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Effects of Goat Manure Fertilization on Grain Nutritional Value in Two Contrasting Quinoa (*Chenopodium quinoa* Willd.) Varieties Cultivated at High Altitudes

J. A. González [1], Sawsan K. M. Yousif [2], L. E. Erazzu [3,4], L. Martínez Calsina [3], E. F. Lizarraga [5,6], Rihab M. Omer [2], D. Bazile [7,8], J. L. Fernandez-Turiel [9], S. E. Buedo [1], M. Rejas [9], P. D. Fontana [3], D. A. González [10], A. Oviedo [5], Fahad Mohammed Alzuaibr [11], Salem Mesfer Al-Qahtani [12], Nadi Awad Al-Harbi [12], Mohamed F. M. Ibrahim [13,*] and C. P. Van Nieuwenhove [5,14,*]

1 Instituto de Ecología, Comportamiento y Conservación, Fundación Miguel Lillo, Miguel Lillo 251, Tucumán 4000, Argentina
2 Department of Chemistry, College of Arts and Science in Baljurashi, Al-Baha University, Al Bahah 65528, Saudi Arabia
3 Instituto Nacional de Tecnología Agropecuaria (INTA), Famaillá, Tucumán 4000, Argentina
4 Facultad de Agronomía y Zootecnia, Universidad Nacional de Tucumán, Tucumán 4000, Argentina
5 Instituto de Fisiología Animal, Fundación Miguel Lillo, Miguel Lillo 251, Tucumán 4000, Argentina
6 Facultad de Ciencias Naturales e IML, Universidad Nacional de Tucumán, Miguel Lillo 205, Tucumán 4000, Argentina
7 CIRAD, UMR SENS, 34398 Montpellier, France
8 CIRAD, IRD, University Paul Valery Montpellier 3, 34090 Montpellier, France
9 Geosciences Barcelona, GEO3BCN, CSIC, 08028 Barcelona, Spain
10 Instituto de Bioprospección y Fisiología Vegetal (INBIOFIV), CONICET-UNT, Facultad de Ciencias Naturales e Instituto Miguel Lillo, Tucumán 4000, Argentina
11 Department of Biology, Faculty of Science, University of Tabuk, P.O. Box 741, Tabuk 71491, Saudi Arabia
12 Biology Department, University College of Tayma, University of Tabuk, P.O. Box 741, Tabuk 71491, Saudi Arabia
13 Department of Agricultural Botany, Faculty of Agriculture, Ain Shams University, Cairo 11566, Egypt
14 Centro de Referencia para Lactobacilos (CERELA-CONICET), Chacabuco 145, Tucumán 4000, Argentina
* Correspondence: ibrahim_mfm@agr.asu.edu.eg(M.F.M.I.); vancarina2@yahoo.com.ar (C.P.V.N.)

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Abstract: In this study, the effects of goat manure fertilization (2, 4, 8, and 12 Tn/ha) on the grain yield, organic compounds, and mineral composition of two quinoa varieties (CICA-17 and Regalona Baer) were evaluated under field conditions in Northwest Argentina. The results indicate that fertilization improved the quinoa grain yield and total protein content. Low manure doses positively affected the fatty acid (FA) profile, and significant changes were determined for the monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acid contents of CICA-17 and on the saturated fatty acid (SFA) contents of R. Baer seeds. The amino acid contents were positively affected in CICA-17 and negatively in R. Baer. Soluble sugars (glucose, fructose, and sucrose), major elements (K, Si, P, Mg, Ca, and Na), minor elements (Fe, Mn, Al, Zn, and Cu), and ultratrace elements (Cr and Li) were detected and discussed in terms of their impact on human nutrition and health. Conclusively, manure addition affected some essential amino acids, the desaturase activity, the n6:n3 and SFA/UFA ratios, the atherogenic index, soluble sugars, and mineral content, and the fatty acid metabolism of each variety was differently affected, especially the C16 and C18 desaturase activity, which responded differently to various manure doses. Manure addition is a promising alternative to improve the nutritional quality and functionality of quinoa grains, but the response is not linear.

Keywords: crop nutrition; grain quality; amino acid content; amino acid type; fatty acids; oil content

1. Introduction

Quinoa (*Chenopodium quinoa* Willd.) is originally from the Andean region of South America. Due to its high nutritional and functional values, quinoa consumption and cultivation have increased in the last few years. It is considered a superfood [1] that may be a complementary crop for different countries [2], especially for those located in geographic areas that are marginal lands for classical crops; e.g., desert or semidesert regions in Latin American, Asian, and MENA countries, among other places in the world.

Quinoa is an important source of proteins (around 15%) and essential amino acids [3], sugars [4,5], minerals [6], vitamins, and antioxidants [7,8], and due to the absence of gluten, it is also a promising food for celiac patients. Its total oil content varies widely according to the quinoa cultivar, ranging from 2.5 to 10.9% [9–11]. High contents of unsaturated fatty acids (UFA, 80–90%) characterize the fatty acid (FA) profile, where the essential linoleic acid (C18:2 n6) is the most abundant (49–57%), followed by oleic (C18:1 C9, 19–29%) and linolenic (C18:3 n3, 9–12%) acids [9].

The quality of dietary fat impacts human health. Monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids have beneficial properties for consumers, helping to prevent cardiovascular diseases [12,13], improve the immune system, and balance the intestinal microbiota [14]. A balanced intake of n6:n3 (2:1 to 6:1) and limited consumption of SFA and trans-FA are recommended to avoid cardiovascular disease risks. An unbalanced ratio of n6: n3 (15:1 to 20:1) in the modern diet is considered one of the major factors in metabolic disorders, cardiovascular risk, and autoimmune disease [8,15].

Currently, several countries are interested in quinoa grains for their healthier and nutritional qualities and their stressful condition tolerance [2,16]. However, the proximal composition of quinoa varies according to different ecotypes and cultivars [8,17], genetic variability [18], and environmental conditions [19]. Thus, and according to the genotype-by-environment interaction effects, different nutritional compositions could be obtained in different places where farmers try to cultivate it [20]. The emerging market for quinoa has led farmers from different countries to use different agronomic practices to increase their yields and cover the high demands of consumers. Since quinoa is promoted as a functional food due to its nutritional value, special attention has been focused on yield and its relationship with nutritional composition. Higher yield and protein content are obtained through different agricultural practices, such as the plant density [21], selected varieties [20], tillage and fertilization [22], irrigation [23], intercropping, and fertilization from a different origin (manure or commercial) [24–26]. Despite the increase in quinoa cultivation, in many parts of the world, the yield is still low, varying between 700 and 1200 kg/ha [27,28]. Farmers usually do not use fertilizers for quinoa crops, and if they use it, as a general rule, they use synthetic nitrogen fertilizers at low doses. It is known that the excessive use of synthetic nitrogen fertilizers may cause serious environmental problems concerning soil fertility, human health, food security, and air pollution [29,30]. On the contrary, some studies have demonstrated that soil nitrogen enrichment using organic fertilizers has produced increases in quinoa yield, with improved protein content [31,32]. However, there is scarce information about the effects of fertilizer addition on the fat content, FA profile, sugar, amino acid, and minerals of different quinoa varieties.

The crop yield and metabolism of quinoa positively respond to the nitrogen addition [31,32], with an increase in the grain protein content, biomass, and harvest index [33,34]. However, the efficiency of nitrogen uptake by plants may be affected by drought conditions [35], and this effect seems to occur in quinoa [36]. In general, the soil where quinoa grows has low organic matter and nitrogen contents, fertilization is scarce, and watering is carried out by furrow irrigation. Although quinoa is now a good alternative for grain production, with a high nutritional value, there is scarce information about the effects of fertilization on its grain yield and different organic and inorganic compounds.

This study aimed to investigate the effects of different organic fertilization levels, without water stress, on the grain yield and its relationship with the protein content and amino acid profile, the sugar soluble content, oil content, fatty acid composition, and min-

eral content of two contrasting quinoa varieties cultivated under the same agroecological conditions of highlands (2000 m a.s.l.) in northwest Argentina. This area has edaphic and weather conditions corresponding to a desert type. Contrasting varieties (CICA-17 and R. Baer), one from high mountains and the other from sea level, were selected to obtain information about potential ecotype differences.

2. Material and Methods

2.1. Plant Material, Field Experiment, and Treatments

Quinoa seeds from the CICA-17 and R. Baer (RB) varieties were grown at the Encalilla experimental field (Amaicha del Valle, 22°31′ S, 65°59′ W, altitude 1995 m a.s.l., Tucumán, Argentina) in the 2017–2018 and 2018–2019 growing seasons. The climate of Encalilla is a desert type (BWkaw) according to the Köppen classification system. The soil is a sandy loam and, according to the FAO/UNESCO soil taxonomy [37], is classified as the Xeric Torriorthent type. In the first 30 cm of soil depth, the pH is 8.8, the organic matter and total nitrogen are low (0.6% and 0.055%, respectively), and the electrical conductivity (EC) is 2 dS m^{-1} [20]. The Encalilla site is an arid place with cold winters and hot summers. The temperature ranges from 9.7 ± 1.3 °C to 30.5 ± 1.7 °C, and the relative humidity (RH) average is 58.1 ± 3.1%. Rainfall is low, with an annual mean of 200 mm. The mean photosynthetic active radiation (PAR) at noon is 1.893 ± 46 µmol m^{-2} s^{-1}. Seeds of the CICA-17 and RB varieties were sown in a randomized complete block design experiment with three replicates for each treatment (30 plots of 10 m^2 each, total experimental area of 300 m^2). The treatments were: CICA without manure and treated with 2, 4, 8, and 12 Tn of manure/ha (C0, C2, C4, C8, and C12, respectively); for the RB cultivar, the groups corresponded to the same amounts of manure per hectare (RB0, RB2, RB4, RB18, and RB12, respectively). Goat manure, obtained from local farmers, was applied by hand along the rows. Manure applications were carried out six months before sowing and at the reproductive phase initiation, with half of the total amount in each application. The manure and soil analyses are summarized in Table 1.

Table 1. Soil and manure analyses.

	Encalilla Soil	Manure Analysis
Soil order	Entisol	-
Sand (%)	48	-
Silt (%)	22	-
Clay (%)	30	-
Soil texture	Sandy loam	
pH	8.40	7.78
EC (dS/m)	2.0	10.4
Organic matter content (%)	0.60	28.80
Total N (%)	0.055	1.60
C/N ratio	10.9	18.0
P (mg/kg)	1965.6	3100
K (mg/kg)	28,828.8	1000
Mg (mg/kg)	18,729.1	2300
Na (mg/kg)	24,609.4	3900
Ca (mg/kg)	22,895.5	10,100
Fe (mg/kg)	39,194.7	4100
Cu (mg/kg)	20.76	5.1

EC: electrical conductivity.

Quinoa seeds were sown by hand (depth of 2–3 cm) in five rows (5 m long) per plot (10 m^2), with 10 cm of interplant spacing and 50 cm between the rows. Twenty days after plant emergence, hand-thinning was performed to reduce the plant density to 100,000 plants/ha. Drip irrigation was applied once a week after adding the manure, twice a week after sowing during the first month, and weekly in the following months,

with 1040 mm of total irrigation. Fungal disease and pest control were carried out during the cropping cycle. During the growing cycle, weed control was performed by hand.

2.2. Grain Yield

At physiological maturity (150 days after sowing), with a seed moisture level of 12% for all treatments, ten plants from the three central rows of each plot were hand-harvested for grain yield determination. After harvesting, the plants were sun-dried for a week, then dry inflorescences were manually threshed, and the grain weights were determined. The grain yield was expressed as kg/ha.

2.3. Total Protein and Amino Acid Contents

The nitrogen content of the seeds was quantified by the micro-Kjeldahl method with colorimetric ammonium (NH_4^+) determination [38], expressed as % seed dry mass. The total protein content (TPC) was calculated from the nitrogen content using a conversion factor of 6.25. The results were given as g/100 g of seed. For the amino acid analysis, powdered seeds were washed twice with n-hexane (chromatographic grade) to remove the lipids and centrifuged (6000 rpm, 10 min), and the pellet was further dried with nitrogen. For hydrolysis, 0.1 g of this solid residue was dissolved in a 6 N HCl solution and heated for 24 h at 110 °C. Then, this solution was evaporated with nitrogen, and the solid residue was dissolved in 2 mL of sodium phosphate (0.5 M, 2 mL), pH 6.8, and further filtered through a 0.22 µm membrane (Millipore).

Amino acid analysis was performed using a Shimadzu fluorescence detector RF10AXL for HPLC, with an automatic injector (Shimadzu Sil 20A HT Tokyo, Japan), column heater (Shimadzu CTO-10AS Tokyo, Japan), control module (Shimadzu CBM-20A Tokyo, Japan), software (Shimadzu Lab Solutions, Tokyo, Japan), and a separation column Kinetex EVO C18 100 A° LC Column 150 × 4.6 mm, Torrance, CA, USA. The flow rate of the mobile phase was 0.8 mL/min at 40 °C. The compounds were compared with the retention time of pure standards (Sigma, 99%. Buenos Aires, Argentina). The amino acid profile included the total essential amino acid content (TEAA) (leucine, lysine, valine, isoleucine, phenylalanine, threonine, histidine, and methionine) and the total non-essential amino acid content (TNEAA) (glutamine, glutamic acid, asparagine, arginine, glycine, alanine, serine, and tyrosine). Due to the acid hydrolysis, tryptophan was degraded and not detected [39].

2.4. Soluble Sugar Content

Soluble sugars were extracted according to Prado et al. [40]. Glucose was determined by the glucose–oxidase–peroxidase coupled assay according to Jorgensen and Andersen [41]. The total fructose was measured by the method of Roe and Papadopoulos [42], and sucrose by the method of Cardini et al. [43]. The total soluble sugars (TSS) were determined by the phenol-sulfuric acid method [44].

2.5. Oil Content and Fatty Acid Profile

Lipid extraction was performed according to the method previously described for seed oil extraction [45]. Briefly, quinoa seeds were crushed and sieved to obtain a fine powder (0.5 mm diameter of sieved particles). The total oil content was estimated by Soxhlet by using n-hexane, further evaporated in a rotary evaporator (Heidolph™ Hei-Vap™ Schwabach, Germany) at 45 °C. The oil content was expressed as g/100 g of seed. To determine the fatty acid profile, the total lipid of quinoa seed flour was extracted by the Folch method [46] using a chloroform/methanol solution (2:1, *v*/*v*), further transmethylated, and analyzed as previously described by van Nieuwenhove et al. [45] using an Agilent Technologies (Palo Alto, CA, USA) gas chromatograph (model 6890N) equipped with a flame ionization detector and an automatic injector (model 7683), in an HP-88 capillary column (100 mm × 0.25 mm × 0.20 µm, Agilent Technologies, USA). The fatty acids were identified by comparing the retention times with the methylated standards (99% pure; Sigma, St. Louis, MO, USA). The results were expressed as g/100 g of fatty acids methyl esters (FAME).

The atherogenicity (*AI*) and thrombogenic (*TI*) indexes were estimated according to the following Ulbricht and Southgate formulae [47]:

$$Al = [C12:0 + (4 * C14:0) + C16:0]/((MUFA + PUFA)\ ) \quad (1)$$

$$TI = (C14:0 + C16:0 + C18:0)/(MUFA * 0.5 + PUFA\ n6 * 0.5 + PUFA\ n3 * 3 + PUFA\ n3/PUFA\ n6) \quad (2)$$

To estimate the activity of desaturases enzymes, for *C*16 and *C*18 FA, the following formulae were applied:

$$\Delta 9 - desaturase\ C16 = C16:1/(C16:1 + C16:0) \quad (3)$$

$$\Delta 9 - desaturase\ C18 = C18:1/(C18:1 + C18:0) \quad (4)$$

Desirable fatty acids (*DFA*) were determined as:

$$DFA = C18:0 + UFA \quad (5)$$

2.6. Mineral Content

The extraction and mineral quantification were performed using a method previously described [48]. Briefly, grains were dried in an oven at 65 °C to a constant weight, then ground into a fine powder, passed through a 60-mesh sieve, and ashed (electric oven at 575 °C for 16 h). After cooling, ash subsamples (0.1 g) were digested with 10 mL of a $HF/HClO/HNO_3$ (5.0/2.5/2.5, *v*/*v*) mixture in a closed Teflon vessel (Savillex, Canada) at 90 °C for at least 12 h. Once the digestion finished, the remaining acid was evaporated on a hotplate to incipient dryness. Next, 1 mL of HNO_3 was added twice and evaporated to incipient dryness. Residual sediment was dissolved in HNO_3 (1 mL) and transferred to a 100 mL volumetric flask. The digestion vessel was rinsed with deionized water several times, and washing water was also transferred to the volumetric flask. The flask volume was made up of deionized water and used for chemical element analysis. Twelve elements, including major (e.g., Ca, K, Mg, Na, and P), minor (e.g., Zn, Fe, and Mn), and ultratrace mineral elements (e.g., Si, Al, Cu, and Co) were quantitatively determined by high-resolution inductively coupled plasma mass spectrometry (Element XR HR-ICP-MS, Thermo Scientific, Bremen, Germany) at the labGEOTOP, Geosciences Barcelona (Spanish Research Council, CSIC, Barcelona, Spain) (Prado et al., 2014) [6]. The element concentrations (mean of 3 replicates) were expressed on a dry weight (DW) basis. The accuracy and precision errors of the analytical determination by HR-ICP-MS were lower than 10%.

2.7. Statistical Analysis

Differences between years are not shown because there were no significant differences between them. All samples were analyzed in triplicate. The results are expressed as the means of the triplicate measurements. The values were statistically evaluated by analysis of variance (ANOVA), and further, Tukey's honestly significant difference tests were performed for mean comparisons (Minitab release 14 statistical software, 2003; Minitab Inc., State College, PA, USA). Differences are considered significant at $p \leq 0.05$ [49].

3. Results

3.1. Grain Yield

The study revealed that manure application improved the grain yield of the two quinoa varieties used under the high valley (about 2000 m a.s.l.) agroecological conditions in northwestern Argentina. Our results show that by using goat manure, the grain yield increased from 2055 kg/ha to 5365 kg/ha when comparing no goat manure addition to a 4 Tn/ha dose, respectively. No significant differences between the varieties were found, nor were any interactions between the variety and manure dose. Regarding the effects of

different manure goat doses, increasing the manure dose from 2 to 4 Tn/ha had a significant effect on the yield, with no differences between 4 and 8 Tn/ha, and a lower yield, similar to that achieved by the 2 Tn/ha dose, for 12 Tn/ha dose (Figure 1). Adding 2 Tn/ha of manure doubled the yield compared to the no-fertilizer treatment, and adding 4 Tn/ha increased the yield by 23% compared to the 2 Tn/ha dose.

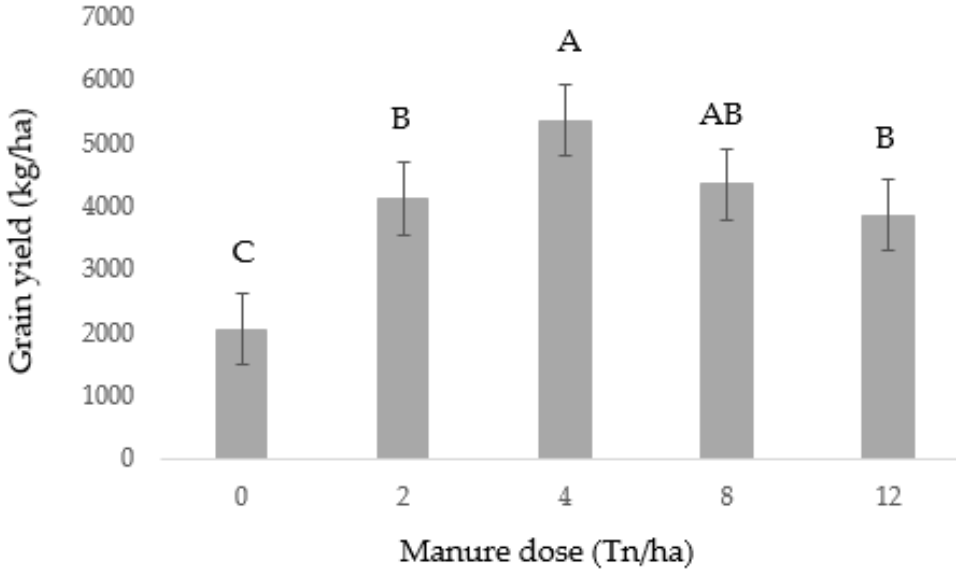

Figure 1. Grain yield (kg/ha) under different doses of goat manure fertilization. Bars show mean ± standard error (n = 12). Different letters represent significant differences among manure doses at $p \leq 0.05$.

3.2. Total Protein and Amino Acid Contents

The total protein content (TPC) significantly increased at higher manure concentrations in both quinoa varieties (see Table 2). Thus, the highest TPC was reached at 12 Tn/ha (22.1% for CICA-17 and 21.4% for RB). The effects of different manure doses on the total amino acids (essential or non-essential) and the amino acid profile varied according to the ecotypes and doses considered. It is evident that the effect of the manure on the synthesis of different amino acids differed between the studied varieties. The total essential amino acid (TEAA) content varied according to the manure addition and varieties (Table 2). Therefore, for CICA-17, the TEAA increased in the C2 treatment and significantly decreased in the C4, C8, and C12 treatments ($p \leq 0.05$). In contrast, the content of TEAA was similar in RB0 and RB2 but a significant reduction was determined in the other treatments (RB4, RB8, and RB12), mainly as a consequence of the lower Val content ($p \leq 0.05$). The EAA ranged from 0.17 g/100 g protein for Thr to 6.26 g/100 g protein in CICA-17 and from 1.19 g/100 g protein for Phe to 8.08 g/100 g protein for Val g/100 in RB. The most abundant essential amino acids in CICA-17 were Phe, Leu, Lys, and Val, whereas Val, Lys, and Leu were predominant in RB. Without manure addition, the total non-essential amino acid (TNEAA) content was lower in CICA-17 than in RB (22.5 and 38.18 g/100 protein for C0 and RB0, respectively) (Table 2). The TNEAA content ranged from 0.43 g/100 g protein for Gln to 10.09 g/100 g protein for Arg in C0 and from 1.13 g/100 g protein for Gln to 10.33 g/100 g protein for Arg in RB0. The non-essential amino acids Arg, Ala, and Glu in C0 were the most abundant in CICA-17, and Arg, Glu, and Ser were the most abundant in RB0.

Table 2. Total protein content, essential and non-essential amino acids in CICA-17 and Regalona Baer varieties under different goat manure dose treatments.

	CICA-17					Regalona Baer				
	C0	**C2**	**C4**	**C8**	**C12**	**RB0**	**RB2**	**RB4**	**RB8**	**RB12**
TPC (g/100 g seed)	15.5 ^{d}	15.0 ^{d}	17.9 ^{c}	19.6 ^{b}	22.1 ^{a}	15.0 ^{c}	15.2 ^{c}	15.9 ^{c}	17.9 ^{b}	21.4 ^{a}
EAA (g/100 g protein)										
Leu	5.97 ^{b}	8.12 ^{a}	4.80 ^{c}	4.33 ^{c}	0.98 ^{d}	5.28 ^{b}	7.03 ^{a}	5.47 ^{b}	5.64 ^{b}	5.52 ^{b}
Lys	5.73 ^{a}	4.76 ^{a}	5.23 ^{a}	5.37 ^{a}	5.12 ^{a}	5.43 ^{a}	5.93 ^{a}	5.77 ^{a}	5.52 ^{a}	5.41 ^{a}
Val	5.05 ^{a}	5.63 ^{a}	3.29 ^{b}	3.07 ^{b}	0.98 ^{c}	8.08 ^{a}	6.79 ^{b}	4.18 ^{e}	4.72 ^{d}	4.95 ^{c}
Ile	2.04 ^{a}	1.88 ^{a}	1.32 ^{b}	1.17 ^{b}	0.55 ^{c}	2.40 ^{a}	2.05 ^{c}	1.79 ^{d}	2.07 ^{b}	2.07 ^{b}
Phe	6.26 ^{a}	6.52 ^{a}	1.10 ^{b}	1.05 ^{b}	1.09 ^{b}	1.16 ^{b}	1.19 ^{b}	1.49 ^{a}	1.38 ^{b}	1.27 ^{b}
Thr	0.17 ^{d}	1.06 ^{a}	0.75 ^{bc}	0.63 ^{c}	0.22 ^{d}	1.17 ^{a}	0.71 ^{c}	1.00 ^{a}	0.81 ^{b}	1.04 ^{a}
Met	0.77 ^{d}	1.65 ^{b}	1.13 ^{a}	1.02 ^{c}	1.09 ^{c}	1.26 ^{a}	1.19 ^{a}	1.00 ^{b}	0.69 ^{c}	0.58 ^{c}
TEAA	25.98 ^{b}	29.62 ^{a}	17.63 ^{c}	16.64 ^{cd}	10.03 ^{d}	24.78 ^{a}	24.89 ^{a}	20.96 ^{b}	20.82 ^{b}	20.84 ^{b}
NEAA (g/100 g protein)										
Asp	1.49 ^{c}	5.63 ^{a}	3.96 ^{ab}	3.62 ^{ab}	1.20 ^{d}	3.49 ^{b}	3.87 ^{b}	4.08 ^{a}	3.91 ^{a}	4.14 ^{a}
Arg	10.09 ^{d}	12.07 ^{d}	10.21 ^{d}	8.32 ^{bc}	2.29 ^{a}	10.33 ^{a}	7.74 ^{d}	8.16 ^{d}	9.20 ^{c}	9.09 ^{b}
Gln	0.43 ^{e}	2.86 ^{c}	3.57 ^{b}	8.35 ^{a}	1.53 ^{d}	1.13 ^{b}	2.53 ^{a}	0.80 ^{c}	0.81 ^{c}	1.04 ^{b}
Glu	1.90 ^{c}	7.00 ^{a}	6.61 ^{a}	5.93 ^{b}	0.44 ^{d}	8.27 ^{a}	7.35 ^{a}	7.96 ^{a}	7.59 ^{a}	8.51 ^{a}
Gly	1.63 ^{a}	1.79 ^{a}	1.35 ^{b}	1.33 ^{b}	1.31 ^{b}	5.14 ^{c}	4.27 ^{b}	3.78 ^{c}	3.80 ^{c}	4.49 ^{a}
Ala	5.26 ^{b}	7.39 ^{a}	2.86 ^{c}	2.43 ^{c}	2.07 ^{c}	2.64 ^{a}	2.69 ^{a}	2.39 ^{a}	2.42 ^{a}	2.42 ^{a}
Ser	0.44 ^{c}	4.54 ^{a}	4.03 ^{a}	3.84 ^{a}	2.62 ^{b}	5.82 ^{a}	4.35 ^{b}	0.50 ^{c}	5.64 ^{a}	5.98 ^{a}
Tyr	1.01 ^{c}	2.13 ^{a}	1.74 ^{b}	1.53 ^{b}	0.44 ^{d}	1.36 ^{a}	1.11 ^{a}	1.29 ^{a}	1.27 ^{a}	1.38 ^{a}
Total NEAA	22.25 ^{c}	43.40 ^{a}	34.32 ^{b}	35.33 ^{b}	11.88 ^{d}	38.18 ^{a}	33.89 ^{a}	28.95 ^{b}	34.62 ^{a}	37.03 ^{a}
TAA	48.2	72.7	52.0	52.0	21.9	63.0	58.8	49.9	55.4	57.9
EAA/TAA	53.9	40.3	33.9	32.0	45.8	39.4	42.3	42.0	37.6	36.0
NEAA/TAA	46.1	59.7	66.1	68.0	54.2	60.6	57.7	58.0	62.4	64.0
EAA/NEAA	116.8	68.2	51.4	47.1	84.4	64.9	73.4	72.4	60.1	56.3

Values are expressed as the means of triplicate analyses. Different letters indicate significant differences among treatments for the same variety ($p \leq 0.05$). TPC: total protein content; EAA: essential amino acids; TAA: total amino acids; TEAA: total essential amino acids; NEAA: non-essential amino acids; TNEAA: total non-essential amino acids.

The total amino acid contents varied according to the manure doses added and differed between the varieties. CICA-17 showed an increase under C2, but under C4, C8, and C12, it exhibited a substantial decrease (Table 2). Meanwhile, RB was similar between RB0 and RB2, and then showed decreases when increasing the manure addition dose. The described behavior is mainly explained by the Leu contents in both varieties. The Lys content showed similar behavior in both varieties. Val, Ile, Phe, and Thr were the most affected EEAs in CICA-17, especially under the C4, C8, and C12 treatments, compared to the changes exhibited by RB, which decreased when adding manure but maintained higher values than CICA-17 for all manure addition doses. The NEAA content showed bimodal behavior in CICA-17, with a remarkable increase in C2, C4, and C8 and a substantial reduction in C12. In contrast, it decreased in RB under all manure addition doses.

3.3. Soluble Sugar Content

The total soluble sugar (TSS) content was lower in C0 than in RB0 (Table 3). The TSS showed a similar increasing pattern in both varieties under different manure dose applications, but the increase was more significant in CICA-17. The soluble sugars (glucose, fructose, and sucrose) varied under different manure addition doses. The glucose content increased from 0.05 g/100 g DW for C0 to 0.16 g/100 g DW for C12 and from 0.05 g/100 g DW for RB0 to 0.12 g/100 g DW for RB8. The highest value of fructose was reached in C4 (0.53 g/100 g DW) and RB8 (0.90 g/100 g DW), whereas for sucrose, the highest values were found in C8 (2.19 g/100 g DW) and RB8 (2.09 g/100 g DW).

Table 3. Total soluble sugar, glucose, fructose, and sucrose contents in the seeds of CICA-17 and Regalona Baer varieties under different goat manure dose treatments.

	CICA-17					Regalona Baer				
	C0	**C2**	**C4**	**C8**	**C12**	**RB0**	**RB2**	**RB4**	**RB 8**	**RB 12**
					(g/100 g DW)					
TSS	0.92 ^{d}	1.39 ^{c}	1.94 ^{b}	2.38 ^{a}	2.59 ^{a}	1.23 ^{c}	1.50 ^{b}	1.49 ^{b}	2.24 ^{a}	2.20 ^{a}
Glucose	0.05 ^{e}	0.07 ^{d}	0.08 ^{c}	0.12 ^{b}	0.16 ^{a}	0.05 ^{d}	0.06 ^{c}	0.11 ^{a}	0.12 ^{a}	0.09 ^{b}
Fructose	0.13 ^{d}	0.20 ^{c}	0.53 ^{a}	0.49 ^{a}	0.45 ^{b}	0.14 ^{e}	0.30 ^{d}	0.43 ^{c}	0.90 ^{a}	0.47 ^{b}
Sucrose	0.90 ^{d}	1.42 ^{c}	2.01 ^{b}	2.19 ^{a}	2.16 ^{a}	0.99 ^{c}	1.08 ^{c}	1.12 ^{c}	2.09 ^{a}	1.99 ^{b}

Values are expressed as the mean of triplicate analyses. The different letters indicate significant differences among treatments of the same variety ($p \leq 0.05$). TSS: Total soluble sugar content.

3.4. Oil Content and Fatty Acids Profile

The oil content in both varieties varied from 6.3 to 5.8% and was not affected by the manure fertilization dose (Table 4). On the contrary, the FA profile significantly changed according to the manure fertilization, affecting some particular FA content (Table 4). As it was expected, the UFA content predominated over the SFA, with a value ranging from 77 to 81 g/100 g of FAME in the CICA-17 seeds and varying from 79 to 83 g/100g of FAME in the RB seeds. Among these, PUFA represented the most abundant fraction (~65–70 g/100 g of FAME) due to both essential fatty acids and linoleic (C18:2, n6) and linolenic (C18:3, n3) acids. Thus, C18:2 exhibited values of around 59 to 65 g/100 g of FAME in both quinoa cultivars, whereas C18:3 reached contents from 4.9 to 7.0 g/100 g of FAME.

Table 4. Fatty acid compositions of quinoa seed oil of CICA-17 and Regalona Baer varieties under different goat manure treatments.

	CICA-17					Regalona Baer				
	C0	**C2**	**C4**	**C8**	**C12**	**RB0**	**RB2**	**RB4**	**RB8**	**RB12**
Oil content (%)	5.83 ^{a}	6.22 ^{a}	6.32 ^{a}	6.03 ^{a}	6.05 ^{a}	5.75 ^{a}	6.25 ^{a}	6.12 ^{a}	6.16 ^{a}	5.99 ^{a}
Fatty acid (g/100 g)										
C14:0	0.21 ^{c}	0.37 ^{b}	0.52 ^{a}	0.22 ^{c}	0.19 ^{c}	0.88 ^{a}	0.86 ^{a}	0.53 ^{b}	0.22 ^{d}	0.35 ^{c}
C14:1	0.08 ^{a}	0.11 ^{a}	0.12 ^{a}	0.09 ^{a}	0.11 ^{a}	0.08 ^{a}	0.08 ^{a}	0.06 ^{a}	0.08 ^{a}	0.07 ^{a}
C16:0	17.50 ^{b}	17.70 ^{b}	16.46 ^{b}	20.32 ^{a}	19.10 ^{a}	16.75 ^{b}	14.97 ^{c}	16.32 ^{b}	18.37 ^{a}	18.30 ^{a}
C16:1	0.35 ^{b}	0.27 ^{b}	0.50 ^{a}	0.53 ^{a}	0.48 ^{a}	0.76 ^{a}	0.67 ^{ab}	0.67 ^{ab}	0.52 ^{c}	0.63 ^{bc}
C18:0	1.92 ^{a}	1.43 ^{b}	1.88 ^{a}	1.90 ^{a}	2.00 ^{a}	1.73 ^{ab}	1.44 ^{b}	1.50 ^{b}	1.88 ^{a}	1.99 ^{a}
C18:1 n9	10.27 ^{c}	14.17 ^{a}	12.37 ^{b}	10.96 ^{c}	11.13 ^{c}	12.97 ^{a}	13.15 ^{a}	13.12 ^{a}	11.65 ^{b}	13.63 ^{a}
C18:2 n6	64.55 ^{a}	58.50 ^{d}	61.46 ^{c}	61.50 ^{c}	62.76 ^{b}	59.41 ^{b}	62.31 ^{a}	60.90 ^{ab}	61.75 ^{a}	58.60 ^{b}
C18:3 n3	4.91 ^{c}	6.98 ^{a}	6.15 ^{b}	4.30 ^{cd}	4.06 ^{d}	5.65 ^{bc}	6.05 ^{ab}	6.62 ^{a}	5.26 ^{c}	6.11 ^{a}
C20:1	0.19 ^{b}	0.49 ^{a}	0.51 ^{a}	0.22 ^{b}	0.21 ^{b}	1.78 ^{a}	0.43 ^{b}	0.29 ^{c}	0.27 ^{c}	0.30 ^{c}
SFA	19.63 ^{c}	19.50 ^{c}	18.87 ^{c}	22.44 ^{a}	21.29 ^{b}	19.37 ^{b}	17.27 ^{d}	18.35 ^{c}	20.47 ^{a}	20.65 ^{a}
UFA	80.35 ^{a}	80.53 ^{a}	81.15 ^{a}	77.51 ^{c}	78.65 ^{b}	80.65 ^{bc}	82.70 ^{a}	81.67 ^{b}	79.54 ^{c}	79.35 ^{c}
MUFA	10.90 ^{a}	15.04 ^{c}	13.51 ^{b}	11.71 ^{a}	11.82 ^{a}	15.55 ^{c}	14.33 ^{b}	14.15 ^{b}	12.52 ^{a}	14.64 ^{bc}
PUFA	69.45 ^{a}	65.48 ^{c}	67.61 ^{b}	65.80 ^{c}	66.82 ^{b}	65.05 ^{c}	68.37 ^{a}	67.52 ^{ab}	67.01 ^{b}	64.71 ^{c}
SFA/UFA	0.25 ^{c}	0.24 ^{c}	0.23 ^{c}	0.29 ^{a}	0.27 ^{b}	0.24 ^{b}	0.21 ^{c}	0.22 ^{c}	0.26 ^{a}	0.26 ^{a}

Values are expressed as the means of three analytical replicates. SFA: saturated fatty acids. MUFA: monounsaturated fatty acids. PUFA: polyunsaturated fatty acids. The different letters indicate significant differences among treatments of the same variety ($p \leq 0.05$).

The changes observed in the FA profile due to the manure addition dose were cultivar-dependent. The most significant changes in the CICA-17 variety were observed for C18 FA after 2 and 4 Tn/ha treatments. In this regard, stearic (C18:0) and C18:2 significantly decreased, while myristic (C14:0), oleic (C18:1 C9), and C18:3 acids increased in C2 compared to C0 ($p \leq 0.05$). Consequently, there was a significant increase in MUFA and a decrease in PUFA content, while the SFA/UFA ratio was not affected under these conditions (Table 4). In the C8 and C12 treatments, changes in the SFA were also observed, mainly attributed to

a higher content of palmitic acid (C16:0), a fatty acid associated with strong atherogenic power. The FA variations consequently affected the SFA/UFA, which had significantly higher levels in both treatments than in the control ($p \leq 0.05$).

In the RB variety, the addition of manure to the soil produced a significant variation in the C16:0. The C16:0 content significantly decreased in RB2 compared to RB0, while in the other treatments, it was similar (RB4) or even higher (RB8 and RB12) than in the RB0 ($p \leq 0.05$). Consequently, similar variations were determined for the total SFA content among the treatments, with the SFA/UFA ratio significantly lower in RB2 than in the other groups.

To infer which FA metabolic pathway could be altered by manure addition, Δ9-desaturase for the C16, C18, AI, TI, and DFA indexes and the n6:n3 ratio were determined (Figure 2A–F). As Figure 2A,B shows, the AI and TI indexes in the CICA-17 variety show a significant increase with increasing manure doses, reaching the highest value with 8 and 12 Tn/ha ($p \leq 0.05$). On the other hand, the RB variety shows the highest AI value in quinoa cultivated without fertilization (Figure 2A), whereas the TI significantly decreased at 2 and 4 Tn/ha (Figure 2B). The manure addition significantly improved the AI of quinoa oil (Figure 2A), showing the lowest value in seeds treated with 2 and 4 Tn/ha, whereas the TI significantly decreased (Figure 2B). Regarding the DFA content, the addition of low manure concentrations (up to 4 Tn/ha) significantly improved the DFA value in both quinoa varieties, but it was negatively affected by higher concentrations (Figure 2C). As Figure 2D shows, the n6:n3 ratio was improved by fertilization up to 2–4 Tn/ha, decreasing in CICA-17 from 13:1 (without manure addition) to 8:1 at 2 Tn/ha. In RB, there was a slight but significant n6:n3 reduction from 10:1 (manure addition) to 9:1 after 4 Tn/ha of manure was applied ($p \leq 0.05$).

The increase in manure addition to the soil significantly modified the desaturase indexes in both quinoa varieties. The Δ9-desaturase for C16 increased at high manure concentrations in the CICA-17 variety (Figure 2E); the highest value was obtained after the addition of 4 Tn/ha. On the contrary, the RB variety showed a tendency to decrease the Δ9-desaturase in C16 by manure addition; the lowest value was determined at the 8 Tn/ha dose ($p \leq 0.05$) (Figure 2E). On the other hand, a similar behavior for Δ9-desaturase in C18 was determined in both cultivars, which was significantly increased by fertilization with a 2 Tn/ha dose ($p \leq 0.05$).

3.5. Mineral Content

The ash and mineral contents of both quinoa varieties are shown in Table 5. No significant variations in the mineral content were detected at low concentrations of manure addition (2 and 4 Tn/ha), but that changed at 8 and 12 Tn/ha. In RB8, the ash content decreased, but it increased in RB12, reaching a value similar to that of RB0. On the contrary, higher mineral content was determined for C8, decreasing in C12 until reaching a value similar to that in the C0 treatment.

The major elements were all affected by fertilization. In C8, the highest values for K, Si, Mg, and Ca were determined, whereas, in C12, the highest contents of P and Na were reached. RB8 showed significant increases in P, Mg, Ca, and Na contents compared to the other treatments, whereas the highest values of K and Si were determined in RB12 and RB4, respectively. There were no differences in the contents of the minor elements Fe, Mn, and Zn between C0 and RB0. The contents of Fe and Mn in both varieties showed a tendency to increase by manure addition, while the Mn content showed a tendency to decrease in the same treatments (Table 5). The Al content was higher in RB8 compared to the other treatments, while in CICA-17, the highest content was determined in C12. The Cu content was higher in C2 and C8 than in the other treatments, whereas in the RB cultivar, the highest Cu value was determined in RB8 and RB12.

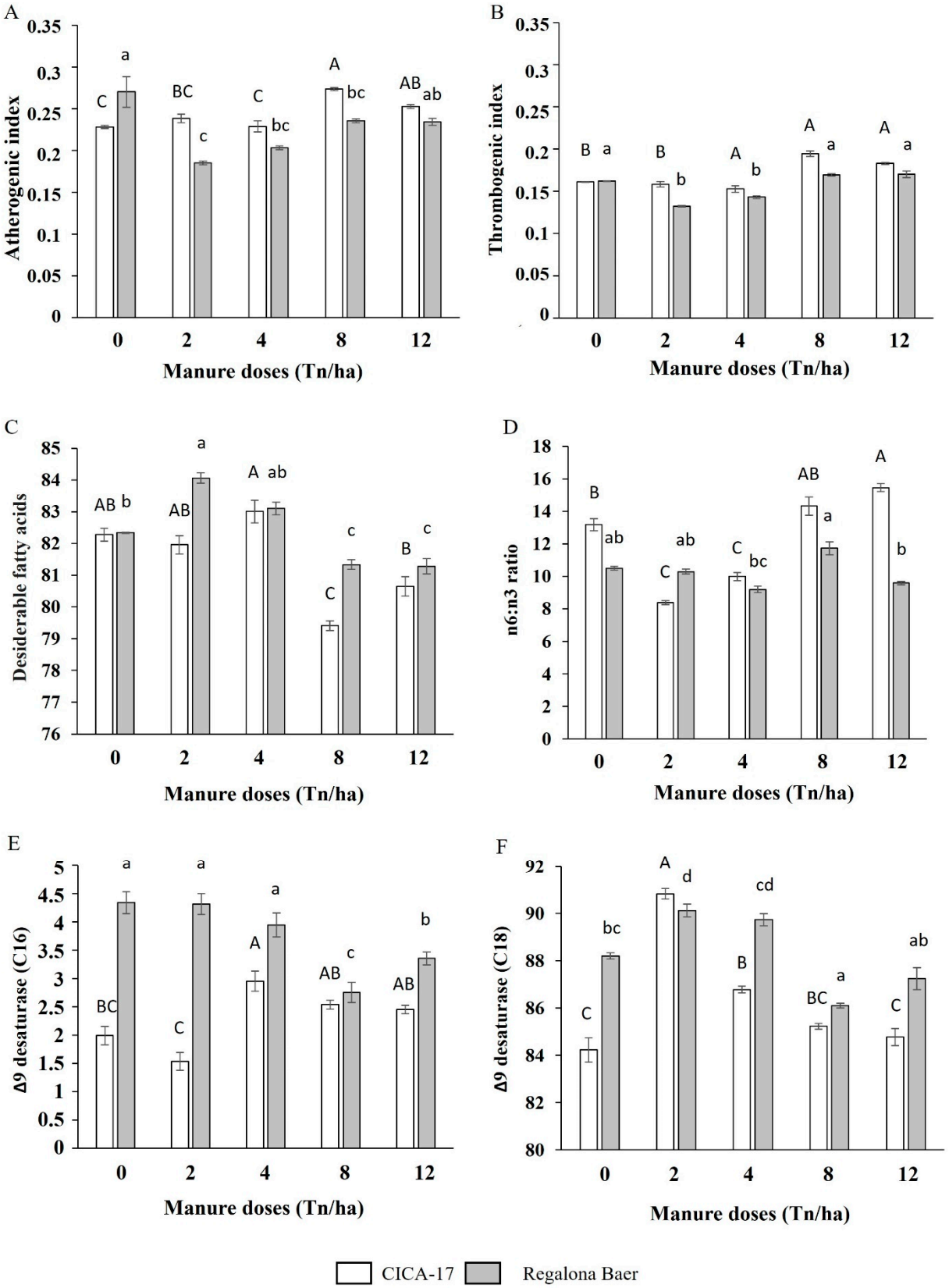

Figure 2. AI (**A**), TI (**B**), DFA (**C**), n6:n3 ratio (**D**), and Δ9 desaturase for C16 and C18 (**E**,**F**) in CICA-17 and Regalona Baer varieties after manure addition to soil. Values correspond to the mean ± SE (n = 3).

Table 5. Ash and mineral content in CICA-17 and RB varieties under different manure treatments.

	CICA-17					Regalona Baer				
	C0	**C2**	**C4**	**C8**	**C12**	**RB0**	**RB2**	**RB4**	**RB 8**	**RB 12**
Ash% DW	3.22 ^{a}	3.35 ^{a}	3.17 ^{a}	3.88 ^{b}	3.19 ^{a}	3.43 ^{b}	3.38 ^{b}	3.47 ^{b}	3.02 ^{a}	3.57 ^{b}
Major elements mg/kg DW										
K	9042.7 ^{a}	9677.5 ^{a}	8726.8 ^{a}	10,260.9 ^{b}	9195.5 ^{a}	9237.5 ^{b}	9071.3 ^{b}	8734.9 ^{b}	8125.2 ^{a}	10,991.4 ^{c}
Si	5303.5 ^{b}	5720.5 ^{b}	5859.0 ^{b}	6304.1 ^{c}	3921.4 ^{a}	6743.9 ^{c}	6772.2 ^{c}	7276.7 ^{c}	3917.9 ^{a}	5760.5 ^{b}
P	2692.6 ^{b}	2663.9 ^{b}	2304.7 ^{a}	2751.1 ^{b}	2924.9 ^{b}	2341.9 ^{a}	2150.3 ^{a}	2123.8 ^{a}	2917.7 ^{b}	2300.3 ^{a}
Mg	1480.4 ^{a}	1361.0 ^{a}	1362.9 ^{a}	2483.9 ^{b}	2215.3 ^{b}	1446.9 ^{a}	1463.1 ^{a}	1501.7 ^{a}	2019.3 ^{b}	1948.0 ^{b}
Ca	660.6 ^{a}	657.7 ^{a}	585.0 ^{a}	1469.6 ^{c}	1132.3 ^{b}	562.4 ^{a}	540.9 ^{a}	655.7 ^{b}	1108.3 ^{c}	924.6 ^{c}
Na	146.5 ^{c}	106.7 ^{b}	74.5 ^{a}	156.3 ^{c}	211.8 ^{d}	26.1 ^{a}	70.9 ^{b}	124.6 ^{c}	146.2 ^{c}	86.2 ^{b}
Minor or trace elements mg/kg DW										
Fe	52.8 ^{a}	52.0 ^{a}	50.0 ^{a}	76.1 ^{b}	70.4 ^{b}	50.0 ^{a}	47.2 ^{a}	46.0 ^{a}	73.9 ^{b}	76.7 ^{b}
Mn	35.2 ^{a}	29.2 ^{b}	29.1 ^{b}	41.9 ^{c}	37.4 ^{a}	26.7 ^{a}	31.5 ^{c}	15.6 ^{b}	35.3 ^{c}	31.2 ^{c}
Al	21.6 ^{a}	30.1 ^{b}	30.2 ^{b}	45.8 ^{c}	35.1 ^{b}	30.8 ^{b}	26.4 ^{b}	21.1 ^{a}	27.4 ^{b}	49.3 ^{c}
Zn	13.2 ^{b}	12.6 ^{b}	11.9 ^{b}	10.7 ^{a}	12.5 ^{b}	14.7 ^{b}	15.1 ^{b}	15.3 ^{b}	10.5 ^{a}	11.5 ^{a}
Cu	6.79 ^{a}	8.1 ^{b}	7.5 ^{a}	7.1 ^{a}	6.2 ^{a}	5.9 ^{a}	5.7 ^{a}	5.7 ^{a}	6.9 ^{b}	6.8 ^{b}
Ultratrace elements mg/kg DW										
Li	0.319 ^{b}	0.252 ^{b}	0.215 ^{a}	0.651 ^{c}	0.241 ^{b}	0.190 ^{a}	0.205 ^{b}	0.238 ^{c}	0.275 ^{d}	0.347 ^{e}
Cr	0.099	0.113	0.072	0.422	0.074	0.089 ^{a}	0.182 ^{b}	0.076 ^{c}	0.485 ^{d}	0.088 ^{a}
Co	0.032 ^{b}	0.033 ^{b}	0.022 ^{a}	0.097 ^{c}	0,028 ^{b}	0.026 ^{b}	0.027 ^{b}	0.089 ^{c}	0.029 ^{b}	0.023 ^{a}

Values are expressed as mean ± SD (n = 3). Different letters indicate significant differences among the same of variety treatments ($p \leq 0.05$).

Among the ultratrace elements, the lithium content increased in C8 and was lower for the other treatments. In contrast, the lithium content in RB showed increases with higher values as the manure dose increased. The chromium content increased in the C8 and RB8 treatments. Finally, the cobalt content increased in the C8 and RB4 treatments.

4. Discussion

This study demonstrated that goat manure fertilization, an abundant resource in the Andean region of Latin American, Asian, and MENA countries, had different effects on the yield and organic compound synthesis of the two evaluated varieties. Increases in the goat manure dose had no linear response, showing a decrease in yield after 8 Tn/ha. Although there is some information about the yield and nutritional value compounds [6,20] of different local quinoa varieties, this is the first report on changes due to different goat manure addition doses. This field study evidenced that the CICA-17 and R. Baer varieties are differently affected by goat manure fertilization, producing changes in some particular nutritional compounds and mineral accumulations. Thus, regarding human nutrition and daily nutrient requirements, it is important to consider how plant nutrition changes the nutritional value of quinoa grain.

4.1. Grain Yield

Our study showed that both varieties assayed, CICA-17 and R. Baer, improved the grain yield when adding goat manure to the soil. It is worth noting that despite the reduction in the yield when applying 8 Tn/ha and 12 Tn/ha of goat manure, the obtained values are still higher than those achieved without applying goat manure. Even so, relevance should be given to the observed yield drops, considering that they may show some nutrient imbalances, which may have adversely affected several metabolic processes, as suggested by Kumar et al., 2021 [50]. According to Romera et al., 2021 [51] a better understanding of the interactions between elements (essential and non-essential) could lead to more rational fertilization practices, preventing interactions that could contribute to unbalanced mineral nutrition of plants. Although that was not the objective of this work, future research about

that knowledge is needed. Considering the different responses obtained among the doses, it would be very interesting to further investigate this topic and how to manage or correct unbalanced mineral nutrition in case it is found. Finally, it is interesting to highlight that in a previous study, a lower quinoa yield increase (up to 95%) was achieved with a 120 kg N/ha dose of nitrogen synthetic fertilizer addition compared to no fertilization [34]. Similar yield increases to those obtained in the present study have been reported by Jacobsen et al. [33], Gomaa [52], and Kakabouki et al. [53].

4.2. Protein and Amino Acid Profile

Quinoa protein content depends on the ecotypes considered and their interactions with environmental factors [6]. This study found similar protein contents (mean of 15.2%) in both quinoa varieties, similar to the 13.5% reported for CICA-17 cultivated in northwestern Argentina [3,52]. Manure application increased the protein content linearly in the studied varieties (r = 0.91 and 0.84 for CICA-17 and R. Baer, respectively; data not shown). At low manure doses, the protein content did not differ from the 0 application, but from 4 to 12 Tn/ha, the protein contents increased in both ecotypes. Nitrogen-containing compounds, such as protein and amino acids, are affected by environmental conditions, such as drought, temperature regime, and nitrogen fertilization [54,55]. The observed increases in the grain protein contents (15.5 to 22.1% for CICA-17 and 15.0 to 21.4% for R. Baer) have an important nutritional impact on human nutrition.

Previous results have shown that environmental conditions, soil properties, and microclimate features are essential for synthesizing and accumulating the essential amino acids in different quinoa ecotypes [3,55]. No significant differences in the TEAA contents were determined between the cultivars, but the TNEAA contents and particular amino acid contents significantly differed. Significant changes were found in the Val and Ile contents for CICA-17, which decreased at high manure doses, whereas the Me and Thr increased. The same behavior was detected in R. Baer. Similar behavior was previously reported for amaranth and quinoa seeds [56]. The requirements of Leu for human nutrition established by FAO/WHO/UNU [57] are around 5.9 to 6.6 g/100 g protein, and were only reached in the C2 and RB2 treatments. The Lys requirements vary from 4.5 to 5.7 g/100 g protein (>18 years old and 0.5 years old, respectively). The Lys contents obtained for CICA-17 were different according to the treatment and partially reached the recommended dose consumption, while all R. Baer treatments reached the established Lys requirements. The Val contents detected in CICA-17 only satisfied all mentioned groups in C0 and C2. However, all of the R. Baer treatments satisfied all age groups. The Ile and Thr amino acid contents neither in CICA-17 nor in RB met any requirements in any age group.

4.3. Soluble Sugar Content

The sucrose, glucose, and fructose contents were similar in both quinoa varieties (0.90–0.99; 0.05 and 0.135 g/100g DW, respectively). Higher levels of sucrose (1.7–2.3 g/100g DW), glucose (0.24–0.24 g/100g DW), and fructose (2.90 g/100 g of DW) have previously been reported by authors for quinoa seed [58,59], probably due to environmental conditions.

4.4. Oil Content and Fatty Acid Profile

The total quinoa grain oil content was not affected by manure addition and was within the range of 2.5 to 10.88 g/100 g established for quinoa [11], similar to values of 6.0–6.8 g/100 g found in different colored quinoa seeds. CICA is a Peruvian variety obtained from Amarilla de Marangani (A. Mújica-Sánchez, personal communication, 2016), with an oil content of 4.97 g/100 g in ungerminated seeds, increasing after germination to 6.00–7.34 g/100 g [60]. CICA-17 cultivated in Al-Fayoum (Egypt) exhibited total oil contents of 4.55 to 5.39 g/100 g [21], while for R. Baer cultivated in Chile, it was 6.4 g/100 g [61]. The influence of quinoa ecotypes on the oil content is controversial. Some authors reported no variation in the oil content of different quinoa ecotypes, but others reported significant

changes in the oil values of six Bolivian and Peruvian quinoa ecotypes [62]. Our results show that the addition of different manure doses did not affect the total oil content neither in the CICA-17 nor the R. Baer varieties. Regarding the FA profile, coincident with our results, similar values for the total UFA content (81–85 g/100 g), with ranges of variation of 15–20 g/100 g for oleic, 45–57 g/100 g for linoleic, and 5–10 g/100 g for linolenic acids, were previously reported for different quinoa cultivars [60]. However, Pellegrini et al. [62] reported lower SFA contents in six commercial quinoa varieties (10.0–11.6 g/100 g).

Changes in particular FA contents according to the ecotype and manure dose were determined in the present study. In plants, FA is synthesized during plastid metabolism from acetyl to CoA, then exported into the cytosol, and finally, oil synthesis occurs in the endoplasmic reticulum (ER) [63]. Several enzymatic reactions occur in the ER and plastids in the C16 and C18 FA pathways, where different enzymes can produce elongation and desaturation. In this way, several desaturases bound to the membrane are involved in the conversion of C18:0 to C18:1 (stearoyl-acyl carrier protein desaturase, SAD), the further conversion of C18:1 to C18:2, and then of C18:2 to C18:3. Indeed, FA desaturase 2 (FAD 2, ER) and 6 (FAD6, in plastids) are responsible for the biological switch of C18:1 to C18:2 [64]. Different factors, such as temperature, light, and flooding, can affect the FAD2 expression of plants [65]. To resist cold and salt stress, plants increase the contents of dienoic FA through FAD2 activity. Moreover, temperature is a critical factor influencing seeds' oil content [66]. FAD3 catalyzes the bioconversion of C18:2 to C18:3.

Geographical factors directly impact the FA profile of seeds. Different seeds grown at high altitudes modified the n6 and n3 contents, evidently by changes in the FAD 2 and 3 [67]. Our results show that manure addition did not affect the total oil content but influenced the metabolism of fatty acids, specifically the C16 and C18 pathways, as evidenced by the changes in the FA profile and the estimation of the Δ9-desaturase enzymes. It seems that a low amount of fertilizer positively affected the AI, TI, and DFA indexes, and the n6:n3 ratio, which had a lower effect on the CICA-17 than on the R. Baer ecotype. Palmitic acid is the most abundant SFA of quinoa seed oil, with values ranging from 9.3 to 21%. The results of Tang et al. and Pereira et al. [67,68] match our results. Among UFAs, the range of variation is also dependent on the cultivar and climate conditions. Vera et al. [60] reported, in order of abundance, linoleic (47–59%), oleic (18–31%), and linolenic (3–11%) acids in four varieties of quinoa. In our study, the linoleic acid content was slightly higher (58.6–64.5 g/100 g of FAME), and the oleic acid content (10.3–14.2 g/100 g of FAME) was slightly lower than those reported values.

Despite the variations in the FA profiles found in this study, the qualification of quinoa grain as a "superfood" is not invalidated. This is because the presence and content of essential (linoleic and linolenic) and healthier (oleic acid) unsaturated fatty acids showed higher values than those registered in other grains used for human consumption. Indeed, quinoa has a higher UFA/SFA ratio (4.9–6.2) than other edible oils, such as corn (4.65), soybean (3.92), and olive (0.65) oil [69]. On the other hand, the relationship between the linoleic and linolenic acid (n6:n3) in any fertilization treatment was around 8 to 15, above the recommended ratio by FAO/WHO [70]. The n6:n3 ratio was significantly improved in both quinoa seeds after adding 4 Tn/ha of manure. A wide variation range for the n6:n3 ratio, from 4.68 to 19.59, was reported by Vera et al. [60] in four quinoa cultivars, coincident with our results. The typical Western diet has an unbalanced ratio between 15:1 to 17:1, which is highly prothrombotic and proinflammatory and could contribute to the development of atherosclerosis, obesity, and diabetes [15]. In CICA-17, the ratio ranged between 8.40 and 15.45, with an average of 12.06, while in R. Baer, it was between 9.20 and 11.70, with an average of 10.20. Palmitoleic (C16:1), oleic, linoleic, and linolenic acids are considered the main precursors of the lipid metabolic pathways in mammals. While palmitoleic and palmitic acids can be synthesized endogenously, the essential C18:2 n6 and C18:3 n3 must be obtained from the diet. Therefore, quinoa may be a good source of healthy fatty acids (C18:1, C18:2, C18:3), especially in many places worldwide where the main crops are grains such as wheat or corn.

4.5. Ash and Mineral Content

It is known that the soil type affects the mineral contents of quinoa and amaranth [6,71]. Our results show that the ash content was similar in both varieties, and the mineral concentrations showed low variation between the two cultivars, except for Na, Si, and Li. Both varieties have grown well at the Encalilla site; CICA-17 has been grown for 15 years, and RB for 10 years. Therefore, both varieties have probably adapted their metabolism to the edaphic and climatic conditions. Among the major elements, potassium increased by 13.5% in C8 and by 19% in RB12, and sodium increased by 44.6% in C12 and by 460% in RB8. The rest of the elements (minor or ultratrace) showed similar responses to manure addition between the CICA-17 and RB varieties. It is remarkable that the most positive changes in the mineral content occurred with 8 or 12 Tn/ha in both quinoa varieties. Li increased by 104.1% in C8 and by 82.8% in RB12. The Cr content increased by 326.2% in CICA-17 and by 444.9% in BR at the same manure dose (8 Tn/ha). The occurrences of both minerals agree with the findings of Li in the seeds of quinoa and amaranth [72] and Cr in CICA-17 grown in saline soil in Egypt [6,48]. The essentiality of Li and Cr for plants has not been recognized but could have a significant relationship with the nutritional aspects of quinoa cultivated in desertic or semi-desertic places [6], which are sites of interest for producing grains with higher mineral concentrations and health effects for humans.

Several studies have shown a close relationship between the mineral compositions and protein contents in cereals and legumes [73,74]. In this study, over 12 minerals were analyzed, and nine positive correlations between the mineral and protein contents in CICA-17 and ten in RB were determined. The most significant correlations ($r \geq$ to 0.70) were found for Mg, Ca, and Al in CICA-17 and for Mg, Ca, Fe, and Cu in RB. In agreement with Prado et al. [6], we found negative correlations for Fe in CICA-17 and for Zn and Si in R. Baer.

5. Conclusions

For the first time, the influence of goat manure addition to soil on the total protein, amino acids (essential and nonessential), fatty acid profile, soluble sugars, and mineral contents of two contrasting quinoa varieties (CICA-17 and R. Baer) is herein reported. Manure addition significantly improved the total protein content. Even the oil content remained unchanged, and several FA were positively affected by low amounts of around 2 and 4 Tn/ha in both varieties. CICA-17 had modified MUFA and PUFA contents, while R. Baer had mostly altered SFA contents. The manure addition affected (in a positive or negative sense) the synthesis of amino acids in both varieties. The contents of essential amino acids sometimes met the requirements of some human age groups (from 0.5 to >18 years old), and sometimes that only happened in a particular fertilization dose or cultivar. Low soluble sugars were detected (especially glucose and fructose), reducing the risk for human health related to the glycemic index. In summary, manure addition can benefit grain yield production and improve protein contents, especially the concentrations of some amino acids such as Leu, Lys, and Val; however, Ile and Thr had decreased contents. The use of goat manure as a source of nitrogen, calcium, and phosphorus, among other minerals and organic matter, is a promising alternative to improve the functionality of quinoa grains, especially in marginal areas such as Latin American, Asian, and MENA countries, where the development of classical crops is complex because of the hard soil and weather conditions. Special care should be given to the study of nutrient balance with goat manure doses higher than 4 Tn/ha. Another interesting future research topic would be mechanized organic fertilization. Despite that, in this study, manure was added by hand due to the experimental design needed, and information obtained about manure's effect on yield and grain quality justifies further studies about manure application by machine. It is worth noting that this would be necessary for producing quinoa at a large scale, particularly in lowlands. Meanwhile, in highlands, where growers mainly produce quinoa at a low scale, adding manure by hand is an interesting option.

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