- The main objective of the presented work is to **produce and asses an innovative fertilizer** based on activated carbon from two different residual materials, analyzing their environmental benefit and comparing them.

1. characterization of the **precursor** materials
2. Process **optimization. Experimental** test campaign
3. Activated carbon **production**
4. **Fertilizer** production
5. **Field** test campaign with the new product
6. Environmental **assessment** and **comparison**

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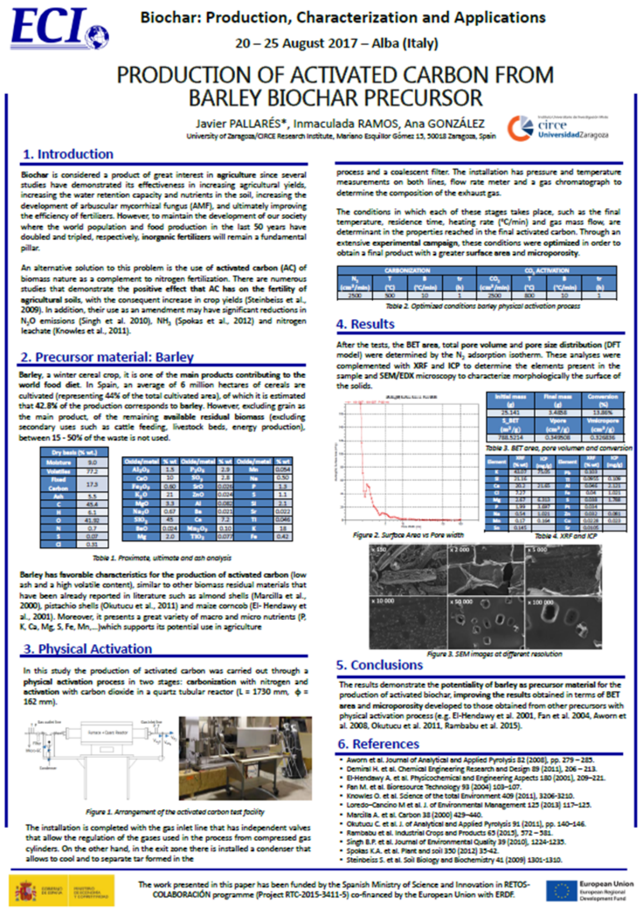
2. BACKGROUND



Biochar: Production, Characterization and Applications

20 – 25 August 2017 – Alba (Italy)

PRODUCTION OF ACTIVATED CARBON FROM BARLEY BIOCHAR PRECURSOR

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1. Introduction

Biochar is considered a product of great interest in **agriculture** since several studies have demonstrated its effectiveness in increasing agricultural yields, increasing the water retention capacity and nutrients in the soil, increasing the development of arbuscular mycorrhizal fungus (AMF), and ultimately improving the efficiency of fertilizers. However, to maintain the development of our society where the world population and food production in the last 50 years have doubled and tripled, respectively, **inorganic fertilizers** will remain a fundamental pillar.

An alternative solution to this problem is the use of **activated carbon (AC)** of biomass nature as a complement to nitrogen fertilization. There are numerous studies that demonstrate the **positive effect that AC has on the fertility of agricultural soils**, with the consequent increase in crop yields (Steinbeiss et al., 2009). In addition, their use as an amendment may have significant reductions in N_2O emissions (Singh et al. 2010), NH_3 (Spokas et al., 2012) and nitrogen leachate (Knowles et al., 2011).

2. Precursor material: Barley

Barley, a winter cereal crop, it is one of the **main products contributing to the world food diet**. In Spain, an average of 6 million hectares of cereals are cultivated (representing 44% of the total cultivated area), of which it is estimated that **42.8%** of the production corresponds to **barley**. However, excluding grain as the main product, of the remaining **available residual biomass** (excluding secondary uses such as cattle feeding, livestock beds, energy production), between 15 - 50% of the waste is not used.

Dry basis (% wt.)	
Moisture	9.0
Volatiles	77.2
Fixed Carbon	17.3
Ash	5.5
C	45.4
H	6.1
O	41.92
N	0.7
S	0.07
Cl	0.31

Oxide/metal	% wt	Oxide/metal	% wt	Oxide/metal	% wt
Al_2O_3	1.5	P_2O_5	2.9	Mn	0.054
CaO	10	SO_3	2.8	Na	0.50
Fe_2O_3	0.60	SrO	0.026	P	1.3
K_2O	21	ZnO	0.024	S	1.1
MgO	3.3	Al	0.082	Si	2.1
Na_2O	0.67	Ba	0.021	Sr	0.022
SiO_2	45	Ca	7.2	Ti	0.046
BaO	0.024	Mn_2O_3	0.10	K	18
Mg	2.0	TiO_2	0.077	Fe	0.42

Table 1. Proximate, ultimate and ash analysis

Barley has favorable characteristics for the production of activated carbon (low ash and a high volatile content), similar to other biomass residual materials that have been already reported in literature such as almond shells (Marcilla et al., 2000), pistachio shells (Okutucu et al., 2011) and maize corncob (El- Hendawy et al., 2001). Moreover, it presents a great variety of macro and micro nutrients (P, K, Ca, Mg, S, Fe, Mn,...)which supports its potential use in agriculture

3. Physical Activation

In this study the production of activated carbon was carried out through a **physical activation process** in two stages: **carbonization** with nitrogen and **activation** with carbon dioxide in a quartz tubular reactor (L = 1730 mm, ϕ = 162 mm).

Figure 1. Arrangement of the activated carbon test facility

The installation is completed with the gas inlet line that has independent valves that allow the regulation of the gases used in the process from compressed gas cylinders. On the other hand, in the exit zone there is installed a condenser that allows to cool and to separate tar formed in the process and a coalescent filter. The installation has pressure and temperature measurements on both lines, flow rate meter and a gas chromatograph to determine the composition of the exhaust gas.

The conditions in which each of these stages takes place, such as the final temperature, residence time, heating rate (°C/min) and gas mass flow, are determinant in the properties reached in the final activated carbon. Through an extensive **experimental campaign**, these conditions were **optimized** in order to obtain a final product with a greater **surface area** and **microporosity**.

CARBONIZATION				CO_2 ACTIVATION			
N_2 (cm³/min)	T (°C)	B (°C/min)	tr (h)	CO_2 (cm³/min)	T (°C)	B (°C/min)	tr (h)
2500	500	10	1	2500	800	10	1

Table 2. Optimized conditions barley physical activation process

4. Results

After the tests, the **BET area**, total **pore volume** and **pore size distribution** (DFT model) were determined by the N_2 adsorption isotherm. These analyses were complemented with **XRF** and **ICP** to determine the elements present in the sample and **SEM/EDX** microscopy to characterize morphologically the surface of the solids.

Figure 2. Surface Area vs Pore width

Initial mass (g)	Final mass (g)	Conversion (%)
25.141	3.4858	13.86%
S_{BET} (m²/g)	Vtotal (cm³/g)	Vmicropore (cm³/g)
766.5214	0.349508	0.326836

Table 3. BET area, pore volumen and conversion

Table 4. XRF and ICP

Figure 3. SEM images at different resolution

5. Conclusions

The results demonstrate the **potentiality of barley as precursor material** for the production of activated biochar, **improving the results obtained in terms of BET area and microporosity** developed to those obtained from other precursors with physical activation process (e.g. El-Hendawy et al. 2001, Fan et al. 2004, Aworn et al. 2008, Okutucu et al. 2011, Rambabu et al. 2015).

6. References

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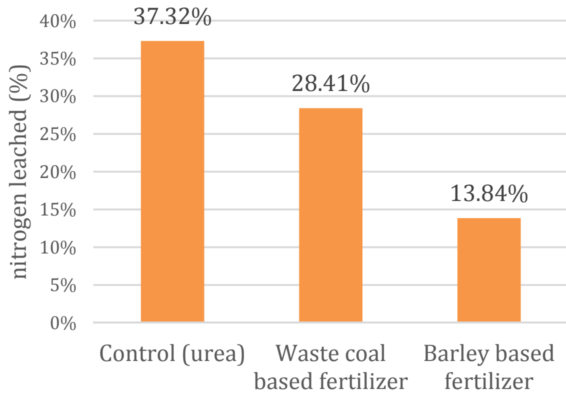
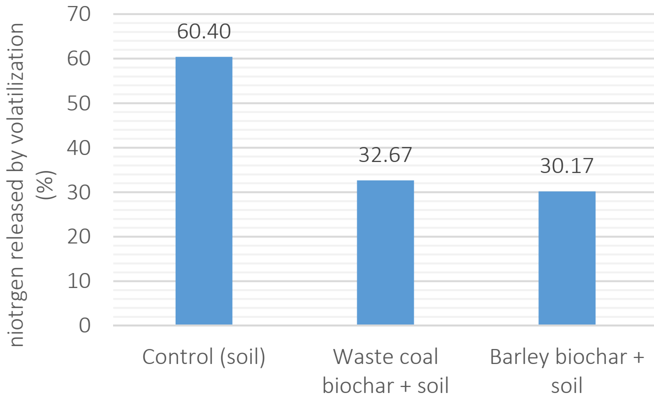
NITRATE LEACHING TESTS



NITROGEN VOLATILIZATION TESTS



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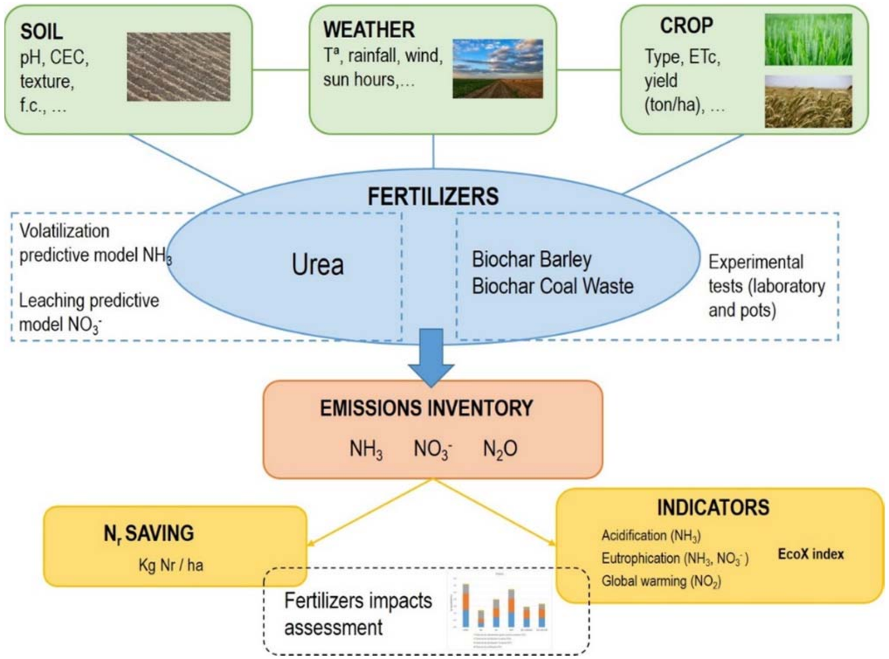
3. ENVIROMENTAL ANALYSIS

To analyze the environmental benefit of the biochar based fertilizers, the study performs a comparative assessment based on LCA procedure and nitrogen footprint tools.



Layout of the environmental analysis

- Life Cycle Assessment (LCA) is a technique used to assess each and every impact associated with all the stages of a process by evaluating its consumptions and emissions (*Basosi et al., 2014*; *Brentrup et al.,2004*).

- Nitrogen *footprint* approach. The 'footprint' concept has been developed over the last decade to serve as a metric of the single or collective impacts of people on the environment, relative to the capacity of the planet to support those people.(*Leach et al., 2012*)

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3. ENVIROMENTAL ANALYSIS

IMPUT DATA

SOIL PROPERTIES	
Bulk density	1,35 g/cm³
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

CROP PROPERTIES (WHEAT)	
Expected production	2 ton/ha
Planting month	October
Dose (according to production)	150 kg N/ha
Uptake N	60 kg N/ha

WEATHER CONDITIONS

Mean data from local weather station (Tª, rainfall, wind, humidity, sun hours)

EMISSION FACTORS

EMISSION FACTORS	UREA	BB BARLEY	BB COAL WASTE
NH_3 volatilization factor (kg NH_3/kg N applied)	0,21	0,08	0,09
N_2O volatilization factor (kg N_2O/kg N applied)	0,01	0,01	0,01
NO_3 leaching factor (kg NO_3/kg N applied)	0,41	0,14	0,28

- Predictive models based on bibliographic data (Urea)
- Experimental tests (BB fertilizers)

EMISSIONS INVENTORY

EMISSIONS INVENTORY	UREA	BB BARLEY	BB COAL WASTE
Ammonia (kg NH_3/ha)	30,88	12,74	13,79
Ammonium ion (kg NO_3/ha)	61,16	20,76	42,62
Nitrous oxide (kg N_2O/ha)	1,49	1,72	1,70

→ LCA INDICATORS

Nr SAVING RESULTS

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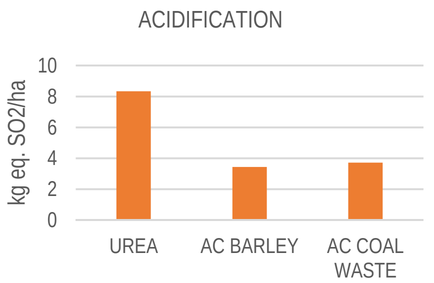
4. RESULTS. Indicators

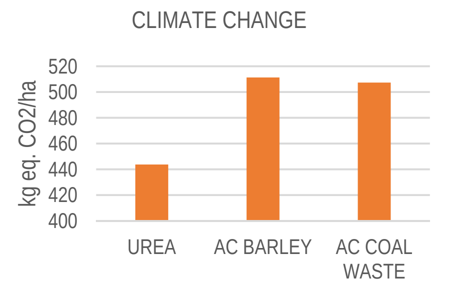
- Calculation of **LCA indicators** based on the main impact categories:

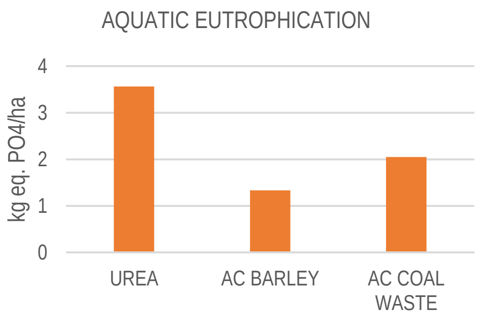
IMPACT CATEGORIES	
Acidification potential (AP)	$AP = m_{NH_3} \cdot AF_{NH_3}$
Terrestrial eutrophication potential (TEP)	$TEP = m_{NH_3} \cdot EF_{NH_3}$
Aquatic eutrophication potential (AEP)	$AEP = (m_{NH_3} \cdot FF_{NH_3 Spain} \cdot EF_{NH_3}) + (m_{NO_3} \cdot RF_{NO_3} \cdot EF_{NO_3})$
Climate change potential (CCP)	$CCP = m_{N_2O} \cdot GWP_{N_2O}$

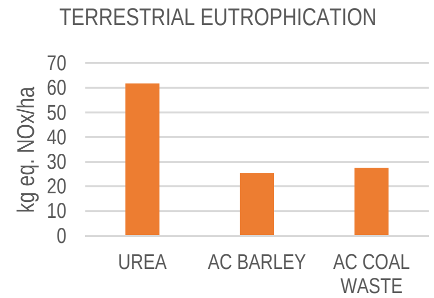
CHARACTERIZATION FACTORS			
Substance	Potential risk	Value	Units
ammonia (NH_3)	Acidification (AF)	0,27	eq. kg SO_2
ammonia (NH_3)	Aquatic eutrophication (EF)	0,35	eq. Kg PO_4
ammonia (NH_3)	Terrestrial eutrophication (EF)	2	eq. kg NO_x
ammonium ion (NO_3^-)	Aquatic eutrophication (EF)	0,1	eq. kg PO_4
nitrous oxide (N_2O)	Climate change (GWP)	298	eq. kg CO_2

Biochar based fertilizers show a great reduction of the potential risk regarding **acidification** and **eutrophication** compared to Urea.









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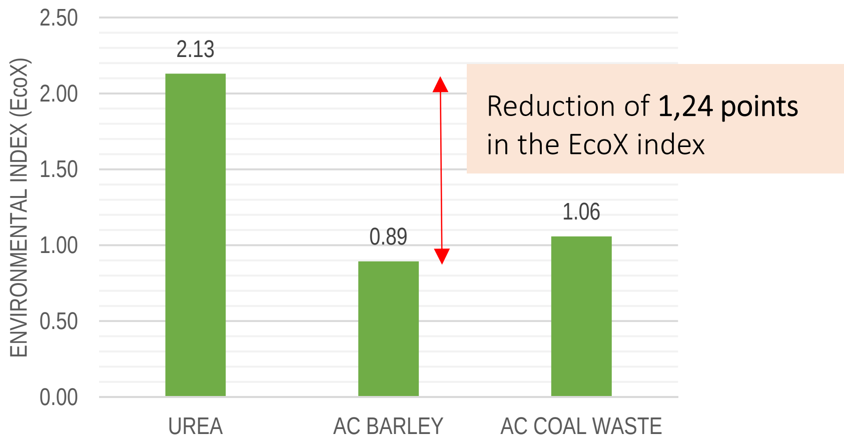
4. RESULTS. Indicators

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 (EcoX indicator*).

$$N_i = \frac{I_i}{NV_i} \qquad EcoX = \sum_i N_i \cdot WF_i$$

NORMALIZATION VALUES AND WEIGHTING FACTORS			
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



** F. Brentrup et al. Environmental impact assessment of agricultural production systems using the life cycle assessment (LCA) methodology II. The application to N fertilizer use in winter wheat production systems. Europ. J. Agronomy 20 (2004) 265-279.*

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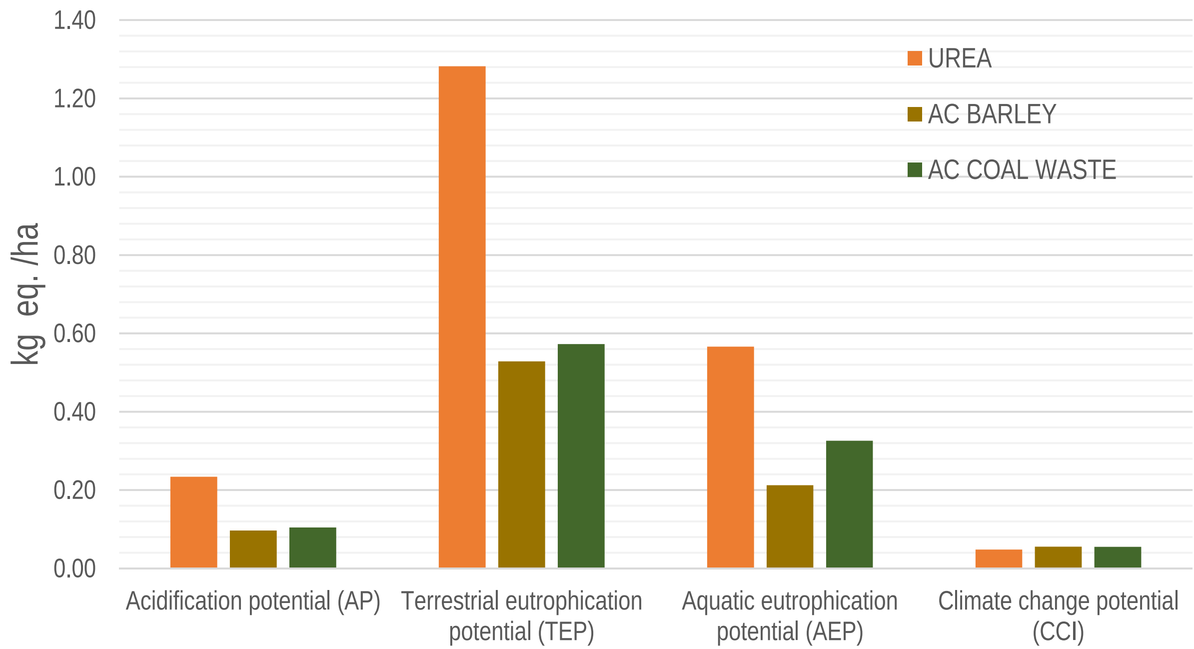
4. RESULTS. Indicators



Environmental impacts assessment → the most important risk in nitrogen fertilization is **eutrophication**, not only due to **nitrate leaching** (**aquatic eutrophication**) but above all, because of the NH_3 emissions that contribute to the undesired increased in biomass production on terrestrial vegetation (**terrestrial eutrophication**), which is quite significant in the case of Urea.

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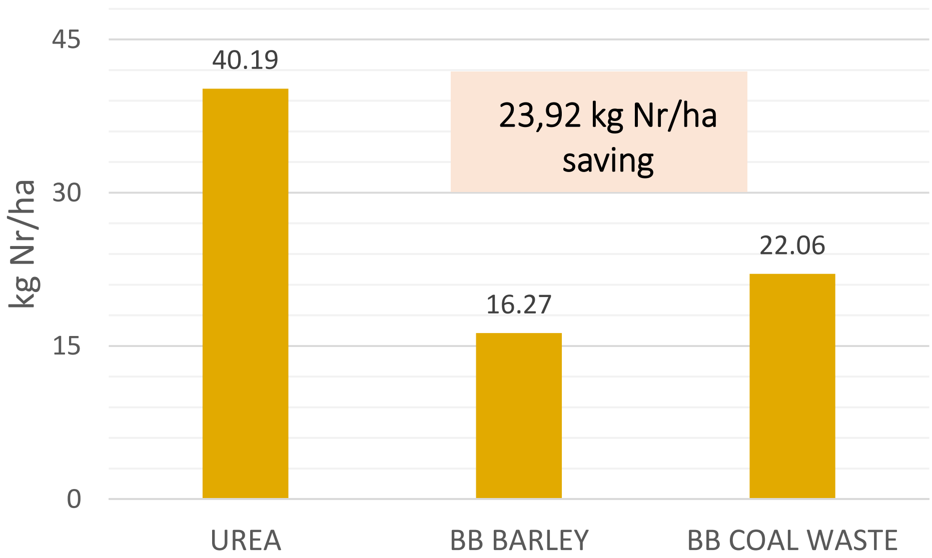
4. RESULTS. Nr saving results

Reactive nitrogen saving: The total Nr emissions are calculated accounting for the contribution of each compound. Then, the Nr reactive savings are determined, using as reference the one which presents the largest Nr emissions (Urea for the particular case study).

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



% saving compared to Urea	
AC BARLEY	59,52
AC COAL WASTE	45,09

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5. CONCLUSIONS

General conclusions

- The production process of AC fertilizer is **viable** and the new product has the **capacity to reduce** the environmental impact compared to traditional fertilizers.
- The proposed methodology is adequate for the assessment of the **environmental risk** involved in the application of nitrogen fertilizers in agricultural practices.
- The analysis of **Nr saving** provides a new tool for assessing the environmental benefit of a product.

Particular case study conclusions

- Biochar based fertilizers show a **great reduction of the potential risk** regarding **acidification** and **eutrophication** compared to Urea.
- Results confirm a **substantial saving** (60% and 45% of Nr saving regarding urea) in the reactive nitrogen emitted when AC fertilizers are applied in a wheat crop under particular conditions.
- Finally, it can be concluded that **residual biomass** material (barley straw) offers **better results** compared to the coal waste material, getting a 14% more of Nr saving.

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