Concentrations of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, and Zn in Uruguayan Rice Determined by Atomic Absorption Spectrometry

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ABSTRACT

The United Nations General Assembly declared the year 2004 the International Year of Rice and the concept "Rice is Life". The largest nutritional problems occurring globally are protein-energy malnutrition, and Ca, Fe, I, Zn, and vitamin A deficiency.

In this report, 49 rice samples (*Oryza sativa L.*) were digested by dry ashing in order to determine As, Cd, Cr, and Pb by ETA-AAS; while Ca, Co, Cu, Fe, K, Mg, Mo, Mn, Na, Ni, and Zn were determined by FAAS; and Hg by CV-AAS using microwave-assisted decomposition. The following concentration ranges were obtained for Ca (9.1–15 mg/100 g), Cd (2.30–4.12 µg/kg), Co (41–60 µg/kg), Cu (1.33–180 mg/kg), Fe (4.41–7.15 mg/kg), K (167–217 mg/100 g), Mg (45–121 mg/100 g), Mo (0.52–0.97 mg/kg), Mn (5.45–25.4 mg/kg), Na (0.95–2.50 mg/100g), Ni (0.53–0.72 mg/kg), and Zn (5.86–12.6 mg/kg).

Mean recoveries of elements from fortified rice were: 87±12% for As, 95.3±8.9% for Ca, 106.2±7.7% for Cd, 103.3±6.5% for Co, 89.4±8.1% for Cr, 99.3±4.6% for Cu, 103±10% for Fe, 96.3±9.3% for Hg, 95.4±12% for K, 98.3±8.0% for Mg, 93.4±7.8% for Mo, 95.3±9.9% for Mn, 89±12% for Na, 90.3±9.7% for Ni, 91.2±5.5% for Pb and 92.0±9.4% for Zn, The concentrations of the minerals and microelements studied fall within the typical range of rice grown around the world. Potassium was the most abundant mineral, followed by Mg and Ca; among microelements, the concentrations of Cu, Fe, Mo, Mn, Na, and Zn in rice were outstanding.

It was also found that the milling process highly affects the K, Mg, Mn, Na, and Zn concentrations, while it has little influence on Ca, Co, Cu, and Fe. On the other hand, there is a loss of Ca, Fe, and Mn during the parboiling process.

Recent studies have shown the potential to exploit the genetic variation of rice seeds with regard to the concentration of some minerals (Ca, Fe, Zn, etc.) without affecting yield or adding new traits.

All rice samples tested showed lower levels of As, Cd, Hg, and Pb in comparison to the maximum limit permitted by government organizations. Thus, the consumption of Uruguayan rice presents no health threat regarding the concentration of toxic elements such as As, Cd, Cr, Hg, and Pb.

INTRODUCTION

On December 16, 2002, the United Nations General Assembly (UNGA) declared the year 2004 the International Year of Rice (IYR) and the concept "Rice is Life". In declaring IYR, UNGA recognized that rice is the primary food source for more than half of the world's population, and that enhancing the sustainability and productivity of rice-based production systems will require the commitment of many parts of society as well as government and inter-governmental action (1).

Rice (*Oryza sativa L*) is considered the main staple food for several countries (Myanmar, Lao People's Democratic Republic, Vietnam, Cambodia, Bangladesh, Indonesia, Thailand, Philippines, Nepal, P.R. China) and is a major source of nutrients. In developing countries, rice accounts for 715 kcal/capita/day; 27% of dietary energy supply, 20% of dietary protein, and 3% of dietary fat. However, while rice provides a substantial amount of dietary energy, it has an incomplete amino acid profile and contains limited amounts of essential micronutrients. Today, more than 2,000 million people suffer from micronutrient malnutrition (Ca, Fe, I, Zn, and vitamin A deficiency). Malnutrition reduces the productivity of adults, reduces children's mental and physical development, and leads to premature death, particularly for women and children. If food systems do not provide sufficient quantities and enough diversity of food on a continuous basis, malnutrition will ensue particularly for the poor, and their health and welfare will deteriorate. Nutritional considerations, therefore, were essential to the International Year of Rice and the concept that Rice is Life (2–5).

Currently, studies are also focused on the improvement of the nutritional quality by genetic manipulation and the fortification of rice.

Since rice is a staple food consumed worldwide, its nutritional vs. toxic composition is of special interest.

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Uruguay has emerged as a medium-size rice producer and is Latin America's major rice exporter, now listed as one of the world's top ten. Although it is a great producer of rice, dietary intake surveys in Uruguay list a consumption of 10 kg per capita/year, lower than the consumption in Asia (81 kg/year), but higher than that in Europe (3 kg/year), and far below Brazil which is the major consumer in the region with a consumption per capita of 39 kg/year (6,7).

Genetic factors, soil and weather conditions, and the use of fertilizers affect the final level of mineral and contaminant components in rice. The human food chain is linked through vegetable, fruit, and tuber consumption to the nature of the soil which supplies, for example, the mineral ions. These are in turn derived from the parent rock and from decaying plant and animal residues.

On the other hand, many industrialized processes give rise to environmental problems with increased levels of contamination from elements such as As, Cr, Hg, and Pb which can have profoundly deleterious effects on health. The joint FAO/WHO (Food and Agriculture Organization/World Health Organization) requires detailed information on the concentration levels of elements in agricultural crops to assess the toxicological and nutritional significance of human and animal intake of these elements. The normal "background" concentrations of toxic elements, such as Pb, Cd, Cr, and As, must be known to develop limitations on the intake of these elements from foods. Information on background levels provides guidance in evaluating the effect of soil additives, such as phosphatic fertilizers and sewage sludge (containing Pb, Cd, Cr, and As), as well as the effect of commercial food handling and processing steps which can result in food contamination. Intake of relatively low doses of these elements over a long period can lead to malfunction of organs and chronic toxicity. Determination of base-line levels of Cd, Pb, Hg, and As in agricultural and horticultural crops is necessary to evaluate their toxicological significance and to establish action levels (8). These potentially toxic metals can be present in the environment from both natural and anthropogenic sources and enter the human body via the two main routes of ingestion and inhalation. The latter pathway is of minor importance except for industrial workers and people living close to emission sources. For the general population, ingestion is the major route of intake with food being the main contributor (9,10).

Cadmium

In the case of Cd, food serves as the major source for the general population. Concentrations of Cd in foods depend on soil contamination and the rate of uptake by plants from the soil. It is well known that among the cereal crops, Cd uptake from soil by rice is high and therefore rice is a major source of cadmium toxicity in rice-consuming countries. Approximately 40–60% of Cd intake in Japan comes from rice alone. Thus, rice serves as an index for environmental monitoring of Cd in rice-eating countries. However, the dietary intake of Cd from rice depends on the consumption level which varies for different occupational groups (11).

Chromium

Chromium is an essential element for the carbohydrate, cholesterol, and protein metabolism, while Cr toxicity depends on the metal's chemical form. Cr(VI) compounds show a toxic, mutagenic, and even carcinogenic character. Cr(III), which is the most frequently found form in foods and beverages, has low toxicity. Although humans can absorb Cr by inhalation or dermal contact, Cr intake through diet is the primary route of entry into humans (12).

Arsenic

Arsenic toxicity also depends on the chemical form of the element, with As(III) being the most potent, followed by As(V), then monomethylarsenate, and finally dimethylarsenate. When ingested, inorganic arsenic may cause acute or chronic toxicity. Epidemiological evidence supports the conclusion that As is a human carcinogen associated mainly with lung, skin, and bladder cancer. These facts show the need for determining As concentrations in food (13).

Lead

Lead is a non-essential element that is toxic to biota at elevated concentrations. In nature, Pb commonly occurs in its monovalent (Pb^{+1}), divalent (Pb^{+2}), and tetravalent (Pb^{+4}) states, with divalent Pb being the most common. Lead can also form organometallic compounds, such as tetraethyllead, which was the largest single source of Pb contamination into the atmosphere in Uruguay prior to January 2004, when it was used as an antiknock additive in gasoline. Studies have shown the carcinogenicity of Pb in the gastrointestinal tract, respiratory system, and kidneys (13).

Mercury

Mercury occurs in different forms such as mercury 0 (liquid and vapor), inorganic mercury (I) and (II), alkylmercury, and phenylmercury. The antimicrobial actions of Hg have also been known for some time. Organomercurials, particularly the alkyl- and arylmercury compounds, are more active as bactericides or fungicides than the inorganic salts. The poisonous properties of Hg have been known throughout recorded history and are reported in ancient oriental and Roman literature (13).

Although the toxic effects of all of these elements have been known for a long time, studies are still on-going to gain a better understanding of their effects within the biosystems.

Atomic Absorption Techniques for Metals Determination in Rice

For the determination of metal ions in rice, atomic absorption spectrometry (AAS) is the technique most widely used because of its versatility, precision, and accuracy. AAS determinations are usually made by flame atomic absorption spectrometry (FAAS) when metal concentrations are high enough (Cu, Zn, Fe, Ca, Mg, K, Na, Mn, Mo, Ni, and Co). For elements with low limits of detection (As, Cd, Cr, and Pb), the more sensitive electrothermal atomization atomic absorption spectrometry (ETA-AAS) technique is used, while cold vapor AAS (CV-AAS) is used for Hg determinations..

Sample Digestion

Prior to analysis, rice samples need to be brought into solution. The two most widely used techniques are based on dry ashing or wet digestion. Both techniques have advantages as well as limitations. The choice of technique should be based on the needs of the specific user. Dry ashing is cheap, provides good detection limits, but is time-consuming (strict temperature control should be observed to avoid metal losses) and sensitive to contamination.

Wet digestion is quick, requires little attendance, and is normally not as sensitive to contamination as dry ashing, but is labor-intensive and usually results in rather dilute solutions.

Since the introduction of microwave energy for wet diges-tion in 1975, microwave–assisted decomposition has been widely employed and numerous applica-tions have been described both for open-vessel and closed-vessel diges-tions. Closed-vessel digestion has several advantages over open-vessel digestion: smaller quantities of reagent (no evaporation), less cont-amination, and a higher reaction rate. The most commonly used acid digestion of biological materials is nitric acid, but various different acid mixtures have also been used (14,15).

The aim of this study was the analysis for the first time in

Uruguay of four different forms of Uruguayan rice (brown, parboiled brown, milled, and parboiled milled) for the determination of As, Cd, Cr, and Pb by ETA-AAS in sam-ples digested by dry ashing. How-ever, microwave-assisted decomposition of the samples was used for the determination of Ca, Co, Cu, Fe, K, Mg, Mo, Mn, Na, Ni, and Zn by FAAS, and Hg by CV-AAS.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer® Model 5000 atomic absorption spectrometer was used, equipped with an HGA®-500 graphite furnace, MHS-10 hydride generation system, and deuterium background correction (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The graphite furnace and flame settings are listed in Tables I and II, respec-tively.

TABLE I
Instrumental Conditions and Furnace Program
for the Determination of As, Cd, Cr, and Pb

	As	Cd	Cr	Pb
Wavelength (nm)	193.7	228.8	357.9	283.3
Spectral Bandwidth (nm)	0.7	0.7	0.7	0.7
Drying (°C)	110	110	110	110
Ashing (°C)	900	250	1200	450
Atomization (°C)	2700	2100	2700	2300
Cleaning (°C)	2700	2700	2700	2700
Sample Injection (μL)	50	10	50	50
Background Correction	D_2 Lamp	D_2 Lamp	D_2 Lamp	D_2 Lamp
Measurement Mode	Peak Area/ Height	Peak Area/ Height	Peak Area/ Height	Peak Area/ Height

TABLE II. Instrumental Parameters for Flame AAS Determination

	Ca[a]	Co	Cu	Fe	K[b]	Mg[a]	Mo	Mn	Na[b]	Ni	Zn
λ (nm)	422.7	240.7	324.8	248.3	769.9	285.2	313.3	279.5	589.0	231.1	213.9
H Slit (nm)	0.7	0.7	0.7	0.2	1.4	0.7	0.7	0.7	0.7	0.2	0.7
Flame Type	AAOF	AAOF	AAOF	AAOF	AAOF	AAOF	NOARF	AAOF	AAOF	AAOF	AAOF
Range (mg/L)	0.2–5.0	0.02–1.0	0.003–1.0	0.1–5.0	2.0–30	0.2–4.0	0.2–5.0	0.01–1.0	1.0–8.0	0.1–2.0	0.004–1.0
BG		D_2 Lamp		D_2 Lamp					D_2 Lamp		D_2 Lamp

AAOF=Air-acetylene oxidizing flame, NOARF=Nitrous oxide-acetylene reducing flame, BG= Background correction.
[a] 0.1% La_2O_3 was used to control the depression of the signal caused by some elements.[b] 0.1% of CsCl was used as ionization buffer.

Rice Samples

Forty-nine commercial samples of long grain rice (*Oryza Sativa L*), cultivated in Uruguay, were selected for this study. The samples were in the form of brown, milled, parboiled milled, and parboiled brown rice.

Prior to analysis, approximately 500 g of sample was ground in an analytical mill (Analytical Mill A10, Kinematica GAC, Luzern, Switzerland) and passed through a 1-mm sieve.

Reagents and Standard Solutions

All chemicals used in the sample preparation and analysis were of analytical grade or better.

Standard stock solutions of 1000 µg/mL were prepared for As, Ca, Cd, Co, Cr, Cu, Fe, K, Hg, Mg, Mo, Mn, Na, Ni, Pb, and Zn (Fluka Chemie GmbH, Germany, and AccuStandard Inc., New Haven, CT, USA), certified by the manufacturer to ± 1% (w/v) and traceable to NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA).

All solutions were prepared with ultrapure water with a specific resistivity of 18 MΩ.cm obtained by filtering distilled water through a Milli-Q™ Plus purifier system immediately before use (Millipore Corporation, Bedford, MA, USA).

Procedure of Sample Decomposition

Dry ashing of the rice samples for the determination of As, Cd, Cr, and Pb by ETA-AAS was performed in a multiplace mineralization block. The sample (~5 g) was weighed into a beaker resistant to high temperatures and, while continuously shaking the suspension, 5 mL ashing aid solution [10% w/v $Mg(NO_3)_2$ in ethanol] was added. Next, the following temperature program was used: heating at

125°C until nearly dry, then heating from 125–450°C for 2 hours, and holding at 450°C for 12–14 hours. If white ashes are not obtained after this temperature cycle, 1 mL HNO_3 should be added dropwise (brown fumes should be seen) and then 1 mL 30% H_2O_2 added; afterwards, repeat the heating cycle until white ashes are observed.

Once white ashes occur from the digestion cycle, 10 mL HNO_3 (10%) was added and the solution obtained was homogenized in an ultrasonic bath and then centrifuged.

Duplicate blanks were prepared by adding 5 mL ashing aid solution for the digestion procedure.

Microwave oven digestion was performed in order to determine Ca, Co, Cu, Fe, K, Hg, Mg, Mo, Mn, Na, Ni, and Zn by FAAS. Samples of 0.50 g were digested in Tetrafluormethaxil (TFM) Teflon™ vessels with 5 mL HNO_3 using a Milestone MLS 1200 MEGA microwave oven (Milestone, Italy) and following the heating program listed in Table III.

For the determination of mercury by CV-AAS, analyte additions were performed before digestion and the microwave oven digestion as described above was followed.

TABLE III
Heating Program[a] Used for the Determination of Ca, Co, Cu, Fe, Hg, K, Mg, Mo, Mn, Na, Ni, and Zn

Step	Power (W)	Time (min)
1	250	1
2	0	5
3	250	5
4	400	5
5	650	5

[a] Caution: Digestion vessels must be cooled for an appropriate time before opening in order to avoid burns from hot and corrosive vapors and to eliminate sample loss.

Calibration and Accuracy Studies

Direct calibration against acidified standard solutions was carried out for Ca, Co, Cu, Fe, K, Mg, Mo, Mn, Na, Ni, and Zn and by the standard additions technique for As, Cd, Cr, Hg, and Pb.

To ensure a high level of analytical reliability, recovery studies were included for each batch to estimate analytical accuracy. The rice samples were spiked with two different concentrations of a certified solution (Trace Metal Standard I and III, J.T. Baker Inc., Philipsburg, PA, USA) and then submitted to the digestion procedure. Each batch also contained a certified reference material (NIST CRM 1568a Rice Flour).

The limits of detection (LOD) obtained in this study are listed in Table III. These values were calculated on the basis of the concentration giving a reading equivalent to twice the standard deviation of the blanks.

The recommendations listed in the EURACHEM/CITAC guide (EuroAnalytical Chemistry/Co-Operation on International Traceability in Analytical Chemistry) were followed to identify and estimate the individual contributions to the total uncertainty of the method employed (16).

RESULTS AND DISCUSSION

The metal ion composition of brown, milled, parboiled milled, and parboiled brown rice is listed in Table IV and was calculated on the wet basis to allow a comparison with the literature data of the product when purchased.

The concentrations of all the elements studied (As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mo, Mn, Na, Ni, Pb, and Zn) in this survey fall within the typical range (as can be seen in Table IV) of rice from around the world (7,11,17–20).

Toxic Elements

All rice samples tested showed lower cadmium and lead concentrations than the maximum limit permitted by the Codex Alimentarius (0.1 mg/kg and 0.2 mg/kg, respectively) (21,22). Uruguayan legislation (23) regulates the levels of As and Hg in foodstuffs (2.0 mg/kg and 0.05 mg/kg, respectively). As can be observed in Table IV, As and Hg concentrations found in this work are far below the maximum concentrations allowed by this regulation. These low levels confirm that the rice growing areas as well as the groundwater employed for irrigation are situated in non-contaminated sites. It is well known that in some countries, i.e., Bangladesh, irrigation of the paddy fields with arsenic-contaminated groundwater has led to arsenic buildup in paddy soil, with subsequent elevations in rice grain arsenic. P.N. Williams et al. (24) have recently reported high levels of As (up to 0.46 mg/kg) in rice from the United States. These high levels are attributed to the use of As herbicides in cotton fields in the early to mid-20th century and currently some of these areas are used for rice production.

Although the Cr content in rice is not yet regulated in Uruguay, it is important to know the Cr levels in foodstuff because of the element's toxicity. The presence of this metal can be attributed to the use of stainless steel equipment or contamination during processing.

The results of our study verify that the levels of As, Cd, Cr, Hg, and Pb concentrations found in commercially available rice are below the legislated limits. These low levels confirm the good agricultural practices employed in the production of rice in Uruguay.

It has been demonstrated that under fasting conditions the gastrointestinal absorption of toxic metals can be significantly increased (13). For instance, Pb absorption in the human adult is in the order of about 10–15% (up to 50% for children) and under fasting circumstances it increases up to 45%. Studies have also shown that certain dietary factors such as milk fasting result in low calcium and vitamin D intake, causing iron deficiency and may enhance lead absorption from the gut (13). Since rice is considered a main staple food and a major source of nutrient for the poor who lack access to diverse foods, strict control should be enforced on the maximum level of toxic metals allowed in this important crop.

TABLE IV
Metal Content in Different Forms of Rice Produced in Uruguay

	Units	Brown	Milled	Parboiled Brown	Parboiled Brown	LOD	Typical Range	CRM (%)	Recovery (%)
As	µg/kg	< LOD	< LOD	< LOD	< LOD	50	0.01–0.61		87±12
Ca	mg/100 g	9.1±1.4	15±1.8	10±1.3	10±1.2	0.010	9–50	99±10	95.3±8.9
Cd	µg/kg	3.43±0.68	4.12±0.72	2.30±0.69	3.75±0.66	1.0	<1–230		106.2±7.7
Co	µg/kg	57±11	41±15	59.6±8.4	50±10	20	10–100		103.3±6.5
Cr	µg/kg	< LOD	< LOD	< LOD	< LOD	5.0	<1–100		89.4±8.1
Cu	mg/kg	1.80±0.16	1.52±0.16	1.45±0.15	1.33±0.16	0.010	1–6	95.2±8.4	99.3±4.6
Fe	mg/kg	7.14±0.64	7.15±0.66	5.90±0.71	4.41±0.77	0.050	2–50	89±11	103±10
Hg	µg/kg	< LOD	< LOD	< LOD	< LOD	1.0	<0.1–29		96.3±9.3
K	mg/100 g	217.3±4.9	167±5.6	210.6±3.7	167.2±5.8	0.10	60–280	99.4±8.4	95.4±5.7
Mg	mg/100 g	121±11	46.4±5.5	116±13	45.4±5.9	0.050	20–150	91.3±7.7	98.3±8.0
Mo	mg/kg	0.82±0.21	0.97±0.19		0.52±0.16	0.10	0.18–3.0		93.4±7.8
Mn	mg/kg	25.4±2.8	6.55±0.85	6.28±0.88	5.45±0.79	0.010	2–36	91±11	95.3±9.9
Na	mg/100 g	2.23±0.21	1.20±0.11	0.95±0.11	2.50±0.21	0.40	1.7–34	96.7±7.8	89±12
Ni	mg/kg	0.62±0.15	0.72±0.13	0.53±0.10	0.613±0.097	0.020	< 0.2–1.2		90.3±9.7
Pb	µg/kg	<LOD	< LOD	< LOD	< LOD	5.0	2–70		91.2±5.5
Zn	mg/kg	12.6±1.0	6.10±0.73	11.6±1.2	5.86±0.75	0.010	6–28	102.8±4.4	92.0±9.4

Minerals and Microelements

In addition to determining toxic elements in rice, the level of minerals and microelements was also studied. As listed in Table IV, potassium was the most abundant mineral (217, 211, 167, and 167 mg/kg for brown, parboiled brown, milled and parboiled milled rice) found in rice, followed by Mg and Ca. Among microelements, the presence of Cu, Fe, Mo, Mn, Na, and Zn in rice was outstanding (for milled rice, the values found were 1.5 mg/kg Cu, 7.25 mg/kg Fe, 0.97 mg/kg Mo, 6.55 mg/kg Mn, 1.2 mg/100g Na, and 6.1 mg/kg Zn).

The concentration of most elements presented in Table IV were similar in brown and parboiled brown rice, except for Mn which was higher in brown rice (25.4 and 6.28 mg/kg, respectively).

It is generally accepted that as greater amounts of rice bran are removed from the grain during milling and polishing, more vitamins and minerals are lost. For all the samples analyzed in this work, milled rice shows a significantly lower content of K, Mg, Mn, Na, and Zn than brown rice. But the milling process seems to have little influence on the Ca, Co, Cu, Fe, and Ni levels. Similar results were reported in rice cultivated in Brazil (7).

The distribution pattern of metal ions in the rice grain is not yet clearly known. Some authors (4,7,26–27) point out that microelements (Cu, Fe, Mn, and Zn) are likely to be uniformly distributed in the grain and macroelements (P, K, Ca, and Mg) seem to be present chiefly in the external layers of the grain (aleurone, pericarp). Research has shown that element concentrations are highly affected by the milling process (25), while others have found a strong interaction between, for instance, iron content and milling, which suggests that much of the iron concentration is in the outer layers (aleurone and pericarp) of rice (25).

The effects of rice grain processing with regard to the mineral levels in the edible product (i.e., milled and parboiled rice grain) are still being evaluated. On the other hand, the parboiling process seems to have little effect on the mineral content in rice (except for Ca, Fe, and Mn) as can be seen in Table IV. The high loss of these minerals was not expected. It is assumed that the minerals spread to the external layers of the grain when soaked and steamed and are subsequently removed by milling. R.J.B. Heinemannn et al. (7) also observed significant losses of Ca and Mn in the parboiled milled rice cultivated in the south of Brazil.

It has been reported that parboiled rice is of superior nutritional value in comparison to milled rice, mainly due to the retention of minerals and water-soluble vitamins (26). The higher retention of micronutrients in parboiled rice has been assigned to their solubilization and migration to the center of the grain and their setting during the starch gelatinization process (26).

Nevertheless, the significance of the nutritional benefits of parboiled rice is still arguable, mostly due to the lack of uniform commercial processes applied in different countries. It is believed that the retention pattern of some minerals is the result of the interaction of different factors such as mineral location in the grain and their solubility during soaking, different ratios of migration, as well as variations in the hydrothermal process and milling resistance of the parboiled grain. Further studies need to be carried out to achieve a more complete understanding of mineral retention.

Staples are generally not considered an important source of minerals in the diet. However, because rice is an important staple food, any increase in mineral concentration might well have a significant effect on human nutrition and health.

Genetic Alteration of Rice

Currently, several research institutions are working toward improving the nutrient content through greater utilization of rice genetic resources. Since 1995, researchers at the International Research Rice Institute (IRRI), Manila, Philippines, have been evaluating the genetic variability of Fe and Zn concentration in rice. Screening tests run to identify germplasm with high iron and zinc found a statistically significant correlation with phytate as the iron and zinc concentrations increased, so did phyate. But the nutritional implications with regard to the bioavailability of the increased Fe and Zn content counterbalanced with increased phytate are still under investigation (5,27).

Scientific programs are also focused on increasing the iron content of the grain and the element's bioavailability once ingested. A two-fold increase was achieved by transferring the coding sequence of ferritin from a bean (*Phaseolus vulgaris*) into rice endosperm (28). At the same time, to increase the bioavailability of iron, β-carotene was inserted, and the phytate gene from *Aspergillus fumigatus* was inserted to break down phytic acid which binds iron (5).

Yet, the controversy and questions remain concerning the advances in biotechnology. Specifically, there is uncertainty regarding the degree to which micronutrient levels can be increased, as well as the effect of this increase on yield, disease resistance, and palatability. The opportunities created through genetic alteration of the rice genome also create new imperatives for biosafety.

Enrichment and Fortification of Rice

As we mentioned previously, the complete milling and polishing that converts brown rice to white rice reduces the amount of vitamins and minerals in the final product. Studies have shown that rice enrichment and fortification techniques restore the levels of vitamins and minerals in milled rice at first removed from the grain during the milling process (7). Enriched rice is coated in a protective material which helps to prevent nutrient loss due to washing. The success of various fortification strategies, particularly those involving fortification with iron, is mixed. The fortification of foods with iron remains technically complex. Those iron compounds with the greatest bioavailability (ferrous sulphate and ferrous fumarate) significantly alter the palatability of food, whereas large declines in the uptake of iron are seen when a more palatable iron compound (elemental iron or ferric orthophophate) is used (28).

Fortified rice holds great potential in reducing micronutrient deficiencies. Its success, however, will depend on making the enriched rice available, affordable, and palatable for the consumer (29).

CONCLUSION

Since rice is a staple food consumed worldwide, its nutritional vs. toxic composition is of special interest. Hence, the knowledge of the metal ion concentrations in rice is crucial to determine the amount of toxic elements and nutrients consumed with rice. It also helps to build up nutrition tables widely used to calculate food nutrient intake.

The report of the 16 elements (As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mo, Mn, Na, Ni, Pb and Zn) in Uruguayan rice here presented has no precedent in the country. Since Uruguay is one of the world's top ten rice producers, the awareness of toxic elements (As, Cd, Cr, Hg, and Pb) and mineral and microelements is vital for the trade market. This type of survey is very important since the determination of elements in rice may help prestigious rice producers from counterfeit rice and permit source confirmation for government certification.

The methodology employed for the determination of As, Cd, Cr, and Pb by ETA-AAS, and Ca, Co, Cu, Fe, K, Mg, Mo, Mn, Na, Ni, and Zn by FAAS, and Hg by CVAAS was appropriate and the results obtained were in general as expected.

The data generated show that the concentrations of the toxic elements As, Cd, Pb, and Hg in the rice samples tested are significantly lower than the maximum tolerance limits established by international organizations. These low levels confirm the good production practices employed in Uruguay and shows that the consumption of this rice presents no health threat.

In addition, the concentrations of all the elements determined in this survey fall within the range typical of rice grown around the world.

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