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Characterisation of nutrient profile of quinoa (*Chenopodium quinoa*), amaranth (*Amaranthus caudatus*), and purple corn (*Zea mays* L.) consumed in the North of Argentina: Proximates, minerals and trace elements

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ABSTRACT

Quinoa, amaranth and purple corn are Andean cereals largely consumed in North of Argentina. Nutrient analysis with the purpose of inclusion in the Argentinean FCDB and e-search EuroFIR has become urgent matter. In this work proximate and mineral profile of Andean cereals cultivated in the North of Argentina were determined and compared with rice. Proximate analysis showed that Andean cereals have similar profile but significantly higher ($p < 0.05$) than rice. Andean cereals are rich sources of iron, copper, manganese and zinc and better than rice. Phosphorus and magnesium quinoa content could contribute up to 55% of consumers DRI. Andean cereals and rice are poor sources of potassium. To guarantee the interchange of data among users and producers of FCDB component values were obtained in compliance with EuroFIR guidelines for compilation process. Present work provides necessary information to FCDB users who wish to have access to food reference analytical parameters.

1. Introduction

Quinoa (*Chenopodium quinoa*), amaranth (*Amaranthus caudatus*) are known as pseudocereals and purple corn (*Zea mays* L.) is a cereal all of Andean origin cultivated in Argentina for thousands of years after domestication at 3000 B.C years ago. The Argentine people supported in their Andean culture and tradition have maintained and preserved quinoa, amaranth and purple corn as a staple food even during the Spanish conquers period when the crop of these Andean cereals was forbidden (Pedreschi & Cisneros-Zevallos, 2006; Rastogi & Shukla, 2013; Valencia, Encina, Binaghi, Greco, & Ferrer, 2010a).

Quinoa and amaranth are considered crops with large genetic variability and therefore adapted to diverse agro-climatic habitats and edaphic conditions. High yields depending on Germplasm lines and quality trials are obtained in salinity regions, at higher and lower elevations, from sea level up to Himalayas even in monsoon climate or regions with mild seasons (Bhargava, Shukla, Rajan, & Ohri, 2007; Rastogi & Shukla, 2013). Purple corn is a rare and ancient Andean cereal with large kernels. It is grown for culinary purposes, but has also recently been studied for its health benefits since it apparently has unusually high levels of antioxidants and anti-inflammatory properties, namely anthocyanin (Pedreschi & Cisneros-Zevallos, 2006; Pedreschi & Cisneros-Zevallos, 2007).

In nineties quinoa has been classified by NASA as an emerging crop with excellent nutritional properties for long term human space missions due to its high content in protein and unique amino acid composition in particular in what respects to lysine and sulfur amino-acids (Schlick & Bubenheim, 1993). Meanwhile quinoa and amaranth were introduced in several countries outside of Andean region. Quinoa is also cultivated in England, Sweden, Denmark, the Netherlands, Italy and France. Recently France has reported an area of 200 ha with yields of 1080 kg/ha and Kenya has shown high seed yields (4 t/ha). Purple Corn is also grown in Ecuador, Bolivia and Chile. The strongest interest in amaranth (investigation and production) in Europe has been in Austria, Czech Republic, Slovak Republic, Germany, Hungary, Poland, Russia, Italy and Slovenia. In Canada, United States, Japan, Australia and European Countries these Andean cereals evidence an increasing acceptance

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regarding food consumer preferences (Hirose, Fujita, Ishii, & Ueno, 2010; Rastogi & Shukla, 2013; Valencia et al., 2010a).

The interest of these non-Andean countries by these cereals can be explained by their properties as functional gluten-free ingredients of bread, pasta and confectionary products. The importance of this healthy gluten-free products gain major interest since protein availability of these set of cereals was demonstrated in animal and human studies as being better than other common products gluten-free.

The successful application of Andean cereals in foods gluten-free was demonstrated in several studies and recently reviewed by Alvarez-Jubete, Arendt, and Gallagher (2010). The authors have demonstrated that a well-balanced diet in protein, fibre, calcium, iron and vitamin E could be obtained whenever these Andean cereals take part in the diet by replacing other gluten-free ingredients. Moreover, due to their rheological properties, sensory characteristics, nutrient profile and stability the gluten-free formulations based on quinoa or amaranth confers a texture similar to corn based formulations. In parallel, the taste, smell and flavor influence and reinforce consumer preferences (Giménez et al., 2012, 2013).

The nutritional properties of quinoa and amaranth seeds cultivated in Andean region and in Europe were compared by several authors and differences were observed in nutrient content, as well as in flavonoid contents. Quinoa and amaranth are a good source of flavonoids and other bioactive compounds with putative health effects (Rastogi & Shukla, 2013; Valencia, Hellstrom, Pihlava, & Mattila, 2010b). In crops cultivated in Japan a higher content in bioactive compounds was observed when compared to those cultivated in South America (Hirose et al., 2010). Schoenlechner, Wendner, Siebenhandl-Ehn, and Berghofer (2010) have analysed quinoa and amaranth folate profile in bread, noodles and pasta and postulated that quinoa could be an alternative for folate source in normal subjects. Studies performed on animals have recently reported a gastro protective activity of quinoa seeds (Schoenlechner et al., 2010; Stikic et al., 2012). These effects are mainly attributed to Arabinose and arabinose-rich pectic polysaccharides that compose the dietary fibre of quinoa. Studies on genetic variability of 27 lines of quinoa grown on the same climatic conditions have demonstrated a high correlation with nutritional quality. These studies indicated that an accurate estimation of dietary intake should be calculated through local crops.

Recognising the importance of quinoa "in providing food security and nutrition and in the eradication of poverty" the General Assembly of United Nations has designated, in its resolution A/RES/66/221, the year 2013 as being the International Year of quinoa.

In the last decade the consumption of quinoa and amaranth has growth substantially across the world (Giménez et al., 2013). In spite of their nutritional importance only a few Food Composition Databanks (FCDB) include quinoa and amaranth as part of their food composition data (EUROFIR, 2013). This information is available in USA and Canada Databanks, both from the same analytical data source (EuroFIR, 2013). Information on purple corn composition is even more deficient. Therefore and as far as the authors are aware, no analytical work that involves quinoa, amaranth and purple corn was reported with the purpose of inclusion in a FCDB.

The aim of this work was to characterise proximate and mineral profile of quinoa, amaranth and purple corn consumed in the north of Argentina and originated from Jujuy Province crops. The study was framed by accepted EuroFIR quality criteria with the purpose of guaranteeing data results reliability and future inclusion in Argentinean Food Composition Data and throught other national food composition databases be included in EuroFIR e-search. A second objective was to compare nutrient profile of these Andean cereals with rice as gluten-free ingredients of cereals based foods.

2. Materials and methods

2.1. Samples and sample preparation

Samples of quinoa, amaranth and purple corn complete seeds were obtained from a Cooperative of Producers (CAUQUEVA-Tilcara, Jujuy, Argentina). White polished rice was obtained from local factories in Portugal (Ribatejo). Primary samples were taken according to a selective sampling plan. In this phase five samples of each material were collected just once for purple corn and amaranths. Quinoa and rice samples were collected in two consecutive years.

The samples were immediately prepared after receipt in the laboratory. Quinoa was washed for 20 min with tap water with the aim to eliminate bitter taste and toxic saponins. Washed grains were dried at 45 °C for 12 h. Dried seeds were packed in vacuum bags and stored at room temperature until they used in analysis and processing. Amaranth, purple corn and white rice samples seeds were homogenised and milled using a high speed grinder, a knife mill GRINDOMIX GM 200 equipped with titanium knives to prevent contamination. The prepared samples were stored in vacuum bags at room temperature until processing. The food products were analysed raw.

2.2. Reagents and chemical standards

All reagents were of high analytical grade. Deionised water of level I, as EN ISO 3696, was used for the preparation of all solutions. The nitric acid (65%) and hydrogen peroxide solutions used were of ultrapure grade, and nitric acid (65%) was first distilled, in acid distillation system (Milestone SubPUR).

A 2% concentration solution of nitric acid was used to prepare working standard solutions, to dilute samples and to prepare blanks. A nitric acid solution with a 2–4% concentration was used to wash up the ICP-OES and ICP-MS sample introduction system.

Working multi-element standard solutions were prepared from mono-element high purity ICP stock standards containing 1000 mg/L of each element (Copper, Manganese, Iron, Zinc, Magnesium, Calcium, Phosphorus, Sodium and Potassium).

Working multi-element standard solutions of Nickel, Molybdenum, Strontium, Vanadium, Lithium, Cobalt, Selenium were prepared from multi-element solution XVI (21 elements diluted in acid nitric), high purity ICP stock standard 100 mg/L.

2.3. Analysis

2.3.1. Proximate

2.3.1.1. Moisture and ash contents. Moisture content was determined by gravimetric method, using a dry air oven from Heraeus Instruments, Hanau, Germany, at 102 °C ± 2 °C during 2 h, using 5 g of sample, until constant weight (AOAC 952.08, 2000); EuroFIR Method indicator ME1103. Total ash analysis was carried out in a muffle furnace M110 (Heraeus Instruments , Hanau, Germany) at 525 °C ± 25 °C for 20 h, using 5 g of sample, until constant weight, according to AOAC 923.03 (2000); EuroFIR Method indicator MI 1018.

2.3.1.2. Extraction and quantification of total fat. Total fat determination was performed with an acid hydrolysis method (AOAC 948.15, 2000) – EuroFIR Method indicator MI 1202 – followed by extraction using a Soxhlet apparatus (Soxtec™ 2050) for 1 h 30 min with petroleum ether (40–60 °C), as the extraction solvent. The residue obtained was dried for 1 h 30 min at 102 °C ± 2 °C, until constant weight.

2.3.1.3. Extraction and quantification of total protein. Each sample was analysed in duplicate for total nitrogen by the Kjeldahl method in combination with a copper catalyst using a block digestion system Foss Tecator 2006 Digestor (Höganäs, Sweden) and a Foss 2800 Kjeltec AutoDistillation unit (Foss Tecator) (AOAC 991.20, 2000); EuroFIR Method indicator MI 1039. The protein content was calculated by using 6.25 for pseudocereals and purple corn and 5.95 for rices the conversion factors, according to FAO, (1973).

2.3.1.4. Extraction and quantification of fibre. The content of total dietary fibre (TDF) was determined by the enzymatic–gravimetric method (AOAC, 2000); EuroFIR Method indicator MI 1307. Samples were weight in duplicate (0.5 g) and enzymatic digestion with α-amylase, protease and amyloglucosidase was applied. A duplicate blank assay was performed using the same procedure than digested samples.

2.3.1.5. Extraction and quantification of starch and amylose. The content of *amylose* was determinate by a test kit (Megazyme kit – K-AMYL 07/11) which is a modification of a Con A method developed by Yun and Matheson (1990). It uses an ethanol pre-treatment step to remove lipids prior to analysis [modified from Morrison and Laignet (1983)]. The concentration of amylose in the starch sample is estimated as the ratio of *Glucose oxidase–peroxidase* (*GOPOD*) reagent absorbance at 510 nm of the supernatant of the Con A precipitated sample, to that of the total starch sample. The content of *starch* was determinated by a test kit (Megazyme kit – K-TSTA 07/11). Total starch assay kit is based on the use of thermostable α-amylase and amyloglucosidase (McCleary, Gibson, & Mugford, 1997). This method has been adopted by AOAC (Official Method 996.11) and AACC (Method 76.13), EuroFIR Method indicator MI 1060.

2.3.2. Mineral and trace elements

Samples digestions were undertaken using a closed-vessel microwave digestion system, Milestone ETHOS 1 Series; EuroFIR Method indicator MI 1196. Cereals samples powders were weighted (0.5 g) to proper Teflon digestion vessels. A mixture of concentrated nitric acid (4 mL), hydrogen peroxide (1 mL) and deionised water (3 mL) was carefully added, and vessels were properly closed and introduced into the microwave oven. A microwave program was established and optimised. Vessels were thereafter cooled to room temperature and digested samples were diluted up to 25 mL with deionised water, for subsequent determination of minerals and trace elements. To assess possible contamination, blank solutions were prepared containing the same reagents and using the same procedure as the samples and standards. An inductively coupled plasma optical emission spectrometer, ICP-OES Thermo iCAP 6000 series, with radial and axial configuration, was used for Cu, Mn, Fe, Zn, Mg, Ca, P, Na and K determinations; EuroFIR Method indicator MI 1305. After an interferences study, measurements were performed at the following emission lines (nm): Cu 324.754, Mn 259.306, Fe 259.940, Zn 213.856, Mg 279.553, P 178.284 or 177.495, Ca 184.006, Na 589.592, K 769.896. ICP-OES operating conditions were optimised as follows: Auxiliar Flow: 0.5 L/min, Plasma Orientation: radial or axial, RF power: 1200 W, Peristaltic pump's speed (Flush pump rate and analysis pump rate): 50 rpm, Pump stabilisation time: 5 s, Integration time in UV and Visible: 15 and 10 s.

An inductively coupled plasma Mass spectrometer, ICP-MS Thermo X series II, was used for determination of the following trace elements: ^{60}Ni, ^{95}Mo, ^{88}Sr, ^{51}V, ^{7}Li, ^{59}Co, ^{82}Se; EuroFIR Method indicator MI 1209. Operating conditions for ICP-MS were optimised as follows: Extraction: −113.7, Focus: 10.0 Pole Bias: −0.1, Hexapole Bias: −3.0, Nebulizer flow rate: 0.87 L min^{-1}, Forward Power: 1404 W, Cool gas flow rate: 13.0 L min^{-1}, Auxiliary gas flow rate: 0.90 L min^{-1}, Sampling Depth: 120, Standard Resolution: 135, High Resolution: 150, Analogue Detector: 1902, PC Detector: 3353.

2.4. Quality assurance and quality control

The optimisation of analytical conditions, including the sample digestion process, was carried out under an Internal Quality Control procedure implemented in laboratory and in accordance with EuroFIR guidelines for laboratory analysis. This included criteria on sample handling, appropriate analytical method and adequate internal and external analytical quality control.

For ICP-OES and ICP-MS analysis two multi-element standard solutions were prepared as working multi-element standard solutions, but from stock standards of a different brand or lot. These quality control solutions were measured during the same assay session in intervals of 10–12 samples and with an acceptance criterion of ±10%. All analyses were carried out in triplicate and/or duplicate.

Methods performances were monitored by analysing appropriate reference materials and are shown in Table 1 – Laboratory performance was guaranteed by regular participation in proficiency testing (PT) schemes launched by PT providers.

3. Results and discussion

3.1. Analytical data quality assurance

Quality assurance results for proximate, mineral and trace elements analysis of cereals and pseudocereals under study are presented in Table 1. This study included appropriate analytical method criteria in terms of precision and accuracy, limit of quantification (LoQ), selectivity, and an effective internal and external quality control program including appropriate use of Certified Reference Materials (CRM) and participation in adequate PT Schemes. Accuracy was determined by Certified Reference Materials or Recovery of spiked samples with chemical standards. For all assays the values obtained were within acceptance criteria range. The laboratory competence was successfully demonstrated in Proficiency testing program launched by providers complying with ISO 17043. All the methods were validated following EuroFIR guidelines.

The choice of internal standards was a critical parameter for ICP-MS analysis. The effect of Internal Standard (IS) concentrations was monitored by comparing the added amount with the recovery percentages.

3.2. Quality index of data enter in FCDB

Another important aspect of quality assurance in FCDB is the quality assessment system applied by compilers to assess the FCDB data quality. This is a global issue in the FCDB data compilation process, and laboratories who intend to produce this type of analysis should be aware of this recommendation. Moreover, quality scores associated to nutrient data are widely accepted for enhancing general information of FCDB users and stakeholders. These circumstances require appropriate methodologies for analytical and compilation activities that guarantee confidence in the values entered into FCDBs. Several countries have developed a Quality System to evaluate the level of data that can be part of published data (Bhargava et al., 2007). In Europe EuroFIR recently published the quality assessment and the quality index guidelines. All categories (food description, sampling, number of samples, analytical method, laboratory performance and quality control) were revised and validated by EuroFIR compilers, and precise guidelines for their assessment were defined. For relevant nutrients and food

Table 1
Quality assurance results for nutrient analysis of cereals under study.

Parameter	Units	Method of analysis	LoQ	SRM/CRM/QCM	Certified Value ± *U*	Analysed values
Proximate						
Protein	g/100 g	Kjeldahl	0.3	(ii) NIST 3244	66.1 ± 1.3	65.6–66.3
Moisture	g/100 g	Oven-drying	0.1	(iii) NIST 1846	1.98 ± 0.27	1.77–1.91
Ash	g/100 g	Ignition in muffle furnace	0.1	(iv) NIST 2383	1.09 ± 0.04	1.09–1.11
Fat	g/100 g	Acid digestion, ether extraction	0.1	(v) BCR 381	1.06 ± 0.20	0.86–0.94
Fibre	g/100 g	AOAC 985.29	0.4	(vi) BIPEA 20/310	23.4 ± 3.0	22.4–22.6
Mineral						
Copper	mg/kg	ICP-OES	0.02	(i) NIST 1548a	2.3 ± 0.16	2.2–2.5
Manganese	mg/kg		0.01		5.7 ± 0.17	5.2–5.7
Iron	mg/kg		0.05		35 ± 3.77	28–34
Zinc	mg/kg		0.05		25 ± 1.79	23–26
Magnesium	mg/kg		0.4		580 ± 26.7	550–600
Calcium	mg/kg		0.2		1970 ± 113	1910–1960
Phosphorus	mg/kg		0.4		3490 ± 245	3300–3570
Sodium	mg/kg		1.0		8130 ± 942	7760–8420
Potassium	mg/kg		1.0		6970 ± 125	6660–7240
Trace elements						
Molybdenum	μg/kg	ICP-MS	0.50	(i) NIST 1548a	260 ± 17	249–254
Strontium	μg/kg		0.50		2930 ± 100	2665–2951
Cobalt	μg/kg		0.25		28[a]	21–27
Lithium	μg/kg		0.25	Recovery	80 – 120 (%)	104–120 (%)
Vanadium	μg/kg		0.25			100–112 (%)
Nickel	μg/kg		0.50			97–102 (%)
Selenium	μg/kg		0.50			80–107 (%)

(i) NIST SRM 1548a Typical Diet, National Institutes of Standards and Technology, Gaithersberg, MD, USA.
(ii) NIST 3244 – Ephedra – Containing Protein Powder, National Institutes of Standards and Technology, Gaithersberg, MD, USA.
(iii) NIST SRM 1846 – Infant Formula, National Institutes of Standards and Technology, Gaithersberg, MD, USA.
(iv) NIST SRM 2383 – Baby Food Composite, National Institutes of Standards and Technology, Gaithersberg, MD, USA.
(v) BCR 381 – Rye Floor – Institute for Reference Materials and Measurements (IRMM), European Commission (EC).
(vi) BIPEA – International Bureau for Analytical Studies, Proficiency Testing Programs – Product riche en fibres – Valeur Caloriqueindicative value (Quality Control Material).
[a] Indicative value for Cobalt.

groups a test of this new system was conducted in EuroFIR Nexus. Therefore, in order to assess data quality produced in this work seven categories are presented in Table 2. For each category only relevant criterion is considered. As it can be verified in what respects to each of the foods being considered in the present study, a positive answer can be obtained. Sampling plan as recommended in guidelines was not applied because data representativity can be aggregated as a normal procedure of compilation process (Westenbrink, Oseredczuk, Castanheira, & Roe, 2009). The aggregation criteria were also discussed in Castanheira et al. (2011). First criterion is food description. Therefore the scientific name and geography origin of cereals are described in Table 3. The name of the components is in agreement with the prioritised list of nutrients published by EuroFIR and they are well characterised as minerals and proximate (Westenbrink et al., 2009). Detailed information concerning quality control and appropriated reference materials are described in Table 1. Therefore for quinoa, amaranth, rice and purple corn detail information for compilers is given. This is a guarantee that values can enter in Argentina and Portugal food composition databank to be part of data used in EuroFIR e-platform and fulfills the check list defined by EuroFIR.

3.3. Proximate analysis

The proximate composition of quinoa, amaranth, purple corn and rice, including dietary fibre, are presented in Table 3. All the values are evaluated by appropriate quality control procedures as a guarantee of reliability and further comparability. The moisture of Andean cereals varies between 10.00 g/100 g (purple corn) and 11.30 g/100 g (quinoa), and 13.10 g/100 g, (rice). These values were in the range usually found in other commercial varieties of Andean cereals (Alvarez-Jubete et al., 2010). The protein contents (>12 g/100 g) of the Andean pseudocereals were much higher than those of rice indicating that both quinoa and amaranth constitute a rich source of protein. These values are in agreement with those reported in Bhargava, Patterson, and Holden (2009), who studied three germaplasm lines originated from Jujuy/Argentine. The current fat levels of quinoa and amaranth (6.31 g/100 g to 6.43 g/100 g) were much higher than in the rice samples (0.60 g/100 g). These values are in line with those reported for white rice, long grain, regular, raw, unenriched reported in several FCDB including USDA (EUROFIR, 2013) and lower than the values determined by Ruales and Nair (1993). The content of dietary fibre present similar values to those reported in USDA FCDB and, once more, lower than the values found by Ruales and Nair (1993). Nevertheless all these crops presented from 7 to times higher fibre content than rice, confirming that the Andean crops constitute a good source of dietary fibre. The starch values are in line to those reported by Atwell, Patrick, Johnson, and Glass (1983), who have reported a range of 51 g/100 g–61 g/100 g, which can have an application in emulsion food products or even as biodegradable fillers in low-density polyethylene (LDPE) films (McCleary et al., 1997). The ash content between quinoa and amaranth does not reveal significant differences, but the rice's ash content was significantly lower than the one found in quinoa, amaranth and purple corn. This finding is expected and complies with the values typically reported in literature (Valencia et al., 2010a,b).

3.4. Mineral and trace analysis

3.4.1. Digestion procedure

The sample preparation including closed vessel microwave digestion is a slow step of overall analytical process. Therefore a consistent development of microwave digestion was necessary and was carried out, using spiked samples as parameters to control the efficiency of decomposition procedure. Recovery rates ($80 < R\% < 120$) of spiked solutions were used to check acceptance criteria following the methodology developed by for Quality Index

Table 2
Evaluation of quality of foods studied and their analysis to score quality index, as defined by EuroFIR.

Category	Criteria of assessment	Answer			
		Quinoa	Amaranthus	Maize	Rice
Food Description	Is the food group (e.g. beverage, dessert, savoury snack, pasta dish) known?	Y	Y	Y	Y
	Was the food source of the food or of the main ingredient provided (best if scientific name included, cutivar/variety, genus/species, etc.)?	Y	Y	Y	Y
	Was information about the geographical origin of the food provided?	Y	Y	Y	Y
	Was the moisture content of the sample measured and the result given?	Y	Y	Y	Y
Component identification	Is the component described unambiguously?	Y	Y	Y	Y
	Is the unit unequivocal?	Y	Y	Y	Y
	Is the matrix unit unequivocal?	Y	Y	Y	Y
Sampling Plan		N	N	N	N
Sampling Handling	If relevant, were appropriate stabilisation treatments applied (e.g. protection from heat/air/light/microbial activity)?	Y	Y	Y	N.A.
	Were the samples homogenised?	Y	Y	Y	Y
Analytical Method	Does the analytical method used in the source match the list of appropriate analyticalmethods given in the guidelines for analytical methods?	Y	Y	Y	Y
	Are the key method steps appropriate for the method described?	Y	Y	Y	Y
Analytical quality control	Were analytical portion replicates tested?	Y	Y	Y	Y
	Was the laboratory accredited for this method or was the method validated by performance testing?	Y	Y	Y	Y
	If available, was an appropriate reference material or a standard reference material used?	Y	Y	Y	Y

Y – yes, N – no; N.A. – not applicable.

Table 3
Proximate and inorganic content of foods under study.

Parameter	Quinoa (*Chenopodium quinoa*) (Jujuy-Argentina)	Amaranth (*Amaranthus caudatus*) (Jujuy-Argentina)	Purple Corn (*Zea mays* L.) (Jujuy-Argentina)	Rice (*Oriza sativa*) (Ribatejo-Portugal)
Proximate	g/100 g			
Moisture	11.30 ± 0.05	10.50 ± 0.04	10.00 ± 0.03	13.10 ± 0.03
Ash	2.01 ± 0.02	2.89 ± 0.01	1.71 ± 0.02	0.42 ± 0.05
Protein	12.10 ± 0.3	13.4 ± 0.2	9.10 ± 0.1	7.10 ± 0.3
Fat	6.31 ± 0.11	6.43 ± 0.09	1.80 ± 0.02	0.60 ± 0.02
Fiber	10.40 ± 0.60	11.30 ± 0.5	11.20 ± 0.4	1.50 ± 0.1
Starch	57.20 ± 0.6	55.30 ± 0.7	57.70 ± 0.6	76.80 ± 0.8
Amylose	19.70 ± 0.5	23.70 ± 0.5	27.10 ± 0.5	29.20 ± 0.6
Trace elements	µg/100 g			
Molybdenum	22.8 ± 0.68	<LoQ	n.d.	30.4 ± 0.34
Strontium	160 ± 11.3	<LoQ	119 ± 7.4	15.1 ± 0.57
Cobalt	<LoQ	<LoQ	<LoQ	<LoQ
Lithium	7.95 ± 0.58	<LoQ	9.48 ± 0.21	<LoQ
Vanadium	6.66 ± 0.62	7.19 ± 0.22	9.01 ± 0.42	n.d.
Nickel	16.3 ± 0.72	16.4 ± 3.7	8.50 ± 0.39	<LoQ
Selenium	<LoQ	<LoQ	2.91 ± 0.16	<LoQ
Minerals	mg/100 g			
Copper	0.59 ± 0.03	0.51 ± 0.01	0.16 ± 0.004	0.12 ± 0.001
Manganese	1.95 ± 0.10	1.51 ± 0.05	0.57 ± 0.01	0.83 ± 0.02
Iron	5.46 ± 0.02	9.62 ± 0.12	2.78 ± 0.31	0.22 ± 0.01
Zinc	2.93 ± 0.07	5.55 ± 0.36	2.54 ± 0.03	0.95 ± 0.03
Magnesium	197 ± 8.1	231 ± 6.9	118 ± 0.83	27 ± 0.09
Calcium	44 ± 1.7	165 ± 9.3	<LoQ	<LoQ
Phosphorus	468 ± 15	527 ± 13	291 ± 3.6	107 ± 2.4
Sodium	<LoQ	<LoQ	<LoQ	<LoQ
Potassium	664 ± 16	530 ± 20	458 ± 3.5	91 ± 3.1

n.d.: not determined.
LoQ: limit of quantification.

of data that enter in FCDBs (Bhargava et al., 2009). Initial setting conditions were applied using manufacturers' instructions for cereals although this was not a useful approach. Thus a strategy based on literature survey was carried out. Different sample quantities (250–500 mg) were submitted to several irradiation powers (1000–1500 W) and irradiation times (2–20 min). Various strongly oxidant media, consisting of nitric acid and hydrogen peroxide mixtures in different ratios, were tested. In food matrices microwave digestion conditions profile (temperature/time) largely depend on the content of major components. The digestion period was carried out in a five step program and presented in Table 4. The first step conducting at 180 °C was applied to start the decomposition of organic matter (mainly proteins) followed by a step of raising the irradiation conditions to destroy lipids, the last step

Table 4
Optimised conditions for microwave assisted digestion of cereals analysed by ICP-MS and ICP-OES.

Step	Time (min)	Temperature (°C)	Power (W)
1	850	180	10
2	0	180	5
3	1100	210	6
4	0	210	5
5	650	90	6

Table 5
Contribution of Andean cereals to the daily dietary intake of prioritised minerals in adults, expressed in % (obtained nutrient value per 100 g of food)/dietary reference intakes.

Life group	Cereals	DRI	Ca	Cu	Fe	Mg	Mn	P	Zn	K
			1000 (mg/d)	900 (μg/d)	8 (mg/d)	420 (mg/d)	2.3 (mg/d)	700 (mg/d)	11 (mg/d)	4.7 (g/d)
19–50	Rice		n.d.	13	3	6	36	15	9	2
	Purple corn		n.d.	18	38	28	25	42	24	10
	Quinoa		4	66	69	47	85	67	26	14
	Amaranth		17	57	120	55	66	75	51	11
			1200 (mg/d)	900 (μg/d)	8 (mg/d)	420/320[a] (mg/d)	2.3/1.8[a](mg/d)	700 (mg/d)	11/8[a] (mg/d)	4.7 (g/d)
>50	Rice		n.d.	13	3	6/8[a]	36/46[a]	15	9/13[a]	2
	Purple corn		n.d.	18	38	28/37[a]	25/32[a]	42	24/33[a]	10
	Quinoa		4	66	69	47/62[a]	85/108[a]	67	26/36[a]	14
	Amaranth		14	57	120	55/72[a]	66/84[a]	75	51/70[a]	11

DRIs – dietary reference intakes.
[a] Female.

runs in the absence of microwave irradiation for safety precautions and to avoid occurrence of uncontrolled reactions. To avoid polyatomic interferences during ICP-MS analysis formation of HN03/H2O2 mixtures were used instead of each reagent alone. Solutions containing HN03/H2O2 (7/1) ratios were not effective for promoting complete sample digestion. Yellowish colour was observed, at high nitric acid contented that can be due to incomplete decomposition of lipids. Suitable conditions (recovery better than 80% and bias under 5%) were achieved by the use of HN03/H2O2/H20 (4/2/2) in combination with the selected program (irradiation time, temperature and power). After this, experimental design was applied for establishing the combination between most critical digestion parameters and sample weight. Maximum analytical amount was calculated in agreement with Dolen and Capar (2002), taking into account the food energy and maximum vessel energy capacity. The mineralisation program that obtained the best performance is presented in Table 4 which was considered for a recovery rate around 95%. This is in agreement with the values reported in literature for samples with similar proteins/fat ratio (Noël et al., 2012).

3.4.2. Contents in mineral and trace elements

Minerals were determined by ICP-OES. The mean values of mineral contents for Andean cereals and rice, respectively for copper, manganese, iron, zinc, magnesium, calcium sodium, phosphorus and potassium, are present in Table 3.

Sodium content is below LoQ (<10 mg/100 g) for all analysed samples. Also for calcium in purple corn and rice the values were below LoQ (<10 mg/100 g). As can be seen in Table 3, Quinoa, amaranth and corn purple contained significantly higher amounts of all the minerals under study, when compared with white raw rice (with corn purple manganese as an exception for being lower then rice). Our results are in agreement with several authors that reported quinoa and amaranth as rich sources of minerals (Alvarez-Jubete et al., 2010; James, 2009; Konishi, Hirano, Tsuboi, & Wada, 2004; Ruales & Nair, 1993; Valencia et al., 2010a; Vega-Galvez et al., 2010). When comparing the three Andean cereals (quinoa, amaranth and purple corn) in what respects to mineral content and as evidenced by Table 3, quinoa presented the highest copper, manganese and potassium content levels, while amaranth reveals the highest content of iron, zinc, magnesium, calcium and phosphorus. Purple corn when compared to quinoa presents the lowest content for almost all minerals with an exception for zinc. James (2009) reported higher amounts of copper, manganese, zinc, calcium and sodium in quinoa originated from other Andean regions. Regarding amaranth, the results shown in Table 3 were compared with those obtained by Rastogi and Shukla (2013) who studied different genotype variability, for cereals grown in India. For phosphorus, potassium and zinc, our results were higher than those reported, but lower for magnesium, iron, copper and calcium.

Quinoa and amaranth's mineral concentration deviations from the results reported by the literature can be explained by different genotypes, type of soil, mineral composition of the soil and fertiliser type (Vega-Galvez et al., 2010). Treatments like dehulling, washing or polishing that can cause the loss of several minerals (James, 2009; Konishi et al., 2004; Stickic et al., 2012), as phosphorus, magnesium and potassium are located on embryonic tissues, while calcium and also potassium are found in pericarp and seed coat. The use of abrasive processes may well explain these eventual losses and therefore the lower contents especially in the case of calcium level (Konishi et al., 2004; Vega-Galvez et al., 2010).

Table 3 presents trace element contents determined by ICP-MS. As can be seen some trace elements were found below the quantification limit. High selenium content was found in purple corn, suggesting that it is a good source of this essential nutrient. When trace element content results obtained in our study are compared to those reported by Ruales and Nair (1993), one can evidence the similarity of results for the cases of molybdenum and selenium (also with lower amounts in quinoa), but higher levels in what respects to nickel. These differences may be explained by the fact that Ruales and Nair (1993) used not only different analytical conditions but also polished and washed quinoa seeds. According with this author the treatment to remove saponins which include polishment and washing reduce the mineral contents. These differences should be taking into account when compilers aggregate data.

3.5. Contributions of Andean cereals to nutrient intake of essential elements

Contributions of mineral intake expressed in % of DRI, based on 100 g of cereals and calculated as determined by the Institute of Medicine of National Academies (IMO, 2013) are shown in Table 5, considering target population age from 19 years old up to senior population. The contribution for DRI varies between 2% (potassium in rice) and 120% (iron in amaranth).

As we can see, the consumption of quinoa and amaranth could cover higher nutritional requirements than rice. Amaranth has higher contribution to mineral intake, even higher then quinoa. This has a high importance for people who have celiac disease, since almost all gluten-free cereals have a poor content of calcium, magnesium and iron (Alvarez-Jubete et al., 2010). Andean cereals and pseudocerals studied can be a rich source of minerals and trace elements for all population. In North of Argentina a shortage of minerals intake was identified which does not occur at moment in Portugal. Although population from both countries with different food habits can consumed Quinoa and Amaranthus as a source of iron and magnesium. Nevertheless studies are necessary to clarify the iron bioavailability present in these products. They can be as

well as a good source of calcium to complement consumption of dairy products.

As we can infer from calculated contribution expressed in Table 5, quinoa and amaranth contribute with slightly upper than 50% of DRI's for copper, iron, manganese, magnesium and phosphorus. For zinc the contribution is higher in amaranth. The contribution of purple corn for the DRI's of copper, iron, manganese, magnesium, phosphorus and zinc range from 18% (copper) to 42% (phosphorus). All the Andean cereals and rice are a poor source of potassium. Our results are in the range of those reported by James (2009).

Calcium, magnesium and iron are minerals that are deficient in gluten-free products and in the gluten-free diet. The high calcium content in amaranth seeds may be of special relevance for celiac subjects due to the well known prevalence of osteopenia and osteoporosis among celiac patients.

4. Conclusions

Quinoa, amaranth and purple corn originated from Jujuy Argentina have higher nutritional values when compared to rice. Furthermore their nutrient profiles in terms of protein content, minerals and trace elements are different from other varieties of quinoa and amaranth produced in other Andean regions. This needs to be taken in consideration when compilers aggregate data. Furthermore, a detailed documentation to trace back aggregate data to original analytical values is necessary as part of compilation process. As far as we know this is the first work reported analytical values on this Andean food products with the purposed to be included in a FCDB.

The differences found in the mineral profile of quinoa and amaranth studied in this work, when compared with the literature, reinforces the necessity to include original data in Argentina food composition databank. Furthermore the data presented in our study indicated that the values are different from those published in other food composition databanks. The findings are in agreement with food composition experts who advocates the need of national food composition data and biodiversity data. Quality control procedures implemented in this work are a guarantee of reliability of the analytical procedures. Moreover guidelines for laboratory performance are paramount to enhance the acceptability of values in LATIN FOODS and other Food Data regional organisations. Quality criteria applied can guarantee that data can be interchanged through e-search EuroFIR platform.

This provides necessary information to the users of Food Composition Databanks who wish to have an overview of the parameters which influence the estimation of nutrient intake, and may affect the diet-disease relationship. Therefore the data obtained can be used to evaluate the nutritional value of the food being consumed by the population and to implement national public nutrition health policies.

Nevertheless, more studies are recommended in order to cover a broader range of components, including all micronutrients and their bioavailability and bioaccessibility. These are crucial for accurate dietary intake estimation. Therefore co-operation between International Organizations such as EuroFIR and LATIN FOODS is underway.

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