Diversity and interrelationships in nutritional traits in cultivated quinoa (*Chenopodium quinoa* Willd.) from Northwest Argentina

S.M. Vidueiros [a, *], R.N. Curti [b, c], L.M. Dyner [d], M.J. Binaghi [d], G. Peterson [e], H.D. Bertero [b], A.N. Pallaro [a]

[a] Department of Nutrition, Faculty of Pharmacy and Biochemistry, University of Buenos Aires, Junín 956- 2nd Floor, 1113 Buenos Aires, Argentina
[b] Department of Plant Production, Faculty of Agronomy, University of Buenos Aires and IFEVA-Conicet, Av. San Martin 4453, 1417 Buenos Aires, Argentina
[c] Botanical Research Laboratory (LABIBO-CONICET), National University of Salta, Argentina
[d] Department of Food Science, Faculty of Pharmacy and Biochemistry, University of Buenos Aires, Argentina
[e] PROPIA, University of La Plata, Argentina

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ABSTRACT

Quinoa (*Chenopodium quinoa* Willd.) is one of the oldest crops in the American continent. It has been recognized as an extremely nutritious grain all over the world. The importance that quinoa could play in nutrition is being emphasized not only in developing countries but also in the developed world. This is the first study reporting the nutritional characterization of Argentinean quinoa germplasm and describing diversity and interrelationships among nutritional traits, less studied in quinoa, which could provide tools for breeding strategies. Nutritional properties of quinoa accessions collected in different eco-regions from Northwest Argentina but grown on the same environment show a wide range of variation with only subtle differences according to the population's region of origin. However, Argentinean quinoa germplasm did not show clear genetic structure across regions based on nutritional traits as is the case with phenotypic and genotypic traits evaluated on a similar set of accessions.

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1. Introduction

Quinoa (*C. quinoa* Willd.) is one of the oldest crops in the American continent (Dillehay et al., 2007). It was cultivated since ancient times and was a staple food of the Inca Empire (Valencia Chamorro, 2003) and played an important role in the diet and culture of the Andean pre-Hispanic inhabitants. However, its production was almost completely abandoned after the Spanish conquest (Cusack, 1984). As a consequence, the habits and traditional foods of local Andean people were replaced with foreign crops such as wheat and barley (Valencia Chamorro, 2003). Nowadays, it remains an important crop among the current rural inhabitants of the Andean Highlands and many different types (from landraces to modern cultivars obtained through conventional breeding) can be found in Bolivia, Ecuador, Perú, Argentina and Chile (Maughan et al., 2007).

The interest in quinoa increased in the last decades because of its enormous plasticity to adapt to different environmental conditions. The quinoa plant shows tolerance to frost, salinity and drought, and has the ability to grow on marginal soils (Stikic et al., 2012).

Quinoa has been recognized as an extremely nutritious grain all over the world, due to both the relatively high quantity (compared to cereals) and quality of its proteins as regards its essential amino acid content (Valencia Chamorro, 2003). Nutritional composition analyses of quinoa seeds revealed protein concentrations ranging from 12 to 23% and fat content ranging from 2% to 10%. Also, it is reported that quinoa seeds are a rich source of essential fatty acids and a good source of minerals (Abugoch, 2009; Vega-Gálvez et al., 2010). However, little is known about mineral bioavailability in these grains.

The importance that quinoa could play in nutrition is being emphasized not only in developing countries but also in the developed world. In the Andean countries, quinoa crops could

achieve an important role in the future of their economies, as a consequence of new export markets, as well as in local food security (Ruiz et al., 2014). Moreover, it is reported that quinoa could be a strategic crop used to complement the diet in rural/marginal regions where energy-protein malnutrition affects a part of the population of the developing countries (Hellin and Higman, 2005).

The nutritional composition of quinoa varies among ecotypes (groups of cultivars and/or landraces defined according to distributional, ecological, agronomic, and morphological criteria, Tapia et al., 1980) due to strong genetic variability in addition to environmental differences in the Andean region (Repo-Carrasco-Valencia et al., 2010). Few studies aimed at describing the diversity and interrelationships in nutritional traits of a representative set of populations or cultivars (Bhargava et al., 2007; González et al., 2011; Miranda et al., 2012). González et al. (2011) recently showed strong interrelationship between seed yield, total protein content and amino acid composition among a set of representative quinoa cultivars from the Andean highlands and valleys growing in two seasons. On the other hand, Miranda et al. (2012) attributed variability in nutritional values in six quinoa ecotypes from Chile to climatic conditions of origin, since their study did not allow discriminating between genotype and genotype-by-environment interaction effects. Recent studies have shown that contrasting Chilean environments affected grain yield and seed composition of at least two varieties of quinoa (Miranda et al., 2013).

Moreover, cultivated quinoa populations from Northwest Argentina (NWA) have recently been characterized according to their phenotypic and genetic diversity (Costa Tártara et al., 2012; Curti et al., 2012). Results of these studies showed a wide range of variation for several morphological traits and microsatellite markers among accessions from different eco-regions; furthermore, accessions from highland and dry valleys displayed more variability than those from humid valleys and a transition zone between drier and more humid valleys.

Although quinoa nutritional properties are described in the literature, this is the first study reporting nutritional characterization of native quinoa germplasm from NWA and describing diversity and interrelationships among nutritional traits, less studied in quinoa, which could provide tools for breeding strategies. A straightforward approach to describe a set of populations in their nutritional values as well as to determine the interrelationships among traits is to grow a representative set of accessions under similar conditions, such that genotypic differences can be assessed. Accordingly, the objectives of this study were to evaluate variation in nutritional traits and describe the interrelationships among them in a set of cultivated quinoa accessions collected in different eco-regions from Northwest Argentina growing on the same environment.

2. Materials and methods

2.1. Quinoa populations

The nutritional value of a set of 21 quinoa populations from Northwest Argentina region was characterized (see Costa Tártara et al., 2012; Curti et al., 2012 for a detailed description of the geographic sub-region of Northwest Argentina where quinoa is grown). Quinoa seeds were collected in different eco-regions of the provinces of Salta and Jujuy. Geographic characteristics like region, province, latitude, longitude and altitude were registered for each quinoa accession (Table 1). Accession is the name given to a sample conserved in a seed bank and these samples originated from a native quinoa germplasm collection and characterization project conducted by the Faculty of Agronomy, University of Buenos Aires during 2006 and 2007, partially supported by INTA, the Argentinian

National Agriculture Technology Institute. Seeds were collected from farmers fields and multiplied in the locality of Calete (23° 12′S, 65° 20′ W; and 2939 m.a.s.l.) Department of Humahuaca, province of Jujuy, Argentina during the 2008—2009 growing season (austral summer) on a sandy soil (Typic Haplargids, Soil Taxonomy, U.S. Department of Agriculture). Growing season rainfall, average daily mean, maximum and minimum temperatures were 168 mm, 12 °C, 27 °C and 3 °C, respectively. Quinoa accessions were sown in two replicate plots per accessions in a fully randomized design. Each plot consisted of three 5 m length rows spaced 0.5 m apart. Sowing density was 14 seeds m^{-1}, equivalent to 280.000 seeds ha^{-1}. The experiment was kept free of weeds and pests and fertilized at a rate of 43 kg N ha^{-1} days after crop emergence (Curti et al., 2012).

2.2. Proximate composition

The proximate composition of raw quinoa seeds was assessed using the Association of Official Analytical Chemists (AOAC) methods (AOAC, 2000), moisture by AOAC N° 925.09, ash by AOAC N° 923.03, protein by AOAC N° 984.13 and fat by AOAC N° 930.09. The factor used to transform % nitrogen into % protein was 6.25 (Stikic, 2012). Total dietary fiber content (TDF) was determined over dried and defatted samples using AOAC N° 985.29 adopted by a Megazyme® commercial kit. Carbohydrates percentage was calculated with the formulas:

$$\% \, Carbohydrates = 100 - (\% \, moisture + \% \, ashes + \% \, proteins + \% \, fats + \% \, total \, dietary \, fiber).$$

2.3. Fatty acids composition

The extraction of total seed's lipids was performed using a solvent mixture of chloroform-methanol (2:1, v/v). After removal of cholesterol and lipids that might interfere with the method of analysis, the chloroform phase was treated with boron trifluoride 10% in methanol in order to convert fatty acids into methyl ester fatty acids, necessary for further analysis. Fatty acids were separated in a Hewlett Packard 6890 gas chromatograph with a flame ionization detector. A capillary column of 30 m × 0.25 mm i.d., with 0.1 μm film thickness was used (Chrompack CP SIL 88). Individual components were identified by comparison with commercial standards mixtures (NuCheck prep) (Tavella et al., 2000).

2.4. Total Fe and Zn content

The total iron and zinc contents were assessed using flame atomic absorption spectroscopy (AAS) after mineralizing the samples with HNO_3—$HClO_4$ (50:50) (J.T. Baker- Carlo Erba).

2.5. Dialyzability determination

Mineral dialyzability, as a predictor of potential bioaccessibility, measures soluble and ionizable mineral after a procedure that involves an enzymatic digestion simulating physiological conditions. It was determined using the method of Miller et al. (1981), modified by Wolfgor et al. (2002). Briefly, aliquots of homogenized samples (composed of 10 g of quinoa seeds and 40 g of water) were incubated successively at 37 °C in a shaking water bath, against a solution of α-amylase and then a pepsin digestion mixture. After this procedure, two 15 g portions of the pepsin digests were placed separately in Erlenmeyers with a dialysis bag (Spectrapore, molecular, weight cut-off 6000—8000, Fischer Scientific, Fairlawn, NJ, USA) containing PIPES (Sigma Chemical CO, St. Luis, MO,USA)

Table 1
Passport data of the 21 quinoa accessions characterized according to nutritional values.

Accession N°	Ecoregion[a]	Origin (location, department)	Province	Latitude (S)	Longitude (O)	Altitude (m.a.s.l.)
CHEN 458	Humid valleys	Morro de Pucará, Santa Victoria Oeste	Salta	22° 10′	64° 58′	2645
CHEN 461	Humid valleys	Poscaya, Santa Victoria Oeste	Salta	22° 27′	65° 04′	3208
CHEN 465	Transition zone	Santa Cruz del Aguilar, Santa Victoria Oeste	Salta	22° 23′	65° 10′	3955
CHEN 435	Dry valleys	Cangrejillos, Yavi	Jujuy	22° 25′	65° 35,′	3583
CHEN 58	Dry valleys	Coctaca, Humahuaca	Jujuy	23° 09′	65° 17′	3215
CHEN 60	Dry valleys	Campo Tapial de Colanzuli, Iruya	Salta	22° 53′	65° 13′	3605
CHEN 182	Dry valleys	QQ 95- NSL 106394, Humahuaca, Humahuaca	Jujuy	23° 12′	65° 20′	2939
CHEN 183	Dry valleys	QQ 101-NSL 106396, Yavi	Jujuy	22° 07′	65° 28′	3457
CHEN 212	Humid valleys	San Felipe, Santa Victoria Oeste	Salta	22° 16′	64° 58′	2507
CHEN 214	Dry valleys	Yacoraite, Tilcara	Jujuy	23° 23′	65° 20′	2700
CHEN 215	Dry valleys	Cieneguillas, Tilcara	Jujuy	23° 40′	65° 27′	2400
CHEN 231	Dry valleys	Ocumaso, Humahuaca	Jujuy	23° 12′	65° 15′	3000
CHEN 232	Dry valleys	Pucará, Humahuaca	Jujuy	23° 08′	65° 16′	3000
CHEN 252	Dry valleys	Río Grande de Colanzulí- Maimará, Iruya	Salta	23° 37′	65° 24′	2334
CHEN 256	Transition zone	Campo Luján, Iruya	Salta	22° 47′	65° 13	3000
CHEN 261	Transition zone	Río Grande de Colanzuli, Iruya	Salta	22° 52′	65° 12	3600
CHEN 273	Not characterized	1483 La Poma, Tumbaya	Jujuy	23° 51′	65° 49′	3480
CHEN 275	Dry valleys	1485 Coctaca, Humahuaca	Jujuy	23° 09′	65° 17′	3215
CHEN 277	Not characterized	1487 Rodero, Humahuaca	Jujuy	23° 06	65° 18′	3200
CHEN 414	Dry valleys	La Poma, La Poma	Salta	24° 42′	66° 11′	3016
CHEN 445	Not characterized	La consulta 659-Juella, Tilcara	Jujuy	23° 31′	65° 23′	2701

[a] Classification according to morpho-phenological and molecular markers (Short Sequence Repeats, SSR) (see Curti et al., 2012; Costa Tártara et al., 2012).

(piperazine-1,4-bis (2-ethanesulfonic acid) buffer and variable pH inside. The buffer's pH was calculated after previous assays of the food matrix in order to obtain a pH of 6.5 ± 0.2 after incubation in pancreatine. At the end of the pancreatin-bile incubation, the dialysis bags were removed and rinsed with water. Bag contents were transferred to tared flasks, weighed and analyzed for iron and zinc content by AAS after mineralization of the samples with HNO_3–$HClO_4$ (50:50) (Merk – Carlo Erba). Iron and Zinc Dialyzability (DFe % and DZn %, respectively) was calculated as the percentage of the mineral dialyzed with regard to the total concentration of the mineral in the sample.

2.6. Statistical analyses

Descriptive and multivariate analyses were carried out to characterize the nutritional diversity of quinoa accessions from Northwest Argentina. The mean, range, standard deviation (SD) and coefficient of variation (CV) were used to estimate and describe the position of the accessions in relation to each trait. Pearson's correlation coefficients were used to calculate the magnitude and type of association between each pair of traits. A set of multivariate analyses [Principal Component Analysis (PCA) and Cluster Analysis (CA)] were used to simultaneously examine several variables for each accession and to describe variation patterns in the germplasm characterized (Franco and Hidalgo, 2003). Principal Component Analysis was performed with Euclidean standardized trait variables and depicted in a two dimensional scatter plot. Eigenvalues >1 were considered as they describe significant variation in a data set (Cuadras, 2010). For classification (CA), the Un-weighted Pair Group Method with Arithmetic Mean (UPGMA) was chosen with the standardized Euclidean distance. A Multivariate Analysis of Variance was performed to facilitate the determination of the optimal numbers of groups. In this approach, groups obtained in each cutting point are considered as treatments and individuals falling within that group are considered as replications for those treatments. The analysis was then performed individually for each cut off point with all traits. The optimal number of groups was determined at that specific cut off point which revealed the highest *F* value (Mohammadi and Prassana, 2003). Groups formed by one accession were eliminated since their lack of replicates precluded analysis. Star charts were used to characterize the combinations of nutritional traits across the groups formed. Statistical analyses were conducted using the statistical software Infostat (Di Rienzo et al., 2014).

3. Results

3.1. Descriptive analyses of nutritional traits

3.1.1. Proximate composition

The proximate composition (g 100 g^{-1} dry basis (db)) of the 21 quinoa populations from NWA is shown in Table 2. According to the descriptive statistics, it was observed that mean protein content was 16.8% (14.5–18.2) and average fat content 5.9% (4.7–7.1). As expected, carbohydrates were the main seed components with an average of 51.4% (46.6–57.4). Besides, mean TDF was 12.1% with a wide range of variation (7.8–16.0).

3.1.2. Fatty acids composition

The fatty acid composition of quinoa lipids (g 100 g^{-1} of total fatty acids) in the 21 accessions from NWA is shown in Table 2. Results indicate that total unsaturated fatty acids (UFA) accounted for 83% (71.3–90.8) of total fatty acids; while total saturated fatty acids (SFA) were 17% (9.3–28.7), mainly palmitic acid (mean 14.5%, range 8.4–22.9; results not shown). Oleic acid (C18:1n-9) accounted for 25.4% (19.8–33.1) of fatty acid composition. Besides, quinoa seeds were a rich source of essential fatty acids such as linoleic (C18:2n-6): 50.4% (43.0–57.5) and α-linolenic (C18:3n-3): 6.6% (3.2–9.4). The oil fraction has a polyunsaturation index (PUFA/SFA) of 3.7 ± 1.1 (1.7–6.3) and an n-6/n-3 index of 8.5 ± 3.2 (4.9–17.4) (results not shown).

3.1.3. Total Fe and Zn content and its dialyzability

Table 2 shows total Fe and Zn content and its dialyzability in quinoa accessions from NWA. It was observed that mean Fe content was 2.5 mg 100 g^{-1} db (0.6–5.8) and average Zn content 2.5 mg 100 g^{-1} db (0.9–5.3) in raw quinoa seeds. Regarding mineral dialyzability, DFe% and DZn% mean values were 13.4% (9.6–22.8) and 11.2% (6.6–25.5), both wide ranges of variation, respectively.

Table 2
Proximate composition, iron and zinc content and its dialyzability (D%) and fatty acids composition of 21 quinoa accessions from NWA.

Accession N°	Moisture[a]	Protein[a]	Ash[a]	Fat[a]	TDF[a]	Carbohy-drate[a]	Fe[b]	DFe %	Zn[b]	DZn%	SFA[d]	UFA[d]	C18:1 n-9[c]	C18:2 n-6[c]	C18:3 n-3[c]
CHEN 458	10.8	14.5	3.9	5.2	13.7	51.9	1.4	11.0	2.0	8.0	18.0	82.0	28.0	52.6	4.7
CHEN 461	10.6	16.7	4.7	5.7	15.8	46.6	0.8	10.2	2.5	7.6	18.5	81.5	27.4	49.9	4.2
CHEN 465	8.6	16.7	4.4	5.0	13.5	51.9	1.3	11.7	1.9	6.6	9.3	90.8	33.1	54.8	3.2
CHEN 435	8.3	17.2	3.6	4.7	16.0	50.2	1.1	9.6	2.6	7.3	12.9	87.1	22.5	57.5	7.5
CHEN 58	8.7	17.4	4.7	5.7	13.1	50.4	3.9	10.6	2.0	12.7	11.9	88.1	26.5	50.1	4.6
CHEN 60	9.2	18.0	5.4	5.6	11.8	50.1	1.0	15.3	1.7	10.5	14.4	85.6	19.8	46.4	9.4
CHEN 182	9.4	16.4	5.6	5.0	14.5	49.1	4.5	16.0	4.1	9.2	13.9	86.1	24.1	54.2	7.7
CHEN 183	9.2	17.3	4.8	6.4	10.8	51.5	0.8	11.1	2.0	9.8	17.1	82.9	28.4	51.0	3.6
CHEN 212	9.0	18.2	5.5	5.9	13.3	48.2	1.0	11.0	2.4	8.6	26.9	73.1	20.7	44.2	8.2
CHEN 214	9.3	15.6	4.2	5.8	7.8	57.4	3.7	22.8	2.3	25.5	13.7	86.3	31.2	49.1	6.0
CHEN 215	9.2	17.2	4.4	5.8	11.9	51.4	0.6	15.7	0.9	8.9	17.2	82.8	25.4	51.3	6.1
CHEN 231	9.1	16.0	4.2	6.0	10.8	53.9	0.9	15.9	2.1	9.1	19.0	81.0	24.2	47.9	8.9
CHEN 232	9.1	16.3	5.0	6.4	11.6	51.7	5.4	10.7	2.8	15.3	18.8	81.2	27.6	48.2	5.5
CHEN 252	8.6	17.3	4.3	5.7	10.8	53.5	0.7	14.9	1.9	7.5	16.3	83.7	24.2	54.2	5.6
CHEN 256	9.0	17.2	6.5	6.0	12.9	48.4	5.8	10.5	3.5	10.6	22.4	77.6	23.1	48.3	6.1
CHEN 261	9.1	16.5	5.1	6.9	10.1	52.4	4.1	16.2	2.5	17.7	13.2	86.8	27.7	51.3	7.8
CHEN 273	9.5	17.1	4.3	7.1	9.7	52.2	1.1	16.3	1.9	9.6	11.0	89.1	25.3	53.7	8.9
CHEN 275	9.3	15.4	4.6	6.8	10.4	53.5	3.8	14.0	2.9	13.3	17.0	83.0	23.3	51.3	8.4
CHEN 277	9.2	17.6	3.9	6.8	9.0	53.6	4.3	17.1	2.7	18.2	16.2	83.8	27.4	49.5	6.9
CHEN 414	9.6	17.2	4.2	5.3	12.7	51.1	5.6	9.6	5.3	11.2	28.7	71.3	21.3	43.0	7.0
CHEN 445	10.3	17.4	5.0	5.0	12.9	49.5	0.8	11.5	1.7	8.1	20.2	79.8	22.8	49.7	7.4
Mean	9.3	16.8	4.7	5.9	12.1	51.4	2.5	13.4	2.5	11.2	17.0	83.0	25.4	50.4	6.6
Range	8.3–10.8	14.5–18.2	3.6–6.5	4.7–7.1	7.8–16.0	46.6–57.4	0.6–5.8	9.6–22.8	0.9–5.3	6.6–25.5	9.3–28.7	71.3–90.8	19.8–33.1	43.0–57.5	3.2–9.4
SD[d]	0.6	0.9	0.7	0.7	2.1	2.4	1.9	3.4	0.9	4.6	4.8	4.8	3.4	3–5	1.8
CV (%)[e]	6.7	5.3	14.6	11.8	17.5	4.6	76.8	25.1	38.4	41.3	28.4	5.8	13.2	7.0	27.6

[a] g 100 g^{-1} db.
[b] mg 100 g^{-1} db.
[c] g 100 g^{-1} of total fatty acids (SFA are the sum of C14:0, C16:0 and C18:0; while UFA correspond to C18:1n-9, C18:2n-6 and C18:3n-3).
[d] SD: Standard deviation.
[e] CV: Coefficient of variation.

3.2. Association between nutritional traits

Of the 66 correlation coefficients evaluated (Table 3), eight exhibited highly significant values ($P < 0.01$) with an $r \geq 0.62$ and three exhibited significant association ($P < 0.05$) with an $r \geq 0.36$. Total dietary fiber content was inversely associated with carbohydrate content (−0.81), Fe and Zn dialyzability (−0.74 and −0.70, respectively) and fat content (−0.71). Carbohydrate content was positively associated with Fe and Zn dialyzability (0.70 and 0.62, respectively), as well as dialyzability between Fe and Zn (0.63) among each other. Similarly, the total content of Fe and Zn were positively associated (0.73) (Table 3). On the other hand, carbohydrate content was inversely associated with protein and ash (−0.45 and −0.54, respectively). The fat content was positively associated with Zn dialyzability (0.46) (Table 3).

3.3. Multivariate analyses: interrelationships between nutritional traits and patterns of variation within the germplasm

The multivariate analysis is shown in Fig. 1. The PCA results show that the first three components concentrate 71% of total variation. The first component (PC1) explained most of this variation (34.7%) and discriminated between accessions according with high TDF, low carbohydrates content, and low Fe and Zn dialyzability to the right and those with opposite trends to the left.

PC2 explained 18.7% of total variation and ordered accessions according to a gradient of the PUFA/SFA and n-6/n-3 ratios and ash content. As indicated in Fig. 1, accessions with higher ash content and low PUFA/SFA and n-6/n-3 ratios were positioned to the lower part on the graph on PC2 while accessions with high polyunsaturated/saturated and n-6/n-3 ratios were placed to the top of

Table 3
Pearson's correlation coefficients among nutritional traits of quinoa accessions.

	Moisture	Protein	Ash	Fat	TDF	Carbohy-drate	Total Fe	Total Zn	DFe%	DZn%	PUFA/SFA	n-6/n-3
Moisture	1											
Protein	−0.39	1										
Ash	−0.03	0.29	1									
Fat	−0.03	−0.03	0.07	1								
TDF	0.15	0.12	0.16	−0.71**	1							
Carbohy-drate	−0.23	−0.45*	−0.54	0.34	−0.81**	1						
Total Fe	−0.13	0.14	−0.12	0.37	−0.43	0.29	1					
Total Zn	−0.03	−0.14	−0.21	0.25	−0.33	0.34	0.73**	1				
DFe%	−0.09	−0.21	−0.15	0.36*	−0.74**	0.7**	0.31	0.21	1			
DZn%	−0.1	−0.24	−0.06	0.46	−0.7**	0.62**	0.04	−0.18	0.63**	1		
PUFA/SFA	−0.36	−0.07	−0.24	−0.02	−0.07	0.26	0.3	0.17	0.28	0.05	1	
n-6/n-3	−0.02	−0.15	−0.18	−0.24	0.24	−0.04	−0.16	0.14	−0.32	−0.23	0.41	1

*Significant at level 0.05.
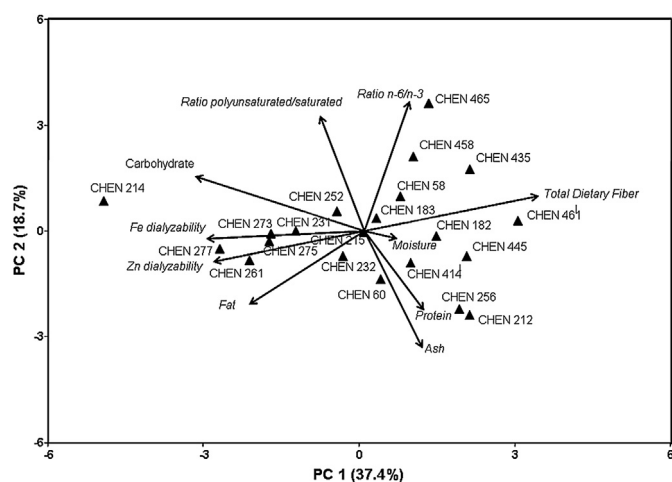**Significant at level 0.01.

Fig. 1. Biplot of the first and second principal components for 21 quinoa accessions described for 10 nutritional traits. Accessions are presented by triangles and traits are represented by vectors. Numbers between brackets indicate the % of total variation explained by each component.

the plot on PC2. It is noteworthy that accession CHEN 215 (from Cieneguillas, Tilcara, Jujuy, a Dry Valley environment) was placed at the centre of the Biplot, which means that it shows equitable contents for all nutritional traits analyzed (Fig. 1). The last principal
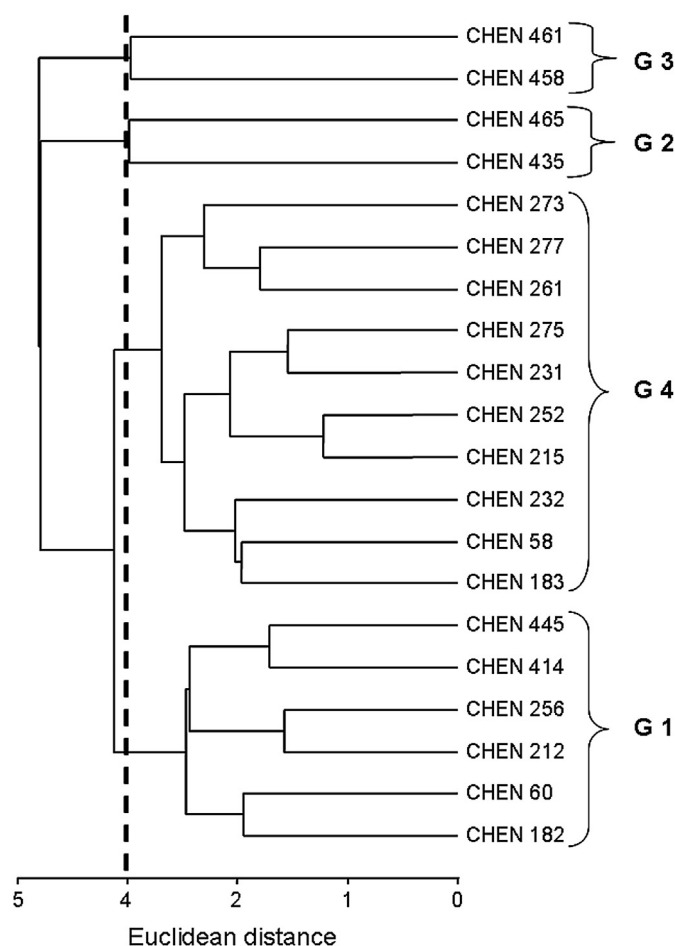
Fig. 2. Dendrogram showing 21 quinoa accessions in the UPGMA according to nutritional traits.

component selected (PC3) explained 17% of total variation and ordered accessions according to a gradient of moisture and protein content. Accessions with high protein content showed low moisture content and vice versa (results not shown), however a clear and significant association between these traits and the origin of accessions was not detected.

The dendrogram resulting from Cluster Analysis shows four main groups formed at a cut-off Euclidean distance of 4 (Fig. 2). In general, cluster results revealed subtle differences between geographic origins, as the majority of clusters (G1, G2 and G4) were formed by accessions from Dry Valleys and Transition Zone, whereas G3 by accessions from Humid Valleys (Fig. 2 and Table 1). According to star charts, G1 showed an equitable amount for all nutritional traits; whereas differences were observed in moisture, PUFA/SFA ratio, carbohydrate and protein content between G2 and G3 groups (Fig. 3). On the other hand, DFe% and DZn%, TDF and fat content showed differences between G4 vs. G2 + G3 (Fig. 3).

4. Discussion

According to Costa Tartara et al. (2012) and Curti et al. (2012), Argentinean quinoa germplasm is highly diverse at phenotypic and genetic levels, reflecting variation in the environment of origin. In our study, results suggest that nutritional properties of 21 different quinoa populations from NWA also show a wide range of variation but with only subtle differences according to the population's origin.

Regarding proximate composition, our results are similar to those reported in quinoa literature. Several studies reports that protein content ranges from 12 to 23% (Abugoch, 2009; Vega-Gálvez et al., 2010). Our result (14.5–18.2%) fits into this range with an average of 16.8%. On the other hand, many studies revealed that quinoa's fat content ranges from 1.8 to 9.5%, with an average of 5.7% (Abugoch, 2009; Vega-Gálvez et al., 2010), similar to our findings (mean 5.9%, range 4.7–7.1). However, ash content found in quinoa seeds from NWA (3.6–6.5%) is higher than that reported by other authors (3.0–3.8%) (Vega-Gálvez et al., 2010).

As is known, total protein content of quinoa is higher than barley (10.2%), rice (6.9%) or corn (9.5%) and closer to wheat (12.4%) (Closa and de Landeta, 2010; Abugoch, 2009). This is explained by the high embryo relative size which can make up to 60% of quinoa seed weight (Valencia-Chamorro, 2003). In *Amaranthaceae* such as quinoa, albumins and globulins are the main protein fraction (44–77%), greater than that of prolamins (0.5–7.0 %). Quinoa is considered a gluten-free grain because it contains very little or no prolamins (Valencia-Chamorro, 2003) so that foods elaborated with quinoa are suitable for celiac patients.

Otherwise, quinoa oil content is higher than corn (0.9%) and lower than soybean (24.2%) (Closa and de Landeta, 2010). Fatty acid composition of quinoa accessions from NWA is similar to previous works, reporting 12–19% saturated fatty acids (palmitic acid mainly), 25–29% total monounsaturated acids (oleic acid mainly) and 52–63% PUFA, predominantly linoleic acid (about 90%) (Abugoch, 2009). The oil fraction of Argentinean quinoa accessions has high quality based on the fact that it has a high content of linoleic and linolenic acid with PUFA/SFA and *n*-6/*n*-3 ratios according to dietary recommendations (NAS, 2005).

Quinoa is considered as a good source of minerals. It contains large amounts of Ca, Fe, Zn, Cu and Mn. However variability in mineral concentrations is observed. For instance, Fe and Zn content (mg kg^{-1} dry weight) ranges from 14 to 168 and 28 to 48, respectively (Vega-Gálvez, 2010). Our results are near the lowest reported values but similar to those of Cervilla et al. (2012) for quinoa seeds from the province of Salta and by Repo-Carrasco-Valencia et al. (2010) for quinoa from Perú (red quinoa, Pasankalla variety).
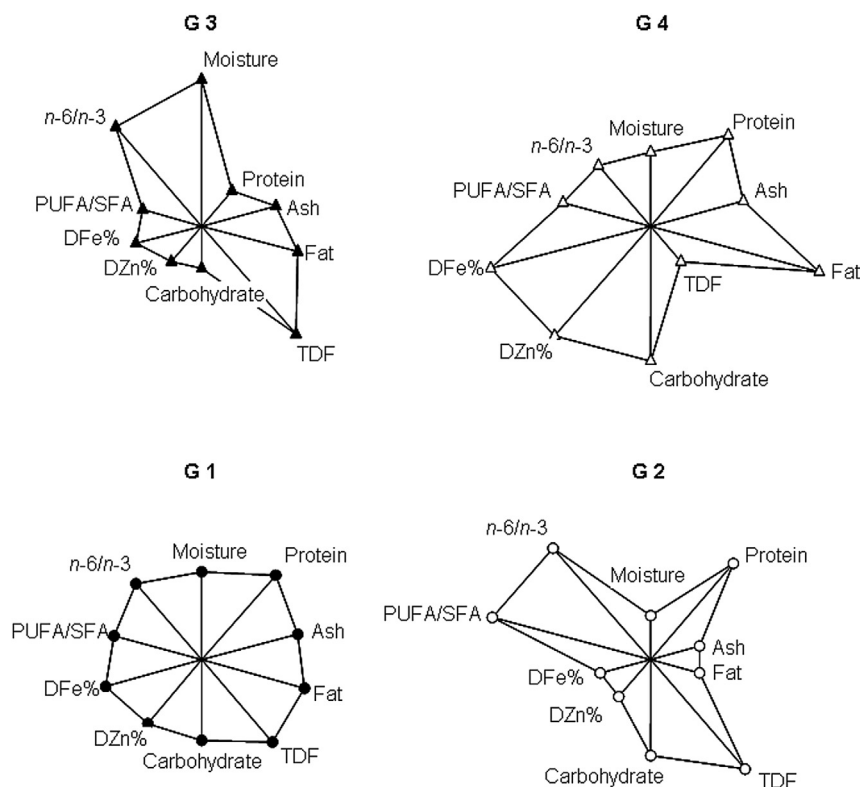
Fig. 3. Star charts for nutritional traits of groups recognized in cluster analysis. Nutritional traits are indicated in the vertex of each graph.

Besides this, 43% of the quinoa accessions characterized in this work presented Fe and Zn content consistent with values for quinoa from Bolivia and Perú (FAO/Latinfoods, 2009). Compared with un-enriched wheat flour (iron, 0.68 mg 100 g^{-1}; zinc, 0.98 mg 100 g^{-1}) (Dyner et al., 2007), concentrations of these minerals are considerably higher in Argentinean quinoa seeds; however, Fe and Zn content are similar in whole meal wheat flour (iron, 3.3 mg 100 g^{-1}; zinc, 3.8 mg 100 g^{-1}) (FAO/Latinfoods, 2009). Also, iron content in quinoa is higher than in rice (1.32 mg 100 g^{-1}) and finger millet (2.13 mg 100 g^{-1}) (Repo-Carrasco-Valencia et al., 2010).

As well as knowing the mineral content, it is important to study its bioavailability, which refers to the amount of minerals that is absorbed in the gastrointestinal tract and utilized for metabolic functions. It is lower in plant than in animal sources because of the presence of certain compounds, like dietary fiber, phytate and oxalate, which have negative effects on mineral absorption. The term bioaccessibility refers to the amount of a substance that is available for absorption. Strictly, bioavailability includes bioactivity as well as bioaccessibility (Fernandez-García et al., 2009) but most of the times, bioavailability and bioaccessibility terms are used indistinctly. Fe and Zn dialyzability were analyzed in this study as a predictor of potential bioaccessibility. According to our findings, mean DFe% and DZn% are ~13 and 11%, respectively. These values are higher than those reported by Repo-Carrasco-Valencia et al. (2010) for raw quinoa seeds from Perú. On the other hand, if we compare mineral dialyzability values in quinoa accessions from NWA with those in wheat flour (FeD% 9.8; ZnD% 10.1) (Dyner et al., 2007), they are similar. However, given the high content of minerals in quinoa, the potential contribution of iron and zinc would differ greatly from that in wheat flour, but *in vivo* impact should be studied in more detail.

This is the first study reporting the interrelationships among nutritional traits in a set of quinoa accessions growing on the same environment, such that differences between them could be ascribed to genetic effects differentiating it from environmental and genotype-by-environment interactions. In this sense, results of interrelationships among traits could be used as a proxy to set out future prospects for breeding programs aimed to improve the nutritional attributes in this species. According to our results, the strong and inverse relationship between total dietary fiber and Fe and Zn dialyzability should be of major relevance given the negative effect that total dietary fiber has on mineral absorption. Meanwhile, a significant relationship was not observed between TDF and total Fe and Zn content. On the other hand, these relationships define subtle differences among accessions from Dry and Humid valleys, showing those from Humid valleys (right side along the PC1 in Fig. 1; accessions CHEN 212, 458 and 461) having higher TDF than those from Dry valleys (left side in Fig. 1) and vice versa for Fe and Zn dialyzability. However, it is important to note that within the germplasm characterized, one accession (i.e., CHEN 215, from Cieneguillas, Tilcara, within the Humahuaca dry valley) showed an equitable amount of all nutritional traits and could be a promising material for future breeding programs. All other interrelationships did not distinguish between accessions from diverse origins, which means that their combination in future breeding lines could be straightforward without considering their origin.

Although only subtle differences were observed between accessions from diverse origins in general, the majority of clusters were formed by mixed populations from Dry valleys and the Transition Zone. In this sense, the Argentinean quinoa germplasm did not show a clear genotypic structure according to nutritional traits as is the case with phenotypic and genotypic traits evaluated on a similar set of accessions (Costa Tártara et al., 2012; Curti et al., 2012). However, it is important to note that in the present study, accessions from the Highlands were not characterized, because of

their low quantity of seed that precluded further analysis for these accessions, and their inclusion in future studies could bring an idea of germplasm structure considering accessions from the whole range of distribution of this crop in the NWA region.

5. Conclusion

This study generates knowledge about nutritional traits and its interrelationships of native quinoa germplasm from Northwest Argentina in order to continue the characterization of this germplasm performed by Costa Tártara et al. (2012) and Curti et al. (2012). As was discussed, nutritional properties of studied quinoa accessions collected in different eco-regions from Northwest Argentina, but grown on the same environment, showed a wide range of variation with only subtle differences according to the population's origin. Nevertheless, Argentinean quinoa germplasm did not present clear genotypic structures according to nutritional traits. For the first time, multivariate analysis is used as a tool to characterize associations between nutritional traits, accessions and environment of origin in Argentinean native quinoa germplasm, a promising avenue to guide breeding for seed quality on quinoa and other crops.

Acknowledgments

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