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Life Cycle Assessment and Soil Nitrogen Balance of Different N Fertilizers for Top Dressing Rye as Energy Crop for Electricity Generation

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Abstract: Nitrogen fertilizers have been identified in energy crops LCAs as the main contributors to global warming, as well as to many other environmental impacts. The distinct production process and application emissions of nitrogen fertilizer types for top dressing produce different GHG savings when energy crops value chains are compared to fossil energy alternatives. In this study, three types of fertilizers (calcium ammonium nitrate, urea and ammonium sulphate) at N top dressing rates of 80 kg N/ha are used to grow rye for electricity generation under the conditions of the Continental Mediterranean climate of central-northern Spain. Complete LCAs for the whole value chain based on real data were performed in conjunction with soil nitrogen balances (SNBs) to assess the accomplishment of European Union (EU) GHG savings sustainability criteria, as well as the sustainability of fertilization practices for soil nitrogen stocks. The results obtained can provide interesting insights for policy making, since calcium ammonium nitrate, the most common fertilizer for rye crops, led to 66% GHG savings, as opposed to the 69% achieved when applying urea and 77% when ammonium sulphate was used. Nevertheless, the three fertilizers produced annual soil deficits greater than 50 kg N/ha. In order to ensure savings above 80%, as required by the EU sustainability criteria, and sustainable SNBs, additional optimization measures should be taken at key points of the value chain.

Keywords: bioenergy; marginal lands; sustainability criteria; calcium ammonium nitrate; urea; ammonium sulphate; biomass; secale cereale; global warming; energy balance

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1. Introduction

Bioenergy is a crucial element within the current development framework for the European Union (EU) Bioeconomy [1]. Bioenergy represents almost 60% of the EU's renewable energy consumption, and it is a contributing factor to reaching the 20% renewable energy target set for 2020. Based on the EU's 2030 targets, bioenergy consumption share is expected to increase, and it plays a key role in the EU's 2050 long-term strategy facts [2,3]. In this context, and considering the limitations of the use of residual biomass, the domestic supply of sustainable biomass from energy crops is being studied intensively within the EU [4–7] to determine its real potential in fulfilling the anticipated demands of biomass industries. Energy crops will be essential in ensuring biomass supply for electricity and heat generation [3,8] and in generating employment in rural areas [9].

Since the entry into force of the first Renewable Energy Directive (RED I) in 2009 [10], life cycle assessment (LCA) has been used to evaluate the sustainability of bioenergy chains [11], as it is designed specifically for this purpose. For transportation fuels to be counted as renewable energy, the directive establishes a binding sustainability criteria of 60% GHG savings with respect to fossil energy references. Simultaneously, the same sustainability criteria were introduced as a strong recommendation for biomass for electricity, heating and cooling [12]. As a result, many bioenergy pathways for biofuel production [13], and electricity and heat generation [14] have been intensively evaluated through LCA. With the publication of the new Renewable Energy Directive (RED II) in 2018 [15], the sustainability criteria for solid biomass has become stricter and binding, increasing GHG savings to 70% for 2021 and 80% for 2026. Due to this fact, it is necessary to optimize the use of dedicated lignocellulosic crops by defining appropriate agricultural management solutions [16]. Many previous LCAs pointed out the crucial role of fertilizers as the main contributors to fossil energy consumption, GHG emissions, and environmental impacts such as eutrophication and acidification, among others [17–19]. Considering this, and that their production and application is responsible for 2.5% of the world's GHG emissions [20], fertilization is one of the best possible targets for optimization. Therefore, many bioenergy sustainability assessments deal with the role of fertilizers [21–23]. These assessments have paid little attention to the effect of different nitrogen fertilizers in productivity and their varying impacts on each production process and use emissions [24]. Moreover, none of them assess the sustainability of the nitrogen fertilization system for soil nitrogen stocks through soil nitrogen balance (SNB). Nitrogen is the main nutrient for plants and it is extracted from the soil to allow their development, besides it can be lost in form of leachates, eroded or emitted to the air in diverse forms. The main source of nitrogen for crops is fertilization and it is targeted in this study, since it should ensure sustainable balances to maintain soil fertility.

According to RED II [15] and its corresponding delegated act [25], biomass should be produced as a low indirect land use change (ILUC) risk feedstock to avoid limitations on the amounts of each biomass type that can be used in each EU country. Rye (*Secale cereale* L.) is a winter cereal with demonstrated potential for use as feedstock for electricity generation [26] and a high possibility of accomplishing low ILUC requirements. It can be cultivated in abandoned lands [27] due to its rustic nature, as well as being a traditional crop well known to many European agricultural smallholders. It can be also produced as additional feedstock within double cropping rotations without reducing current food production [28,29]. For all these reasons, rye has been chosen as the target energy crop for testing different types of fertilizers.

The goal of this work is to optimize rye management when grown as an energy crop for electricity generation, by selecting the best nitrogen fertilizer in terms of producing the lowest possible LCA environmental impacts, while achieving and maintaining good soil properties and a sustainable nitrogen balance. The environmental impacts of rye are compared with those of natural gas for electricity generation, as it is currently the cleanest fossil energy source. Greenhouse gases savings are calculated to assess the extent of compliance with the RED II's GHG sustainability criteria. This will help to provide a more holistic approach to assessing the sustainability of an energy crop suited for growth in the EU under the new RED II low ILUC requirements.

The biomass production conditions are those of the Spanish province of Soria, which is located in central-northern Spain and belongs to the region of Castilla y León, one of the most important and extensive cereal producing areas in the country, where the low profitability [30] of the poorer and more marginal lands leads to their abandonment. This creates a unique opportunity for the production of low ILUC biomass.

The bioenergy system used takes into consideration the soil characteristics, as well as crop production and composition of the biomass obtained in the experimental trials. Data on the transportation of bales and their processing for electricity generation, combustion emissions, and transport to the waste management point were taken from a 25 MWe biomass power plant in northern Spain. The fossil energy system used as a reference considers the average life cycle data of natural gas transformation into electricity in Spain [31]. The results of electricity generated from rye were compared to those of natural gas in order to determine compliance with the RED II GHG sustainability criteria. Primary energy consumption and other important indicators such as acidification and eutrophication were also evaluated due to their relevance. Primary fossil energy and GHG savings were considered alongside annual biomass yields, soil nitrogen balances and total fertilization efficiencies.

2. Materials and Methods

2.1. Experimental Design: Plots, Soils, Biomass Production and Analytical Methods

Field trials of rye (*Secale cereale* (L.) M.Bieb.) Petkus cultivar were established in two locations of the Spanish province of Soria. Tests were carried out during one agricultural season in two experimental plots located in the municipalities of Lubia and Escobosa de Almazán, with an approximate surface area of 1800 m^2 each. Twelve narrow strips (≈3 m wide) of 150 m^2 were established per location following a randomized complete block design, and considering a sowing dose of 120 kg/ha, base fertilization with 300 kg/ha of NPK compound fertilizer (8-24-8) and four types of top dressing (none–NUL-, calcium ammonium nitrate–CAN-, ammonium sulphate–AMS-, and urea –URE-) in three replicates. CAN (27% N), AMS (21% N), and URE (46% N) [32] were applied at an annual fertilizer rate of 80 kg N/ha, on 13th March in Escobosa and 16th March in Lubia. No N top dressing was applied in the control plot (NUL). Calcium ammonium nitrate is the preferred rye fertilizer of the farmers of the region, due to it being both fast at absorbing nitric nitrogen and ammonia nitrogen that needs time to transform and become available, as well as calcium, which is an important secondary nutrient. It also produces low losses in the form of NH_3, but has the highest emissions of GHGs per nitrogen fertilizer unit (NFU). Ammonium sulphate nitrogen is 100% ammonia and can acidify soils due to its sulphur, but has the lowest GHG emissions per NFU. Urea is the cheapest fertilizer of the three, and its nitrogen is slowly released and its GHG emissions per NFU are between CAN and AMS, but it has high losses of nitrogen as NH_3 (63% more than CAN). In general, farmers in the region consider the price of fertilizer per NFU, the type of nitrogen, the secondary nutrients and the losses in the form of NH_3, because it implies that less nitrogen is available for the crops at the end. However, they are not aware of the GHGs emissions per NFU of the fertilizer that they buy.

No pesticides were applied in any of the two sites. Both sites were fallow the year prior to the establishment of rye according to the typical crop rotation (rye-barley-fallow) conducted in the region for rain-fed agriculture in relatively poor soils, such as the ones selected.

The edapho-climatic conditions at the two experimental sites, as well as relevant information on the duration and the location of the trials, are shown in Table 1. Several soil samples were taken in zig-zag from the first 30 cm of the soil. They were mixed and dried to a constant weight in an oven maintained at 40 °C. These samples were sieved (2 mm size mesh), and stones (fraction over 2 mm) were separated. The fraction below 2 mm was used for determining the soil properties; pH was potentiometrically determined (1:2.5, soil: water), soil organic C was analyzed by oxidation with dichromate in sulphuric acid (Walkley–Black method), and the total soil N content was analyzed by micro-Kjeldhal (Bouat–Afora method). Available soil phosphorus was determined with the Bray and Kurt method, using a UV-visible spectrophotometer (Spectronic–Genesys–Unicam, Madrid, Spain). The available soil potassium concentrations were determined by neutral extraction with ammonium acetate (1 N), followed by atomic absorption spectrometry (Varian AA-1475; Midland, ON, Canada). Average precipitations obtained from the last six available years from the nearest meteorological stations were 319 mm for Lubia and 281 mm for Escobosa (November–June).

All the aerial biomass produced on each entire plot was harvested using commercial machinery at the doughy state (8 on the Zadoks growth scale), leaving approximately 10 cm of stubble. Dry matter yields were estimated by taking into account the total surface harvested, as well as the total weight and moisture content of the aerial biomass collected.

Table 1. Experimental sites characteristics and trials duration.

1. Location	Lubia (Soria)	Escobosa de Almazán (Soria)
Coordinates	41°36′40.0″ N 2°28′55.6″ W	41°29′31.3″ N 2°21′59.6″ W
Altitude	1035 m	1081 m
2. Experimental period		
Duration (sowing harvest)	08/11/2011–26/06/2012	13/11/2011–25/06/2012
Average temperature	10.3 °C	10.8 °C
Total rainfall	293 mm	335 mm
3. Soil type	Soil 1 (S1)	Soil 2 (S2)
Texture	Sandy loam	Sandy loam
Clay/silt/sand (%)	12/12/76	20/28/52
pH	7.1	8.7
Organic matter (%)	1.3	1.3
Nitrogen (%)	0.100	0.110
Available K (ppm)	192	222
Available P Olsen (ppm)	11	12

A combined sample per replicate plot (three combined samples per fertilizer regime and location) was analyzed to determine the main properties and the chemical composition of the above-ground biomass. Every combined sample was formed by manually collecting three subsamples (1 kg each) from different random locations in the replicate plot. At least ten roots were also collected per plot by digging a pit of ≈1.3 m; they were carefully cleaned without using water with compressed air and brushes to determine their weight and chemical composition; samples for characterization were obtained as previously for above-ground biomass.

Biomass chemical analysis was performed in the CIEMAT Laboratory of Biomass Characterization following the corresponding international standards for solid biofuels. Moisture content was measured by oven-drying at 105 °C until constant weight, following ISO 18134-2:2017. Sample preparation was performed according to ISO 14780:2017. Ash content was determined by calcination of the biomass at 550 °C following the ISO 18122:2015 standard. C, H, and N were determined according to ISO 16948:2015 using a TruSpec (Leco, Tres Cantos, Madrid, Spain) elemental analyzer equipped with infrared detectors and a thermal conductivity detector. The determination of Cl and S was carried out by ion chromatography (883 Basic IC Plus, Metrohm, Madrid, Spain) after sample combustion in a calorimetric bomb and the later recovery of chloride and sulphate in an aqueous solution (ISO 16994:2016). The oxygen content related to the combustible part of the solid biofuel was calculated according to ISO 16993:2016. Calorific value was determined using an automatic calorimeter (C-5000, Ika Verke Staufen, Germany) by applying ISO 18125:2017. The net calorific value at constant pressure was calculated on a dry basis (NCVp,0), as well as on a wet basis, considering a moisture content of 12% (NCVp,12), as this is the average moisture content of the rye biomass consumed by the power plant selected for this study. The ash, H, Cl, S, and O contents of the fuel were not shown, but used to calculate the net calorific value at constant pressure.

The ratio between the aerial and root biomass as well as the C and N ratios between both fractions were the same as those considered by the authors elsewhere [33].

2.2. Life Cycle Assessment Methodology

The LCA methodology has been described previously [33]. It considers seed production, fertilizer production, diesel and motor oil consumption and combustion emissions and agricultural machinery manufacture. It also considers field and fertilizer derived emissions, which included emissions of nitrous oxide, nitrogen oxides (NO_x) and ammonia emissions to the air, nitrate leaching to ground water and the nitrogen emission from eroded particles that reach the surface water. Besides the emissions of phosphorous to the water as well as the emissions of heavy metals to agricultural soil, surface water and ground water were also included. Nitrogen emissions in form of nitrous oxide were calculated as 1% of the N of fertilizers and crop residues and of the N emissions in form of ammonia, plus 0.75% of the nitrogen emissions in the form of nitrates. When urea was used as fertilizer, it was considered that 1.570 kg of CO_2 per kg of applied N was released [34], none CO_2 emissions were considered due to the application of calcium ammonium nitrate or ammonium sulphate.

The impact assessment method chosen to evaluate the GWP was the 2013 version of the IPCC for 100 years' time horizon [35]. The corner–middle–layer (CML) method was also chosen to evaluate the effects of the systems on other important impact categories [35]. Cumulative energy requirement analysis (CERA) [35] was the method chosen for energy assessment.

Figure 1 describes the bioenergy system under study, including the processes, emissions and subsystems considered, as well as the limits of the assessment. As mentioned earlier, electricity production from rye biomass was compared to natural gas. This fossil fuel was selected as a reference because it is the cleanest fossil feedstock for electricity generation. For both systems, rye and natural gas, the functional unit chosen is 1 TJ of electrical energy generated from their respective consumptions.

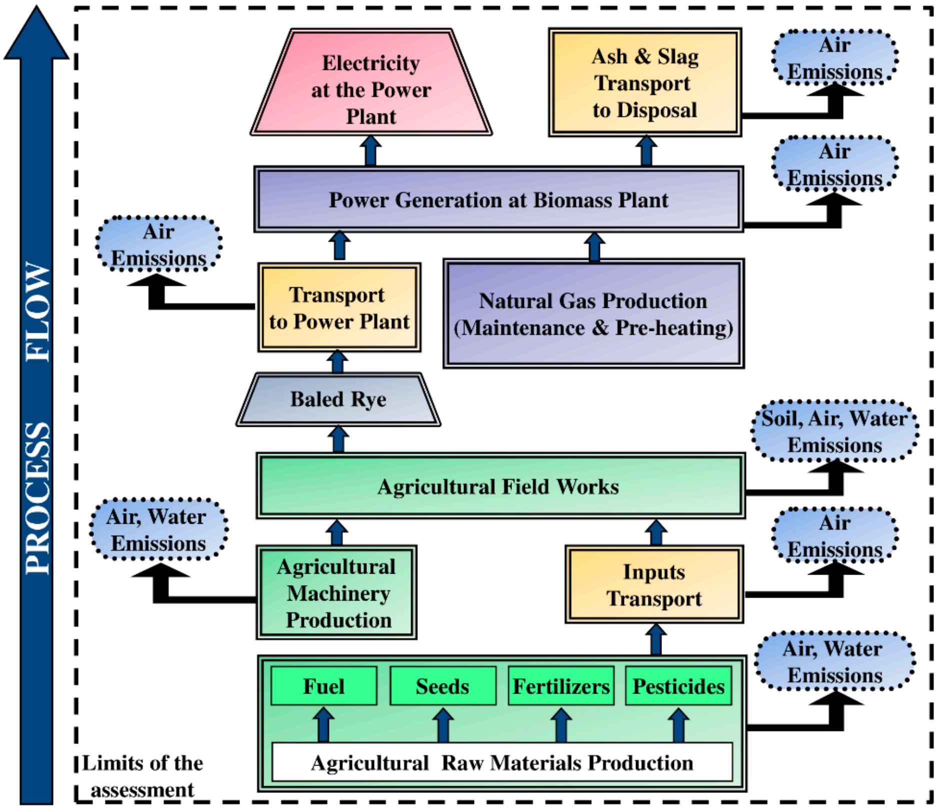

Figure 1. Bioenergy system limits and phases included in the analysis.

Field operations constitute an essential part of the agricultural system when growing rye. Table 2 includes the characteristics and fuel consumption of the agricultural machinery used. Together with fertilizers and seed consumption, fuel consumption derived from the use of agricultural machinery can be considered relevant inputs of the agricultural system.

Table 2. Field operations performed for rye cultivation.

Operation	Tractor		Implement			
	Weight	Power	Type	Weight	Operating Rate	Fuel Consumption
	(kg)	(kW)		(kg)	(h/ha)	(L/ha)
Primary tillage	5470	103	Plough	1390	1.00	20
Secondary tillage	5470	103	Harrow	400	0.66	10
Base fertilization	3914	66	Spreader	110	0.20	4
Sowing	5470	103	Seeder	830	0.60	8
Top dressing [a]	3914	66	Spreader	110	0.20	4
Rolling	3914	66	Roller	1000	0.40	8
Mowing-swathing [b]	3914	66	Mower	150	1.88–0.65 (1.17) [c]	18.84–6.50 (11.60) [c]
Baling [b]	9000	144	Large square baler	1700	1.32–0.44 (0.82) [c]	31.68–10.60 (19.64) [c]
Automatic bale loading	5470	103	Atomatic bale loader trailer	2500	0.48	10.9
Bale loading to lorry	5470	103	Forklift	1870	0.40	4

[a] No top dressing was applied in control treatment (NUL). [b] Field work fuel consumption and operating rates depend on biomass production. [c] Maximum-Minimum (Average) values.

The biomass power plant data used for the modelling of this part of the system (Table 3) were provided by a real 25 MW plant located in northern Spain, which averaged a 29% conversion efficiency of biomass to electricity.

Table 3. Biomass power plant consumptions, residues and emissions.

Items	Type	Amount	Units
Natural gas	Consumption	0.0389	MJ Natural Gas/kg dry biomass
Slag	Residue	93.72	g Slag/kg dry biomass
Ashes	Residue	9.38	g Ash/kg dry biomass
Carbon dioxide from natural gas combustion	Emission	2.16	g CO_2/kg dry biomass
Nitrogen oxides	Emission	1.85	g NO_x/kg dry biomass
Carbon monoxide	Emission	1.05	g CO/kg dry biomass
Sulphur dioxide	Emission	0.36	g SO_2/kg dry biomass
Particulate matter	Emission	0.27	g Particulate matter/kg dry biomass

Table 4 summarizes the inventory data for the modelling of the transport system, including all material to be transported, as well as their origin and destination points, the distances between them, and the vehicles used.

Table 4. Transport system characteristics.

Material	From	To	Distance	Vehicle
Seed	Field	Processing center	30 km	Lorry 16–32 t
	Processing center	Regional storehouse	100 km	Lorry 16–32 t
	Regional storehouse	Demonstration plot	10 km	Tractor and trailer
Fertilizers and pesticides	Manufacturer	Regional storehouse	600 km	Train
			100 km	Lorry > 16 t
	Regional storehouse	Demonstration plot	10 km	Tractor and trailer
Rye bales	Demostration plot	Biomass plant	60 km	Lorry 16–32 t
Ash and slag	Biomass power plant	Disposal site	37 km	Lorry 16–32 t

2.3. Soil Nitrogen Balance Methodology

Soil nitrogen balance was performed by using the data shown in Sections 2 and 3, and the methodology used has been previously described elsewhere [33]. The inputs considered included the nitrogen provided by fertilizers (N_Fert), seeds (N_Seed), atmospheric deposition (N_AtDep), and free living soil organisms (N_FrLiv). The following outputs have been taken into account: N removal by crop harvest (N_HarvEx); losses of nitrogen in the form of nitrates ($N\_NO_3{}^-$), which were calculated considering the influence of the precipitation, clay content of the soil, crop root depth, as well as nitrogen supplied with fertilizers, crop nitrogen uptake and organic nitrogen content of the soil; losses of nitrogen due to soil erosion (N_Eros) were calculated considering erosion factor specific for the watershed, the nitrogen content of the top soil, a nitrogen enrichment factor for the first cm of the soil and a factor to estimate the fraction of nitrogen that effectively leaves plots and goes to rivers and not the near plots; emissions of nitrogen in the form of ammonia (N_NH_3) estimated as a fraction of the nitrogen content of each type of fertilizer (2% for calcium ammonium nitrate, 15% for urea, 8% for ammonium sulphate and 4% for the multinutrient fertilizer); nitrogen emissions in the form of nitrous oxide due to the decomposition of crop residues and fertilizer application ($N\_N_2O_{Cr+Fert}$) estimated as 1% of the nitrogen provided by both crop residues and fertilizers and nitrogen emissions in form of other nitrogen oxides (N_NO_x), which were estimated as 21% of total N_2O emissions. The soil nitrogen balance (SNB) methodology was adjusted to make it coherent and consistent with the LCA methodology by matching the outputs of the SNB to the nitrogen emissions, which are accounted for in the LCA and affect the environmental impact results.

2.4. Statistical Analysis

Statistical analyses were performed using the Statgraphics Centurion XVII.I (Statpoint Technologies INC., Warrenton, VA, USA, 2017) software.

The effects of the different fertilizer regimes (NUL, AMS, CAN, and URE) and locations (Lubia and Escobosa) on biomass production and composition (calorific values, C and N contents), as well as on soil nitrogen deficits, global warming potential, electricity produced per fossil energy consumed, natural gas savings, total fertilizer efficiencies and all the impact categories (CML method) were evaluated by means of the analysis of variance (ANOVA) procedure. A multifactorial two-way ANOVA (Type III sums of squares) with a maximum order interaction of 2 was used. Two factors were considered in the statistical model; the different fertilizer type used for top dressing (F) and the energy crop location (L). Both factors (F and L) and their interaction (F × L) were considered to be fixed effects. All F-ratios were based on the residual mean square error. A main factor or an interaction effect was considered significant when its significance level or *p*-value was lower than 0.05 at 95.0% confidence level. Mean differences across fertilizer types and locations were assessed using multiple range tests according to Fisher's least significant difference (LSD) test.

3. Results

3.1. Biomass Production and Composition

Table 5 shows dry matter yields, calorific values and N and C contents of the biomass produced under different fertilizer conditions and locations.

The calorific value and the C content of the biomass differed significantly depending on the type of fertilizer used for top dressing, obtaining the highest values when AMS was applied. The different types of fertilizers border on significance (at 95% confidence level) in the case of biomass production and N contents, with *p*-values between 0.065 and 0.079. Ammonium sulphate provided the highest mean yields and NUL the lowest N average levels in both aerial biomass and roots.

With regard to the site of the energy crop, Escobosa provided higher yields and N biomass contents than Lubia. The C content in the aerial biomass and roots and the calorific values did not differ across locations.

No statistical significant interaction between the type of fertilizer used for top dressing and the location of the energy crop was detected.

Table 5. Calorific value, biomass yield and composition (means ± standard deviations) depending on the N fertilizer type used for top dressing and location.

	Annual Aerial Yield	**N in Aerial Biomass**	**N in Roots**	**C in Aerial Biomass and Roots**	**$NCV_{p,0}$**	**$NCV_{p,12}$**
	(Mg/ha, d.b.)	**(%, d.b.)**	**(%, d.b.)**	**(%, d.b.)**	**(MJ/kg)**	**(MJ/kg)**
Fertilizer type for top dressing						
NUL	10.4 ± 0.9	1.28 ± 0.20	1.93 ± 0.29	44.1 ± 0.4 b	16.20 ± 0.17 b	13.96 ± 0.15 b
AMS	11.2 ± 1.2	1.49 ± 0.09	2.23 ± 0.14	44.9 ± 0.3 a	16.62 ± 0.09 a	14.34 ± 0.08 a
CAN	10.8 ± 1.6	1.40 ± 0.19	2.10 ± 0.28	44.1 ± 0.4 b	16.28 ± 0.14 b	14.03 ± 0.13 b
URE	9.6 ± 0.8	1.48 ± 0.16	2.22 ± 0.23	44.4 ± 0.6 ab	16.35 ± 0.23 b	14.09 ± 0.20 b
Energy crop location						
Lubia	10.0 ± 1.1 b	1.33 ± 0.20 b	2.00 ± 0.30 b	44.5 ± 0.6	16.37 ± 0.27	14.11 ± 0.23
Escobosa	11.0 ± 1.3 a	1.49 ± 0.09 a	2.24 ± 0.14 a	44.3 ± 0.5	16.36 ± 0.19	14.10 ± 0.17
				p-values (*)		
F	0.0786	0.0647	0.0657	0.0172	0.0052	0.0052
L	0.0405	0.0107	0.0111	0.2608	0.8588	0.8496
F × L	0.1927	0.2692	0.2714	0.3530	0.8253	0.8432

d.b.: dry basis, $NCV_{p,0}$: Net heating value at constant pressure and 0% humidity, $NCV_{p,12}$: Net heating value at constant pressure and 12% humidity; (*) Statistical significance (*p*-values from Fisher's tests) of the considered factors for each property from a multifactorial ANOVA (order 2), taking into account the fertilizer regime used for top dressing (F) and the location of the energy crop (L) as factors. Different letters indicate significantly different means between fertilizer regimes or locations for that property at the 95% confidence level according to multiple range tests. Root biomass was considered as 9.1% of the aerial biomass yield for all plots based on our measures.

3.2. Soil Nitrogen Balance, Global Warming Potential and Cumulative Energy Demand

All SNBs yielded negative values irrespective of the dosage and type of fertilizer applied or the location of the trial (Table 6). Control plots that did not receive any N top dressing also displayed negative balances. Crop harvest (N_HarvEx) was responsible for 81% of all N outputs. Other N outputs such as nitrates leaching (N_NO_3^-) were lower, and averaged 12%. Analogously, nitrogen fertilization (N_Fert) was the main nitrogen input, and averaged 90% for all the alternatives that included conventional fertilizer annual doses of 80 kg N/ha.

Among other indicators, Table 7 shows the annual N deficits depending on the fertilizer type used for top dressing and the location of the energy crop and its statistical significance (*p*-values < 0.01).

As expected, the highest deficits were obtained in control trials (NUL), which reached more than 120 kg N/ha. Conventional fertilizer applications of calcium ammonium nitrate, urea and ammonium sulphate also produced remarkable deficits (60–90 kg N/ha).

The global warming potential of control plots (27 Mg CO_2/TJ el) was significantly lower than those of the rest of fertilizer treatments, which ranged 37–54 Mg CO_2/TJ el, depending on the type of fertilizer used for top dressing (Table 7).

Table 6. Soil nitrogen balance (means ± standard deviations) depending on the N fertilizer type used for top dressing and location. Input and output codes were described in Section 2.3.

	Inputs (kg N/(ha·y))				Outputs (kg N/(ha·y))						Soil Nitrogen Balance
	N_Fert	N_Seed	N_AtDep	N_FrLiv	N_HarvEx	N_NO$_3^-$	N_Eros	N_NH$_3$	N_N$_2$O$_{Cr+Fert}$	N_NO$_x$	(kg N/(ha·y))
Fertilizer type for top dressing											
NUL	24	1.91	7	3	132 ± 22	18.4 ± 0.6 b	n.a.	1.0	0.59 ± 0.06 c	0.25 ± 0.02 c	−121 ± 22 b
AMS	104	1.91	7	3	167 ± 20	20.9 ± 1.2 ab	n.a.	7.4	1.49 ± 0.05 a	0.56 ± 0.02 a	−85 ± 19 a
CAN	104	1.91	7	3	152 ± 34	22.9 ± 3.5 a	n.a.	2.6	1.44 ± 0.09 ab	0.54 ± 0.02 b	−67 ± 31 a
URE	104	1.91	7	3	143 ± 23	23.1 ± 2.7 a	n.a.	13	1.42 ± 0.06 b	0.57 ± 0.02 a	−69 ± 21 a
Energy crop location											
Lubia	n.a.	1.91	7	3	134 ± 25 b	22.2 ± 3.6	3.97	n.a.	1.19 ± 0.40 b	0.47 ± 0.14 b	−71 ± 28 a
Escobosa	n.a.	1.91	7	3	163 ± 20 a	20.5 ± 1.6	4.36	n.a.	1.27 ± 0.39 a	0.49 ± 0.14 a	−100 ± 28 b
							p-values (*)				
F	n.a.	n.a.	n.a.	n.a.	0.0506	0.0047	n.a.	n.a.	0.0000	0.0000	0.0003
L	n.a.	n.a.	n.a.	n.a.	0.0020	0.0556	n.a.	n.a.	0.0018	0.0008	0.0013
F × L	n.a.	n.a.	n.a.	n.a.	0.4295	0.2813	n.a.	n.a.	0.4372	0.4950	0.4028

n.a.: not applicable; (*) Statistical significance (*p*-values from Fisher's tests) of the considered factors for each property from a multifactorial ANOVA (order 2), taking into account the fertilizer regime used for top dressing (F) and the location of the energy crop (L) as factors. Different letters indicate significant different means between fertilizer regimes or locations for that property at the 95% confidence level according to multiple range tests. N_Fert: N provided by fertilizers, N_Seed: N in seeds, N_AtDep: N from atmospheric deposition, N_FrLiv: N from free living soil organisms, N_HarvEx: N removal by crop harvest, N_NO$_3^-$: losses of N in the form of nitrates, N_Eros: N loss by soil erosion, N_NH$_3$: emissions of N in form of ammonia, N_N$_2$O$_{Cr+Fert}$: N loss in form of N$_2$O due to crop residues decomposition and fertilizer application, N_NO$_x$: N emissions in form of other nitrogen oxides, NUL: none top fertilization, AMS: ammonium sulphate, CAN: calcium ammonium nitrate, URE: urea.

Table 7. Global warming potential, energy produced, natural gas savings, total fertilizer efficiency and annual N deficits (means ± standard deviations) depending on the N fertilizer type used for top dressing and location.

	Annual N Deficit [1]	Global Warming Potential [2]	E Produced per Fossil E Consumed [3]	Natural Gas Savings [4]	Total Fertilizer Efficiency [5]
	(kg N/ha)	(Mg CO$_2$/TJ el)	(TJ el/TJ Fossil)	(%)	(GJ/kg N)
Fertilizer type for top dressing					
NUL	−121 ± 22 a	27 ± 2 c	3.6 ± 0.2 a	83 ± 1 a	7.0 ± 0.6 a
AMS	−85 ± 19 b	37 ± 3 b	3.2 ± 0.2 b	77 ± 2 b	1.8 ± 0.2 b
CAN	−67 ± 30 b	54 ± 8 a	2.5 ± 0.3 c	66 ± 5 c	1.7 ± 0.3 b
URE	−69 ± 21 b	49 ± 4 a	2.3 ± 0.2 c	69 ± 3 c	1.5 ± 0.1 b
Energy crop location					
Lubia	−71 ± 28 b	44 ± 14 a	2.8 ± 0.6	73 ± 9 b	2.9 ± 2.5
Escobosa	−100 ± 28 a	40 ± 9 b	3.0 ± 0.5	75 ± 6 a	3.1 ± 2.4
			p-values (*)		
F	0.0003	0.0000	0.0000	0.0000	0.0000
L	0.0013	0.0215	0.0709	0.0242	0.4086
F × L	0.4028	0.0410	0.2169	0.0396	0.7514

[1] Annual nitrogen deficits derived from the soil nitrogen balance; [2] Global warming potential, 100 years, according to IPCC 2013; [3] Electrical energy produced per fossil energy consumed; [4] GHG savings according to IPCC 2013 (Natural Gas as reference); [5] Total fertilizer efficiency (GJ generated per kg of N applied); (*) Statistical significance (*p*-values from Fisher´s tests) of the considered factors for each property from a multifactorial ANOVA (order 2), taking into account the fertilizer regime used for top dressing (F) and the location of the energy crop (L) as factors. Different letters indicate significant different means between fertilizer regimes or locations for that property at the 95% confidence level according to multiple range tests. NUL: none top fertilization, AMS: ammonium sulphate, CAN: calcium ammonium nitrate, URE: urea.

Figures 2 and 3 display the GHG savings that could be obtained if the tested rye energy crops were used to produce electricity instead of natural gas. In Figure 2, GHG savings were depicted as a function of the yields obtained under the four fertilizer regimes tested. As can be also seen in this graph, GHG savings were higher for control plots than for the alternatives that used the typical annual top fertilizer doses of 80 kg N/ha. We also noted how GHG savings tend to rise with increasing yields. With regard to the type of fertilizer used, significant differences in GHG savings were found in the following order in our trials (Table 7): AMS > (Urea = CAN). Similarly, the use of AMS averaged higher yields (11.2 Mg/ha) than those obtained when other fertilizers were applied (9.6–10.8 Mg/ha). In turn, plots fertilized with urea averaged lower biomass productions (Table 5). Therefore, under our experimental conditions, the fertilizer with better results in terms of GHG savings and dry matter productions was ammonium sulphate, whereas calcium ammonium nitrate, the most common fertilizer in the region studied, provided worse results. Additionally, when comparing GHG savings from the biomass in the two locations under study, the biomass grown in Escobosa had higher GHG savings (75%) than the biomass from Lubia (73%), probably due to the significantly higher yields obtained in the Escobosa plots (Table 5). Of practical relevance is the fact that the threshold set for 2018 (60% GHG savings) could be met in both cases, with the exception of CAN for one of the locations. However, none of the energy crops fertilized with common annual top-dress doses (80 kg N/ha) were able to fulfill the 80% threshold set from 2026 onwards, no matter the type of fertilizer applied. The plots where no N fertilizer was applied for top dressing could reach 80% GHG savings because yields obtained were high and they avoided the GHG emissions of N fertilizer production and its field application.

Figure 3 shows the correlation between the GHG savings obtained under the four fertilizer regimes considered and their resulting soil nitrogen balances. The variations in the SNBs across sites and fertilizer regimes could explain 66% of the variation in the GHG savings ($R^2 = 0.66$ in the regression). Among the three types of fertilizers tested, the use of ammonium sulphate led to the highest GHG savings (77%), but also caused elevated N deficits in the soil (85 kg N/ha). Energy crops fertilized with urea and calcium ammonium nitrate produced medium and similar GHG savings (66–69%) and N deficits (67–69 kg N/ha). Under the experimental conditions of this study, our results suggest that a reduction of 1 kg N/ha in the soil N deficit implies a simultaneous reduction in GHG savings of 0.31% (Figure 3).

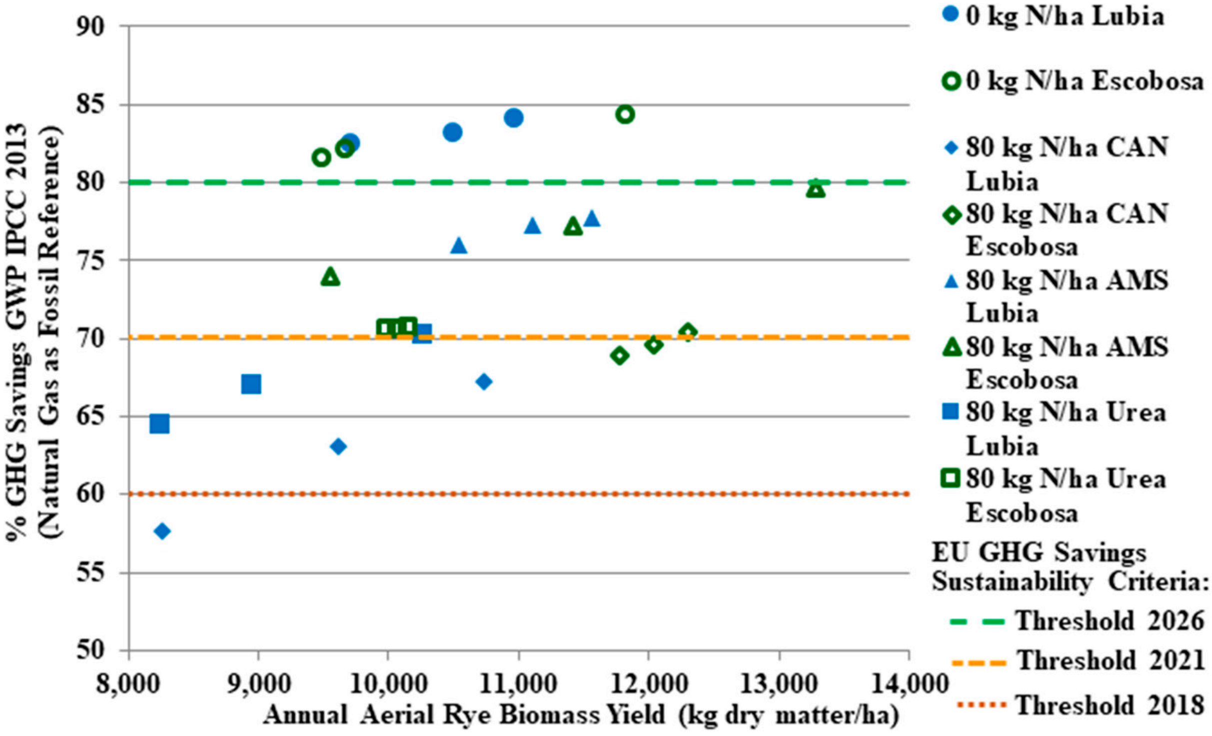

Figure 2. Relationship between the GHG savings obtained when producing bioenergy with rye energy crops grown under different fertilizer regimes with respect to natural gas and depending on the aerial biomass production (calculated with the GWP IPCC 2013 100 years method). GWP: Global warming potential, IPCC: Intergovernmental panel on climate change, CAN: calcium ammonium nitrate, AMS: ammonium sulphate, EU GHG: European Union greenhouse gases.

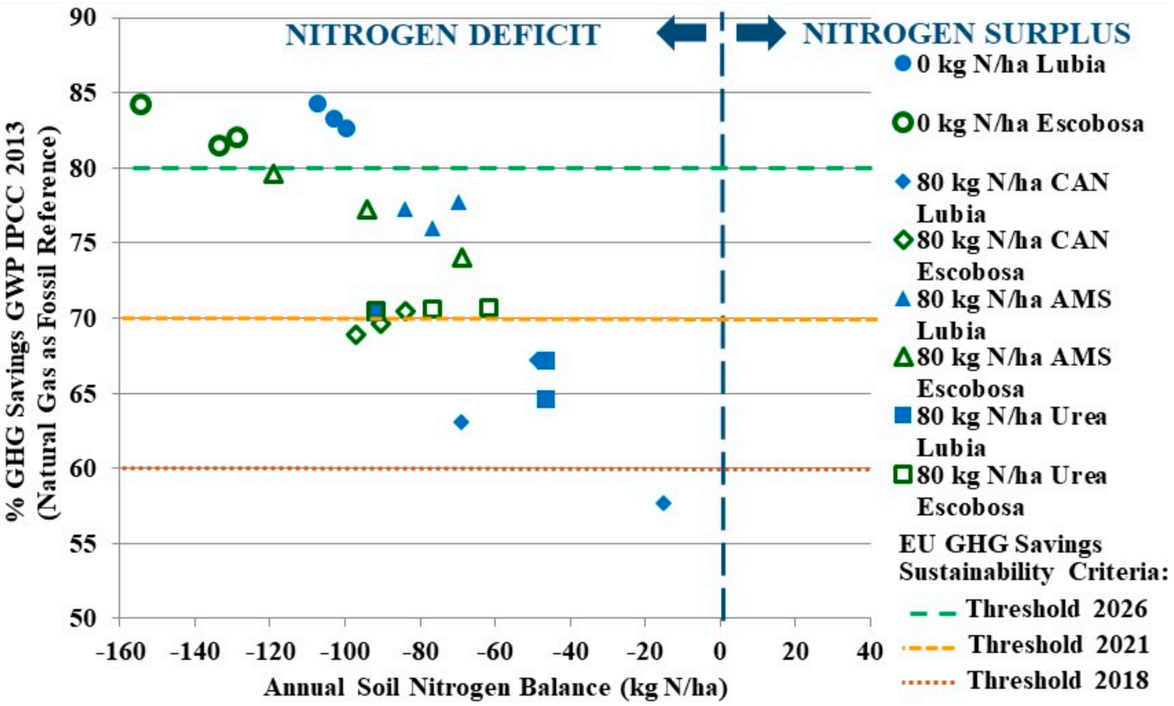

Figure 3. Relationship between the GHG savings obtained when producing bioenergy with rye energy crops grown under different fertilizer regimes with respect to natural gas in relation to the soil nitrogen balances (calculated with the GWP IPCC 2013 100 years method). GWP: Global warming potential, IPCC: Intergovernmental panel on climate change, CAN: calcium ammonium nitrate, AMS: ammonium sulphate, EU GHG: European Union greenhouse gases. Regression equation: $y = -0.0019x + 0.5731$.

Figures 4 and 5 show the electricity produced by the rye energy crops per unit of fossil energy consumed (fossil energy return), as a function of two different parameters (biomass production and soil N balances). The statistical significance of the type of fertilizer and the location with regard to this parameter can be seen in Table 7. Figure 5 especially shows the electricity production of the energy crops grown under the four fertilizer regimes, depending on their biomass productions. Control plots produced the best energy returns, followed by those fertilized with ammonium sulphate, whereas ammonium calcium nitrate and urea provided the poorest energy returns (Table 7 and Figure 5). Additionally, energy plots fertilized with ammonium sulphate produced 0.5 TJ more of electricity per TJ of fossil energy consumed than plots where urea or calcium ammonium nitrate was applied.

A positive correlation ($R^2 = 0.65$) was found between the electrical energy produced by the energy crops per fossil energy consumed and the resulting N deficits in the soil (Figure 5). At a given location, control trials produced the highest energy returns and nitrogen deficits (Table 7, Figure 5) as, even with less N inputs, these plots yielded biomass productions within the same range as some of those fertilized with annual top doses of 80 kg N/ha (Table 7). It is also worth mentioning that the rest of the trials provided highly variable energy returns, ranging between 2.0–3.5 TJe per TJfosssil, and N deficits in the soil averaging 67 to 85 kg N/ha, depending on the fertilizer used.

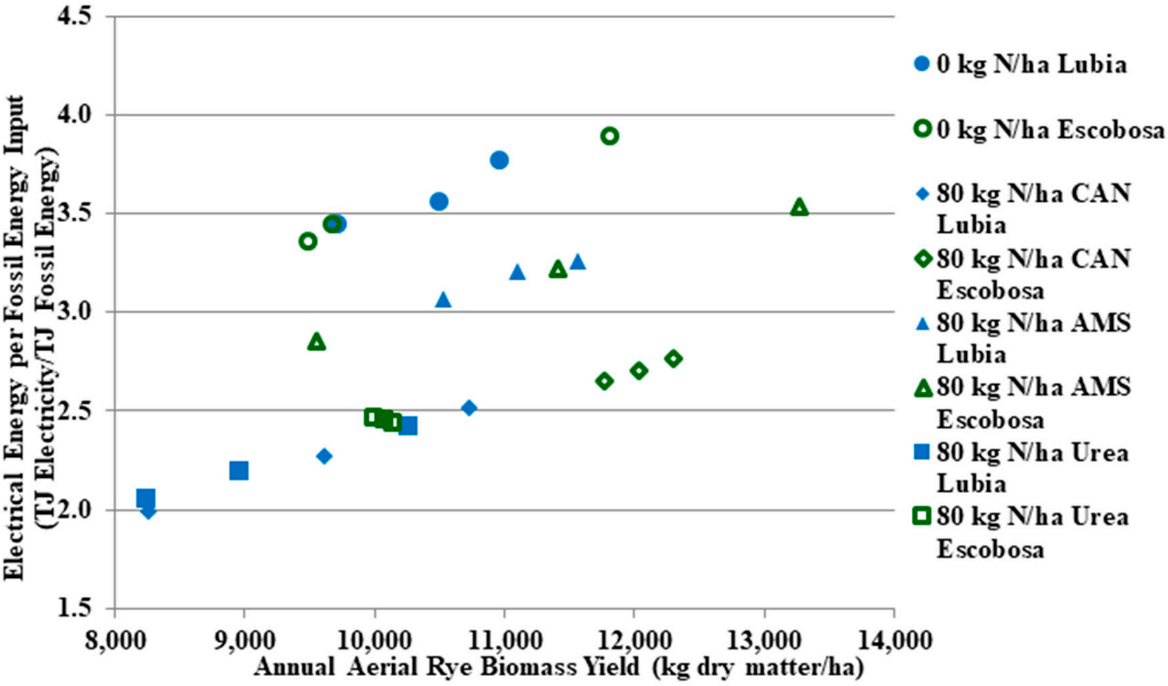

Figure 4. Relationship between the electrical energy produced per fossil energy consumed as a function of the biomass yields obtained from the rye energy crops grown under different fertilizer regimes. CAN: calcium ammonium nitrate, AMS: ammonium sulphate.

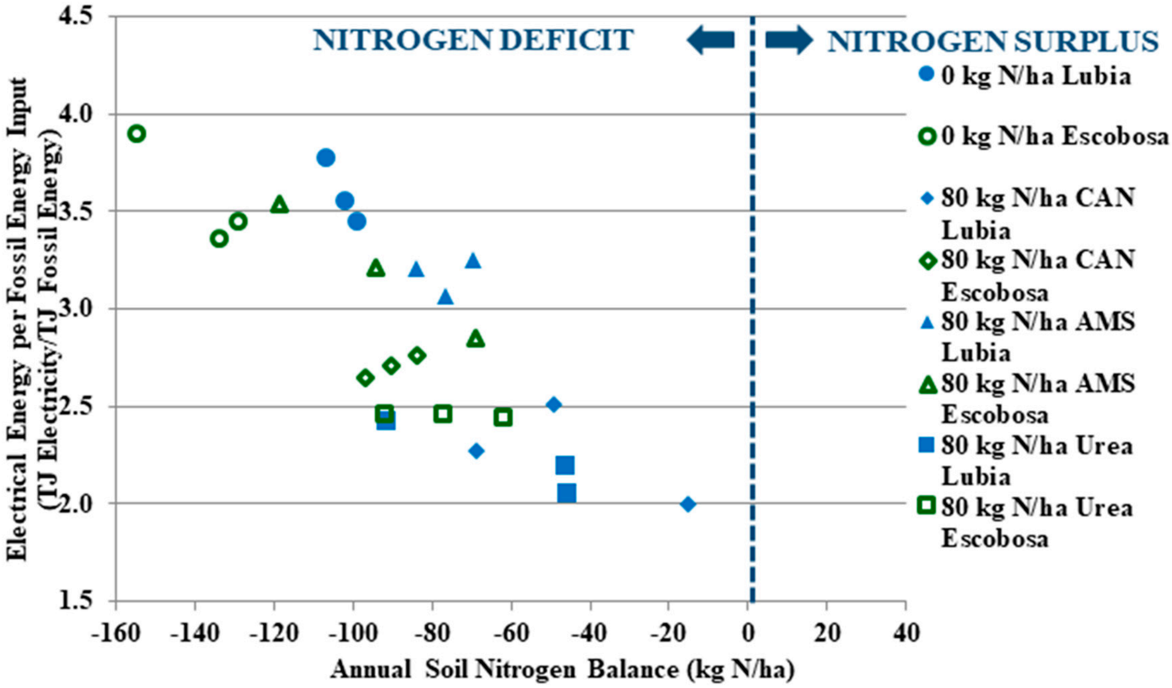

Figure 5. Relationship between the electrical energy produced per fossil energy consumed as a function of the soil nitrogen balance obtained for the rye energy crops grown under different fertilizer regimes. CAN: calcium ammonium nitrate, AMS: ammonium sulphate. Regression equation: $y = -0.0145x + 1.6511$.

Control plots provided significantly higher natural gas savings (83%) than for the alternatives that used the typical annual top-fertilizer doses of 80 kg N/ha (Table 7). Among the three types of fertilizers used, AMS resulted in significantly higher natural gas savings (77%) than the CAN and URE treatments (66–69%, Table 7). Figure 6 shows the type of primary energy consumed (renewable or non-renewable) per TJ of electrical energy generated by natural gas and by the rye energy crops cultivated under different fertilizer regimes. To produce 1 TJe, the rye energy crops consumed 36–41% more primary energy (3.89–4.06) than natural gas (2.89). However, 3.60 TJ of all the energy consumed by the rye crops to produce 1 TJe came from renewable sources, which represents an 89–93% of the total energy consumption, depending on the fertilizer regime, but only 0.29–0.45 TJ (7–11%) came from non-renewable energy sources. As can be seen in Figure 6, the total energy consumption, as well as the type of energy consumed (renewable vs. non-renewable), is very similar across the four fertilizer regimes. In turn, the energy consumption of natural gas to produce 1 TJe, is 2.89 TJ, with 2.87 TJ (99%) from non-renewable sources. The higher values of total primary energy of rye crops are due to the accounting of the rye's own biomass renewable energy due to its consumption as fuel to generate the electricity in the power plant. Figure A1 shows the contribution by the phases considered in the life cycle of rye en-ergy crops fertilization alternatives to the consumption of three types of renewable primary energy and three types of non-renewable primary energy.

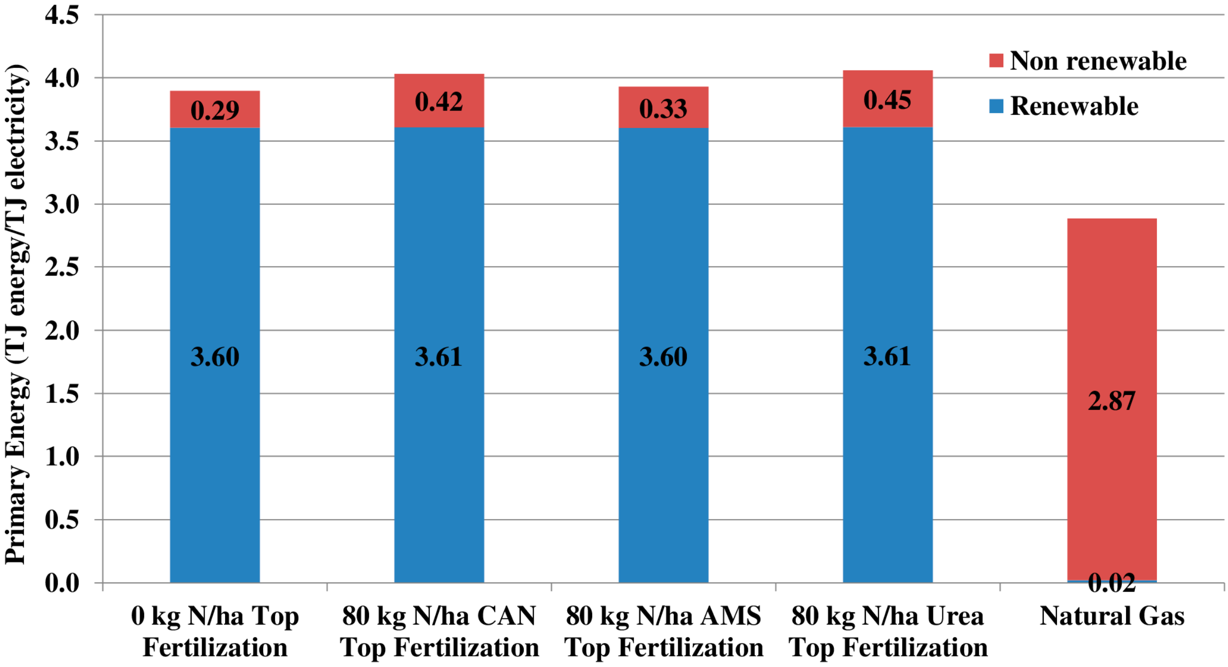

Figure 6. Average total primary energy consumed in the generation of 1 TJe by rye biomass for the four different fertilizer regimes evaluated and by natural gas. CAN: calcium ammonium nitrate, AMS: ammonium sulphate.

3.3. Impact Categories of CML Method

Table 8 shows the results obtained for the impact categories of the CML method depending on the fertilizer type used for top dressing and the location of the energy crop and their statistical significance.

According to Table 8, control plots performed significantly better than the alternatives that used the typical annual top-fertilizer doses of 80 kg N/ha in the following categories: abiotic depletion, global warming potential, human toxicity and acidification. Additionally, the use of rye biomass from crops fertilized with ammonium sulphate produced impacts similar to those derived from control plots, as regards ozone layer depletion, photochemical oxidation, as well as fresh water, marine and terrestrial aquatic ecotoxicities. Among all the fertilizer types, AMS also performed better in terms of abiotic depletion, global warming potential, human toxicity and eutrophication.

Table 8. Impact categories (means ± standard deviations) depending on the N fertilizer type used for top dressing and location.

	Abiotic Depletion [1]	**Global Warming Potential** [2]	**Ozone Layer Depletion**	**Human Toxicity** [3]	**Fresh Water Aquatic Ecotoxicity**	**Marine Aquatic Ecotoxicity**	**Terrestrial Ecotoxicity**	**Photochemical Oxidation**	**Acidification**	**Eutrophication**
	(MJ ×10^5/TJel)	**(kg CO_2eq ×10^4)**	**(mg CFC-11eq)**	**(Mg 1,4-DBeq)**	**(Mg 1,4-DBeq ×10^3)**	**(Mg 1,4-DBeq)**	**(kg 1,4-DBeq)**	**(kg C_2H_4eq)**	**(kg SO_2eq ×10^3)**	**(kg PO_4^{2-} eq ×10^3)**
Fertilizer type for top dressing										
NUL	2.8 ± 0.2 c	2.8 ± 0.2 d	3.0 ± 0.2 c	11 ± 1 d	8.0 ± 0.6 c	22 ± 2 b	61 ± 5 b	16.4 ± 0.5 b	0.45 ± 0.01 d	0.39 ± 0.04 c
AMS	3.1 ± 0.2 b	3.8 ± 0.3 c	3.1 ± 0.2 c	13 ± 1 c	8.9 ± 0.9 c	24 ± 2 b	61 ± 6 b	16.5 ± 0.6 b	0.65 ± 0.04 b	0.44 ± 0.05 cb
CAN	4.1 ± 0.5 a	5.7 ± 0.8 a	4.1 ± 0.5 b	18 ± 3 a	11.7 ± 1.9 b	30 ± 5 a	76 ± 13 a	18.8 ± 1.4 a	0.59 ± 0.05 c	0.47 ± 0.10 b
URE	4.3 ± 0.3 a	5.2 ± 0.4 b	4.6 ± 0.3 a	16 ± 1 b	10.2 ± 0.9 a	28 ± 3 a	79 ± 8 a	19.4 ± 0.8 a	0.97 ± 0.06 a	0.58 ± 0.08 a
Energy crop location										
Lubia	3.7 ± 0.9 a	4.6 ± 1.5 a	3.8 ± 0.9 a	15 ± 4 a	10.2 ± 2.3 a	28 ± 5 a	73 ± 14 a	18.1 ± 1.9 a	0.68 ± 0.22 a	0.50 ± 0.11
Escobosa	3.4 ± 0.5 b	4.2 ± 1.0 b	3.5 ± 0.6 b	14 ± 2 b	9.2 ± 1.1 b	25 ± 3 b	66 ± 8 b	17.4 ± 1.1 b	0.64 ± 0.19 b	0.44 ± 0.07
					p-values (*)					
F	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0003	0.0000	0.0000	0.0004
L	0.0205	0.0255	0.0205	0.0209	0.0269	0.0302	0.0299	0.0297	0.0281	0.0520
F × L	0.0675	0.0376	0.0927	0.0521	0.0731	0.0875	0.0956	0.0711	0.1330	0.1435

[1]: Abiotic depletion (fossil fuels); [2]: Global warming potential, 100 y, according to IPCC 2007; [3]: 1,4-dichlorobenzene. (*) Statistical significance (*p*-values from Fisher´s tests) of the considered factors for each property from a multifactorial ANOVA (order 2), taking into account the fertilizer regime used for top dressing (F) and the location of the energy crop (L) as factors. Different letters indicate significant different means between fertilizer regimes or locations for that property at the 95% confidence level according to multiple range tests. NUL: none top fertilization, AMS: ammonium sulphate, CAN: calcium ammonium nitrate, URE: urea.

Additionally, the eleven categories included in the CML impact assessment of electricity generation from rye crops cultivated under four different fertilizer regimes, and from natural gas, are represented graphically in Figure A2. The contribution of the phases considered in the life cycle to these impacts assessment categories for the four types of fertilization evaluated is shown in Figure A3.

4. Discussion

All treatments in which N top dressing was applied resulted in lower GHG emissions per unit energy than the energy produced with natural gas, and averaged mean GHG savings of 71%. Of all of the fertilizers tested, ammonium sulphate is the most promising fertilizer, as it produced the highest GHG savings (77%), followed by urea (69%) and ammonium nitrate (66%), the latter being the most common fertilizer in the region. Therefore, exchanging calcium ammonium nitrate for ammonium sulphate could improve GHG emissions by 11% under the conditions of this study. However, ammonia-based fertilizers are known for being major contributors to soil acidification upon repeated use, by decreasing soil pH due to the nitrification process [36]. This may have a positive effect on alkaline soils for a limited period of time, but may negatively affect the productivity of crops grown in acidic soils [37]. In any case, it should be also taken into account that soil acidification may be amended by using products that increase soil pH. According to the Fertilizer Technology Research Centre (FTRC) [38], the acid-producing potential of ammonium sulphate is greater than the same N application with urea or calcium ammonium nitrate (approx. 3.5 kg lime equivalent per kg N). Therefore, the use of a lime amendment to increase soil pH when using ammonium sulphate would raise the CO_2 emissions of this fertilizer by 320 kg CO_2 eq./ha, which is equivalent to 6.1 Mg CO_2 eq. per TJ of electricity produced, at the same time decreasing GHG savings by 3.8%. Consequently, GHG savings from ammonium sulphate would be reduced from an initial value of 77% to 73%, although they would still be at levels higher than those obtained if urea (69%) or calcium ammonium nitrate (66%) were applied to the rye energy crops.

Moreover, the use of urea may also have drawbacks, as this fertilizer is known for causing atmospheric ammonia emissions through volatilization after application. The use of urea in Spain could definitely contribute to exceeding the ammonia emissions limits set for this country in EU regulations [39]. However, it is also worth mentioning that these emissions could be reduced by using urease inhibitors [40]. With regard to soil nitrogen balances, both control (with no N top dressing) and fertilized plots had serious N deficits. All the fertilizers entailed remarkable and similar annual deficits, ranging from 67 ± 30 kg N/ha when applying calcium ammonium nitrate to 85 kg N/ha for ammonium sulphate. Under the conditions studied, positive balances would be difficult to achieve, even if legumes are periodically introduced in crop rotation for N fixation [41]. Nitrogen outputs are mainly dependent on dry matter productions and biomass N contents. Given that biomass production should be as high as possible from an energy and economic perspective, the nitrogen content of the biomass should be maintained as low as possible. Nitrogen content in rye energy crops where the whole plant is usually collected (aerial biomass without root) can vary within a wide range, commonly between 0.8% and 1.5% [33,42,43], depending on the cultivar, growth stage, and location, including meteorological conditions and soil characteristics [42]. The N content of rye straw is lower, usually in the range of 0.2–0.6% [44,45] and with typical mean values of 0.5% [43,46], due to the absence of grains that typically exhibit N contents as high as 2% [43,46]. The N content of the biomass produced in this study is relatively high (1.1–1.7%), mainly due to the crop's stage of development at harvest, which was doughy grain (8 on the Zadoks growth scale). However, slightly lower N contents were found in the biomass from control plots, with mean contents of 1.3% as opposed to 1.4–1.5% from plots with N top dressing, and from the Lubia location, which averaged 1.3% as opposed to 1.5% in Escobosa. Therefore, the N content of the biomass could be minimized, at least to a certain extent, by selecting cultivars with less proportion of grains and locations where low N biomass can be produced due to soil characteristics, as well as by harvesting the crop at an earlier stage when the grains are less developed and milky (7 on the Zadoks growth scale). However, the effects of these strategies on productivity should be assessed.

With the use of rye energy crops under the conditions considered in this study, it would be very difficult to comply with the new RED II GHG savings sustainability criteria of 80% when N fertilizers are applied for top dressing. However, if calcium ammonium nitrate, the most common rye fertilizer, was replaced by ammonium sulphate, GHG savings would increase from 66% to 77%. In order to achieve GHG savings over 80%, additional actions must be taken throughout the different phases of the process. At the agricultural phase, minimum tillage could be applied to reduce diesel consumption derived from field works. Harvest procedures could also be optimized at this phase to minimize dry matter loses and decrease the N content of the fuel. More efficient vehicles consuming renewable energy should be used for transportation. Finally, GHG emissions could also be reduced if the efficiency of the energy conversion process at power plants was improved.

Since the unique treatment that resulted in average GHG savings above 80% required by the RED II (81%) was suppression of the N fertilizer for top dressing (NUL), this practice, or at least a significate reduction of the N provided, could be considered as a suitable option given that yields (9.6 Mg dm/ha) were similar to the ones obtained when N fertilization was applied (10.8 Mg dm/ha) and that the N content of the biomass was lower (1.28% vs. 1.46%). The high negative annual SNBs produced (>120 kg N/ha) could be at least partly compensated with the fallow that it is already present in the crop rotation (rye, barley, and fallow), and to a greater extent, with the introduction in the rotation of a legume crop with high nitrogen fixing capacity. This new approach for rye cultivation for bioenergy purposes should be further investigated and tested to verify that rye yields are not reduced in the long term.

Nevertheless, and in spite of implementing all these potential improvements and changes in the fertilization approaches, we believe that it would be very difficult to achieve GHG savings above 80% from rye energy crops in the low productive abandoned lands that are currently available for bioenergy in the Mediterranean semi-arid regions, particularly under rain-fed conditions. This is due to the impossibility of obtaining better yields with clear biophysical constraints in these areas, often characterized by poor soils and water scarcity. Having strict and equal GHG sustainability criteria [7] for diverse EU agricultural realities is unfair and seriously hinders the implantation of energy crops in certain areas, where this practice could lead to social benefits such as job creation. In our view, social indicators and the specific characteristics of different regions should be considered when defining sustainability criteria. In this sense, a more holistic approach would also boost aspects such as job creation in rural unpopulated regions, similar to those under study. This could be done through a reduction of the savings required for regions considered unpopulated, plus an additional reduction of the savings for abandoned or marginal lands; 10% for each condition would be fair in our view.

5. Conclusions

The use of conventional fertilization practices and traditional crop management techniques in rye energy crops seems to be unable to accomplish the binding criteria of 80% GHG savings with respect to natural gases established by the new RED II for electricity generation, at least under the pedoclimatic conditions given in this study. GHG savings greater than 80% might be achieved with yields above 13,500 kg dm/ha, but this is rarely feasible in the rain-fed conditions of the area under study. In principle, a reduction in the top N dressing rate could be a potential possibility for fulfilling this threshold. The use of ammonium sulphate as top-dressing fertilizer appears to be a better choice than calcium ammonium nitrate, which is the most common fertilizer applied to rye crops. Under the conditions of the study, ammonium sulphate provided the highest GHG savings, almost 10% higher than those obtained, with the application of the other fertilizers considered for similar yields, and it led to better energy balances and lower impacts for most of the categories analyzed. The better performance of this fertilizer might not be enough to achieve the GHG savings set in the new sustainability criteria (>80%), unless higher dry matter yields could be obtained. Other optimization strategies should be implemented at the different stages of the value chain to achieve this goal. Moreover, the change suggested in the fertilizer used for top dressing rye should consider that both calcium and sulphur are nutrients for crops with different effects and that ammonium sulphate has higher potential for soil acidification. Long-term results under different pedoclimatic conditions would also be very useful to support these conclusions to provide further insights and help policy makers to make well founded decisions.

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Appendix A. Supplementary Results

This appendix contains additional results that can be of interest to readers.

Figure A1 shows the different types of primary energy consumed in the entire process of producing 1 TJe from the energy crops under study. For each type of primary, the consumption share of the following phases was shown: production and transportation of seeds, fertilizers, and pesticides, field works, bales transportation and power plant operations. Plant operation is the highest contributor to the total primary energy, due to the consumption of rye biomass. It is also worth mentioning that 95% of the non-renewable energy consumed is derived from fossil fuels consumed, being the production and transportation of fertilizers its main contributor in case of plots with annual top-dressing fertilization; and field works in case of control plots. Seed and pesticides production and transport as well as bales transport and plant operation had much smaller contribution than field forks or fertilizer production for non-renewable and fossil energy types. Among all the types of fertilizers considered, using ammonium sulphate produced the lowest nonrenewable and fossil energy consumption. No significant differences in fossil energy consumption were found between the application of urea and calcium ammonium nitrate.

The use of rye biomass to produce electricity proved to be a better option than natural gas when it came to the following four categories: global warming, ozone layer depletion, abiotic depletion (fossil fuels), and photochemical oxidation. In turn, natural gas had less impact than any of the three alternatives with top dressing rates of 80 kg N/ha for the remaining categories, with the exception of marine ecotoxicity, where ammonium sulphate had a slightly lower impact. It should also be mentioned that this fertilizer had a lower impact than urea and calcium ammonium nitrate in all of the categories considered, except acidification (Table 8 and Figure A2). The application of ammonium sulphate led to impacts that were only 10% higher than control plots for global warming, eutrophication, abiotic depletion, human toxicity, and fresh water and marine aquatic ecotoxicities, being roughly 20% higher in the case of acidification.

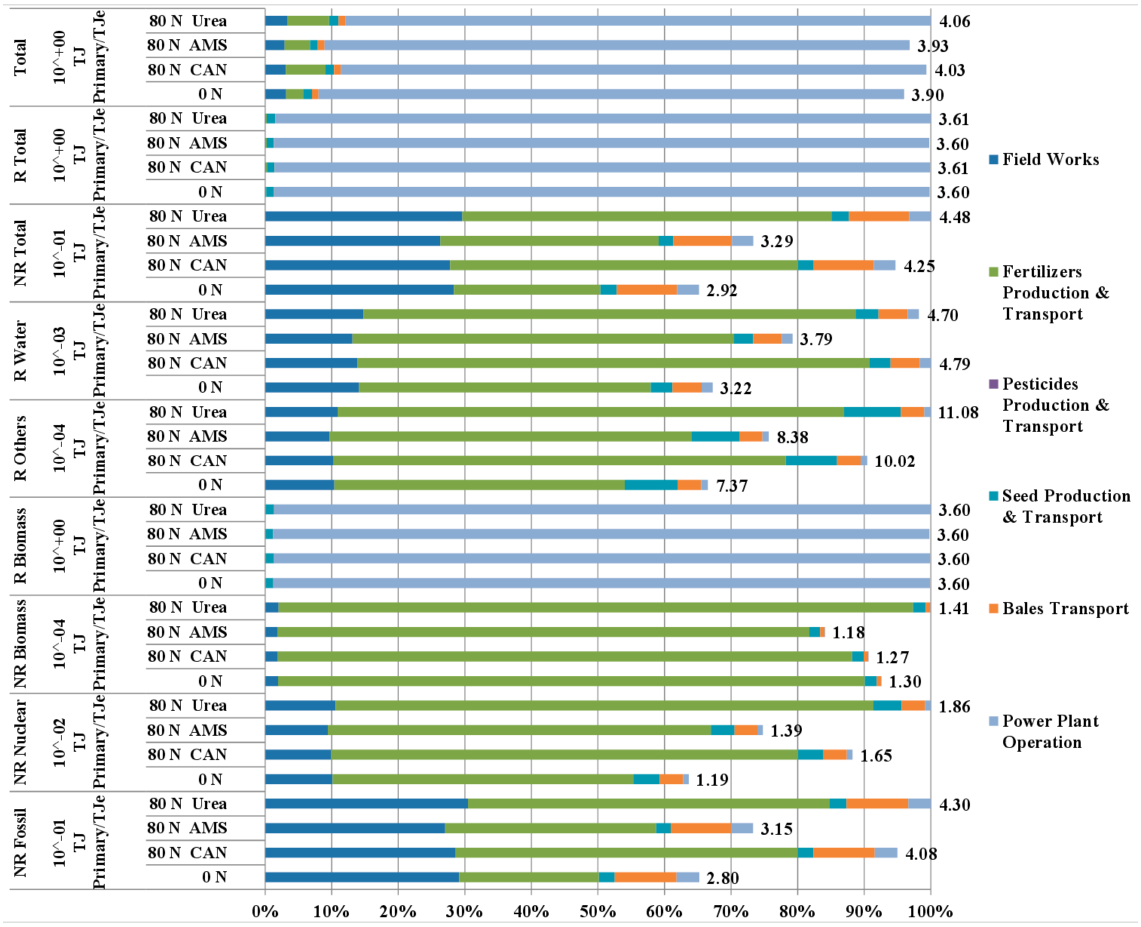

Figure A1. Types of energy consumed by phases considered in the life cycle of the rye energy crops grown under four different fertilizer regimes when producing 1 TJe. R: renewable energy; NR: non-renewable energy; R: Others: wind, solar, geothermal renewable energies among others, AMS: ammonium sulphate, CAN: calcium ammonium nitrate. Nitrogen fertilizers aplication rates at the *y*-axis are in kg/ha. The percentages of the *x*-axis represent the relative contribution of each one of the four fertilizer alternatives studied with respect to the one which produced the highest impacts (100%).

Figure A3 shows the CML impacts of all the phases of the production life cycle of rye biomass under the four fertilizer regimes used for producing 1 TJe with rye as energy crop. For each impact category, the share of the following phases was shown: production and transportation of seeds, fertilizers, and pesticides, field and fertilizer emissions, field works, bales transportation and power plant operations. The production and transportation of fertilizers, together with field emissions and fertilizer applications, produced the highest impacts in all categories, except for acidification and photochemical oxidation, where power plant operation was the main contributor, owing to the effects of atmospheric emissions derived from biomass combustion. The high contribution of field and fertilizer emissions to eutrophication is due to the effect of phosphorus emissions to the water and nitrate leachates. Moreover, it may be observed that ammonium sulphate production had a lower impact than the production of the other two fertilizer types (urea and calcium ammonium nitrate). Finally, it must be highlighted that control plots provided the best results of all of the fertilizer regimes considered, while ammonium sulphate was the best performance fertilizer for plots with fertilizer doses of 80 kg N/ha.

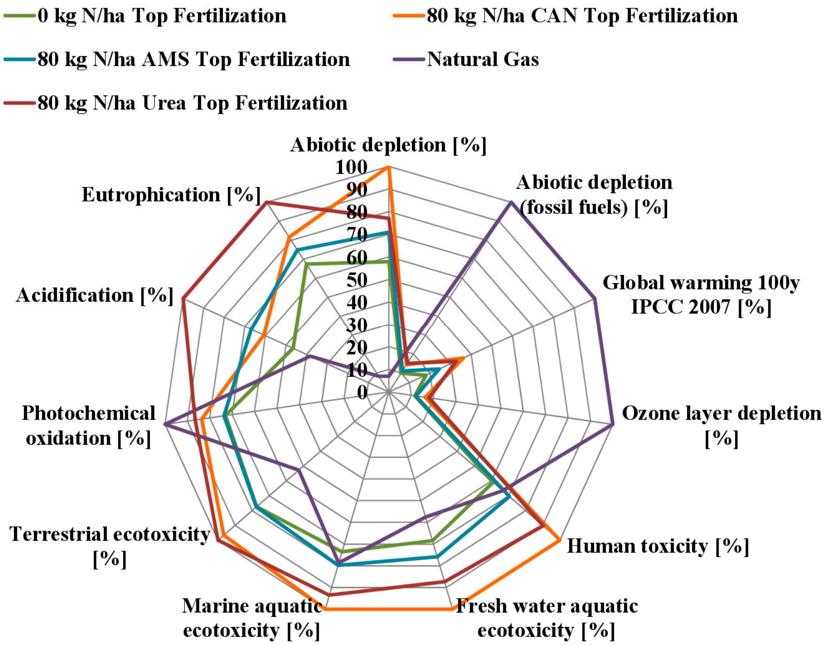

Figure A2. Corner-Middle-Layer (CML) method impacts derived from the life cycle assessment of natural gas and from the life cycle assessment of rye energy crops grown under four different fertilizer regimes to produce electricity. NUL: none top fertilization, AMS: ammonium sulphate, CAN: calcium ammonium nitrate, URE: urea.

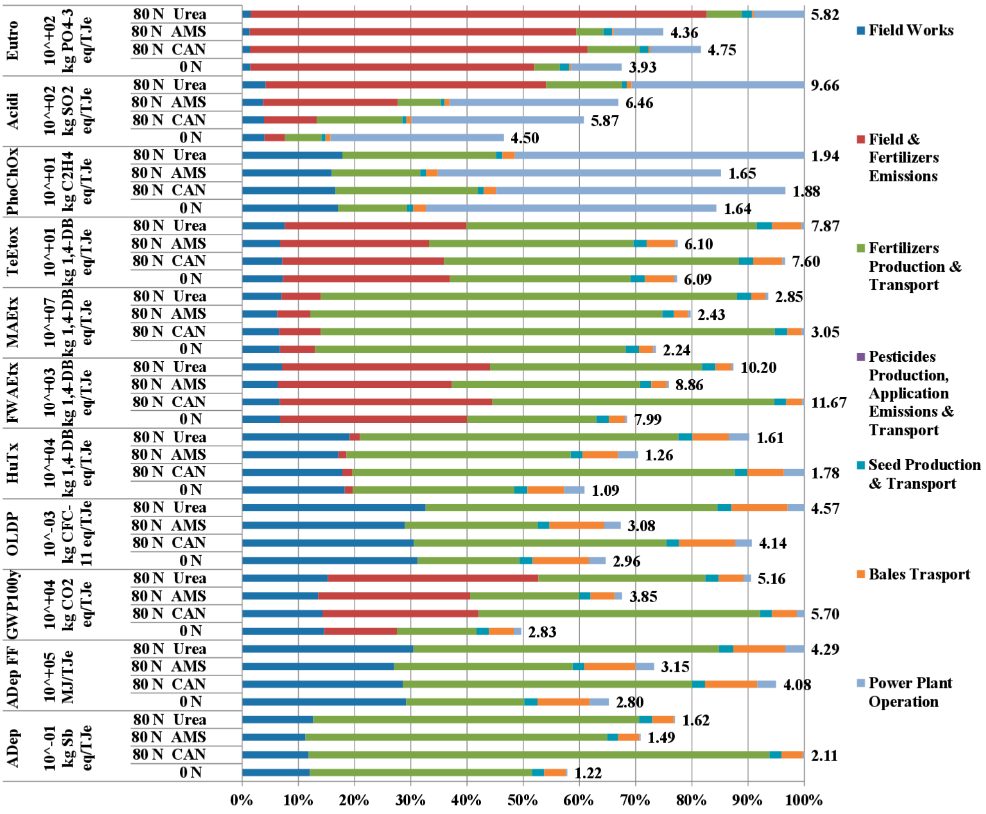

Figure A3. Corner-Middle-Layer (CML) method impacts by phases considered in the life cycle assessment of rye energy crops when producing 1 TJe under four different fertilizer regimes. AMS: ammonium sulphate, CAN: calcium ammonium nitrate. Nitrogen fertilizers aplication rates at the *y*-axis are in kg/ha. The percentages of the *x*-axis represent the relative contribution of each one of the four fertilizer alternatives studied with respect to the one which produced the highest impacts (100%).

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