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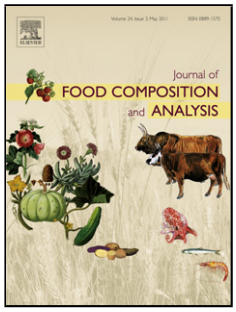

Fate and health risks assessment of some pesticides residues during industrial rice processing in Argentina

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Fate and health risks assessment of some pesticides residues during industrial rice processing in Argentina

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Highlights

- Dietary exposure to pesticides of the Argentinean men, women and children was low.
- Chromatographic methods for pesticides in husk rice, brown rice, husk and bran were validated.
- Husk rice pesticides were reduced in the range of 66.1 to 74.7 % during industrial rice processing.
- Bran contained 2.5 times more pesticides residues than polished rice.

Abstract

The residues of deltamethrin, penconazole, kresoxim-methyl, cyproconazole, epoxiconazole and azoxystrobin were determined in husk rice, brown rice, husk and bran, fifty samples of each matrix, obtained from industrial rice facilities, to estimate the distribution of contamination levels during industrial rice processing; and to estimate the exposure to these pesticides through rice intake. The analytical methodologies required were validated. QuEChERS extraction and gas chromatography-mass spectrometry were used. All methods showed good linearity ($r^2 > 0.9996$), adequate recoveries (between 80.0– 102.0%) and relative standard deviations lower than 9.9%. A total of 250 samples were analyzed, finding that the polishing stage reached the greatest pesticide reduction.

Considering the overall process, the initial concentration of pesticides in husk rice was reduced in the range of 66.1 to 74.7%. Process factors were lower than 0.69 and 0.36 for brown and polished rice, respectively. Estimated Dietary Intake were below 0.83%, 2.34% and 3.70% of ADI, for men, women, and children, respectively. Hazard quotient was estimated, and it was lower than 1 in all cases, showing a low potential risk for human health in terms of residue ingestion.

Key words: Food Analysis; Pesticide distribution; Industrial rice processing; Health risk; Chromatographic determination

1. Introduction

Rice (*Oryza sativa L.*) is one of the most consumed cereals in the world (Sadeghi et al., 2016; Sharafi et al., 2015), with the highest caloric intake (De Bernardi, 2017). According to the Food and Agriculture Organization of the United Nations (FAO, 2004), rice provides 20% of the dietary energy supply of the world. The rice harvested in Argentina was about 1.23 million tons in 2019 (Fontanini, 2019). According to Fontanini (2019), in the 2018/2019 campaign, the rice-producing provinces in Argentina are Corrientes (45%), Entre Ríos (35%), Santa Fe (13%), Formosa (5%) and Chaco (2%). Although the province of Corrientes is the one that has the highest primary productivity, it is the province of Entre Ríos which has a higher processing volume, about 79% of the total national production. Argentinian rice is not only consumed locally but also exported.

The main causes of loss in the pre and post-harvest rice production are fungal diseases that affect not only the plant but also the seeds, along with insect attacks (Benavidez, 2006). These pests and diseases may cause different extent losses that can be translated into a reduction in economic terms. Therefore, pesticides are used to control them. Systemic pesticides are absorbed by the vegetal, incorporated into the sap and translocated. These movements inside the plant make possible its distribution in the different layers that constitute the rice seed (Barberá, 1989, Cremlyn, 1995).

The rice seed consists of a husk, which is constituted by the lemma and the palea (Figure 1). Beneath the husk, there are layers called pericarp, tegmen and aleurone, forming the rice bran or miller´s bran, and along with the endosperm and the germ compose the caryopsis, known as brown rice (Pinciroli, 2010). The rice production consists of removing the rice husk with rubber rollers (husker) that rotate at different speeds in opposite directions. This way, two streams are obtained: on one hand, the husk and, on the other, brown rice (Buggenhout et al., 2013). From this last stream and through a process called milling or polishing, where abrasion and/or friction forces

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intervene, white rice is produced. The main processing rice byproducts are husk and bran. Near 20 – 22% of rice grain is husk, while approximately 10% is bran (Nadaleti, 2019).

The behavior of pesticides residues after food processing (washing, peeling, bleaching, etc.) will depend on their chemical structure, physicochemical properties, such as water solubility, polarity, octanol / water coefficient (Kow), volatility, boiling point, etc. (Aliste et al., 2018; Jankowska et al., 2019); and the characteristic of the raw material (Aliste et al., 2018).

Nowadays, consumers prefer products with higher nutrients content. White rice processing causes an important reduction of vitamins and minerals due to the elimination of the bran (Lamberts et al., 2007; Monks Fernandes et al., 2013; Saman et al., 2019), and that is the reason why brown rice consumption is increasing.

Several authors found higher concentration of pesticides in wheat bran samples, compared to polished grain samples. (Balinova et al., 2006; Dors et al., 2011; Kaushik et al., 2009; Mahugija et al., 2017; Sgarbiero et al., 2003). Medina et al. (2019) have studied the residual levels of pesticides commonly used in Entre Ríos Province, Argentina, in 100 samples of polished rice from supermarkets, and have found deltamethrin, penconazle, kresoxim-methyl, cyproconazole, epoxiconazole and azoxystrobin, in 94 samples. Due to these results, it is probable that brown rice contains higher concentration of pesticide due to its remaining bran layer. Information on the fate of the pesticides during rice process, and the final concentration in brown and polished rice, is needed to assess the human risk associated with its consumption, primarily for children who consume three to five times more cereal than adults per body weight (FDA, 2016).

Pareja et al. (2011) highlighted the importance of studying the effect of the different stages of polished rice production, on pesticides fate. Likewise, Alister et al, (2018), state that industrial knowledge is limited and that most studies have been carried out in laboratory conditions. For these reasons, and to expand the knowledge on the effect of industrial-scale processing on the final pesticide content, this work was carried out in the main processing area of Argentina.

The quality control of rice, related to pesticides, and the assessment of their impacts on the health of consumers are relevant. Sharafi et al. (2019a) studied the quality and health risk assessment of rice related to heavy metals in Iran. Butinof et al. (2014) evaluated the health risk assessment related to pesticides in vegetables from Cordoba Province in Argentina. However, they do not work with rice.

Medina et al. (2019) validated a methodology to analyze pesticides in polished rice. However, due to the matrix effect, the validation of analytical methods for husk rice, brown rice, husk and bran is needed.

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Therefore, the purposes of this research work are firstly, to validate a chromatographic methodology to analyze pesticides in husk rice, brown rice, husk and bran; secondly, to study the influence of polished rice production process on the final content of pesticides and its fate in products and by-products of grain milling in an industrial scale, and confirm results obtained on a pilot scale; and finally, to estimate the health risk related to the intake of brown and polished rice.

2. Materials and methods

2.1. Reagents and materials

The pesticides standards of deltamethrin, penconazole, kresoxim-methyl, cyproxonazole, epoxiconazole and azoxystrobin were supplied by Sigma-Aldrich (Seelze, Germany). The stock solutions (1000 mg/L) were prepared by dissolving the standards in methanol HPLC grade (99.9%) purchased by Sintorgan (Buenos Aires, Argentina), and stored under freezing condition (-18°C ± 1°C) in dark bottles sealed with PTFE/silicone caps. The working standard solutions (50 mg/L) were prepared in acetonitrile (ACN) of high purity grade for residue analysis, provided by Merck (Darmstadt, Germany).

Deionized water obtained from an E-pure water purification system (Barnstead/Thermolyne, Bedford, MA, United States) was used for sample swelling in the extraction step.

For extraction and partitioning, sodium chloride and anhydrous sodium sulfate were purchased from Biopack (Buenos Aires, Argentina); sodium hydrogencitrate sesquihydrate and sodium citrate dihydrate were obtained from Sigma-Aldrich (Seelze, Germany). For clean-up using d-SPE, C18 and PSA bulk powder were obtained from Agilent Technologies (Santa Clara, United States).

2.2. Samples

A total of 250 samples of rice and byproducts were obtained from rice industry located in Concordia, Entre Ríos Province, Argentina, during 2018/2019 harvest season.

Samples belonged to 50 different rice lots and consisted of paddy rice, husk, brown rice, bran and polished rice, which means that husk and brown rice were obtained from the paddy rice that was introduced into the rice husker, and bran and polished rice were obtained from the brown rice that was introduced into the rice polisher.

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In order to obtain an aggregate sample, several incremental samples of 200 – 300 g. of each matrix were taken during a working day, with a sampling frequency of one hour. Each aggregate sample weighed about 1600 – 2400 g. The samples were identified, labeled, and transported to the laboratory preserving the cold chain and were kept in the freezer (-18 ± 1°C) until their processing for the analysis.

All samples, except for rice bran (as it is not necessary), were ground until they were powdered in a stainless-steel mill and sieved with Mesh No. 230.

2.3 Pesticides extractions and chromatographic determination

The extraction procedure and determination by gas chromatography – mass spectrometry (GC-MS) of azoxystrobin, cyproconazole, deltametrhrin, epoxiconazole, kresoxim-methyl and penconazole in rice samples, were described by Medina et al. (2019). Briefly, a modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) methodology technique, with 10 g rice, 10 mL water and 10 mL ACN, was used. The addition of water was proposed for cereals and other products with moisture lower than 25%. This allows extraction solvents access to the samples' pores (Diez et al. 2006; Kolberg et al. 2011).

Chromatographic analyzes were performed with a GC Agilent 6890N fitted with a micro-electron capture detector (µECD), and confirmation was performed with an Agilent 6890 N GC coupled with an Agilent 5973 MS. Both chromatographs had a fused silica capillary column HP-5MS (30 m x 0.25 mm i.d. x 0.25 µm film thickness). The oven conditions were: 80 °C (0.2 min), 40 °C/min up to 195 °C, 12 °C/min up to 280 °C and 5 °C/min up to 290 °C (held for 8 min). Helium (99.999 % purity) was used as carrier gas at a constant flow of 1 mL/min. The injector and detector were set at 250 ºC and 290 ºC, respectively. Electron Impact (EI) mass spectra were got at 70 eV and the system was programmed in selected ion monitoring (SIM) mode. Ion source and MS quad temperature were set at 230 °C and 150 °C, respectively.

The methodologies validation was performed as recommended by the European SANTE Guidelines (EC 2019) and Eurachem (2014).

Four different pesticides extraction methods were tested for husk and bran, varying the amount of sample, water and ACN. They were called A, B, C and D. In method A, 5 g of powdered sample, 10 mL of deionized water and 10 mL of acetonitrile were used. In B, 10 g of sample, 10 mL of deionized water and 10 mL of acetonitrile. In C, 10 g of sample, 17 mL of deionized water and 10 mL of acetonitrile. In D, 5 g of sample, 10 mL of deionized water and 5 mL of solvent were used.

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2.4 Laboratory rice mill

This investigation was carried during industrial rice processing. The process was repeated on a laboratory scale to ensure that there were no errors during sampling.

The laboratory rice mill was used to verify not only the husk, bran and polished rice percentages obtained from an industrial scale milling process, but also the reduction of pesticides under investigation, in each stage of the process.

From the 50 paddy rice samples collected from the industrial mill, 10 were randomly taken. The laboratory mill (MACHINA ZACCARIA S/A., Brasil) has a feed capacity of 100 grams and as the process was carried out in triplicate, 300 grams of paddy rice were used from each sample.

Feeding is carried out through the upper part of the machine; the feed hopper has a door through which paddy rice is introduced. Paddy rice is then pulled down by gravity until it reaches the husking and polishing chamber. Both operations are performed simultaneously in the same place. The chamber has a rubber brake that stops paddy rice grains from moving forward and when they stop, they come across with other rice grains (friction forces are involved) and a hard stone for polishing (abrasion). Distance between the rubber brake and the stone is 1.8 mm.

The husking and polishing chamber has a mesh opening that allows air inlet. This flow is generated by a fan, and it drags not only the husk but also the bran towards a cyclone separator. Through the bottom of the separator, a mixture of husk and rice bran is eliminated, as they enter tangentially and, while following the direction of the centrifugal force generated, they strike its walls and fall. The airflow exits through the top as it has lower density or it is lighter than the husk and bran flow.

Therefore, in the rice mill, along with a husk and bran flow, a flow of polished rice and broken grains is obtained. This flow is divided into whole and broken grains through a separator located in the mill, which applies centrifugal force. To separate bran and husk flows, a sieve that does not belong to the equipment was used (Mesh N° 35).

2.5 Process Factor

Food processing may have an effect on the pesticide residues. FAO/WHO (2006) indicated that the Process Factor (PF) is calculated dividing the residue level in processed commodity (mg/kg) by the residue level in raw commodity (mg/kg). If PF is higher than 1, the pesticide concentration has increased; while if it is lower than 1, the concentration has decreased (Cámara et al., 2020; Mekonen et al., 2019). Keikotlhaile et al. (2010) mentioned

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that this effect could be related to physico-chemical properties of pesticide or the physical location of it in the commodity.

2.6 Dietary exposure and health risk assessment

The dietary exposure to pesticides was determined according to FAO/WHO (1997), and is shown in Equation 1

$$EDI = \frac{(C\text{x}FP\text{x}D_i)}{Bw} \qquad (1)$$

where EDI (mg / kg Bw) is the estimated daily intake of each pesticide, C is maximum residue concentration of each analyte (mg/kg), FP is process factor; D_i is the daily intake of rice in Argentina, and Bw is the average body weight of consumers (kg).

According to Reffstrup et al. (2010), an important point in the risk assessment is whether there is or is not interaction between the pesticides in the mixture. Although interactions among chemicals at high doses are well-known, there is currently no simple approach to judge upon potential interactions at the low doses to which humans are exposed from pesticide residues in food. We do not have information about interactions between pesticides.

For the estimation of the long-term health hazard, the hazard quotient (HQ) was used (USEPA, 2000). HQ was calculated with the ratio between the estimated daily intake and the acceptable daily intake (ADI). The ADI values were taken from FAO/WHO (2017).

The analysis of each HQ value is important because when HQ ≤ 1 there is an acceptable risk for human health; while when HQ > 1 the risk is unacceptable (Cámara et al., 2020; Kumari & John, 2019; Reffstrup et al., 2010; Wu et al., 2017). Several authors evaluated EDI, and HQ related with pesticides in different vegetables, fruits, honey and beeswax (Bommuraj et al., 2019; Golge et al., 2018; Li et al., 2016).

2.7 Statistical analysis

The comparison between pesticides concentration in samples obtained from industrial and pilot scale, were carried out by using the software STATGRAPHICS Centurion version XV (Statgraphics Technologies, Inc., United States) applying two non-parametric tests, Mann–Whitney and Kolmogorov Smirnov.

3. Results and discussion

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3.1. Extraction method of rice husk and bran

In the case of rice bran, extraction method B is chosen (10 g of powdered sample, 10 ml of deionized water and 10 ml of acetonitrile) due to the fact that chromatographic responses are higher for deltamethrin, penconazole and kresoxim - methyl, than method A (Figure 2). This method is the best for cyproconazole. Methods C and D fail to extract azoxystrobin, but they are better for epoxiconazole than method B. Method C is better than method B for kresoxim – methyl. However, as a compromise solution, this method was chosen as it allows to extract all 6 pesticides.

Regarding the husk, according to Figure 2, the higher chromatographic response for all pesticides is produced in extraction C, where 10 g of sample, 17 ml of deionized water and 10 ml of acetonitrile were used. No statistically significant differences were shown at a 95% confidence level for epoxiconazole in methods B and C.

3.2 Analytical methodology validation for husk rice, brown rice, bran and husk

For the validation of analytical methodologies used for husk rice, husk, brown rice and bran, the method described in Medina et al. (2019) for polished rice was followed. It was done because of the presence of matrix effects. The extraction of husk and bran was performed following the procedure described above. The validation procedure was performed with samples blanks without pesticides. The obtained results are briefly described below.

Calibration curves were built with 5 pesticides concentrations, ranged from 0.005 to 1.5 mg/kg (n=9), according to the European SANTE Guidelines (EC, 2019) recommendations. Regression coefficients were higher than 0.9996, in all cases. Individual values are shown in Supplementary Data 1.

Samples of each matrix were spiked with azoxystrobin, cyproconazole, deltamethrin, epoxiconazole, kresoxim-methyl and penconazole at 0.05, 0.5 and 1.5 mg/kg of each pesticide (n=9), to determine the repeatability of the method, which is expressed as a relative standard deviation (RSD%). These values were lower than 10% in all cases, showing that the precision of the proposed methods was satisfactory to control residue analysis. The selectivity was evaluated by observing that there were not interfering peaks at the retention time of each pesticide in a blank chromatogram of each matrix sample without spiking.

Recovery experiments were carried out on untreated husk rice, brown rice, husk and bran samples for accuracy determination. Triplicate of the samples were spiked with 0.05, 0.5 and 1.5 mg/kg of the standard solutions. The limits of detection (LOD) and limits of quantifications (LOQ) of each pesticide were estimated by considering a signal to noise ratio of 3 and 10 respectively, in comparison with the background noise of a blank sample (n=5). These results are shown in Table 1.

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Quality control is performed daily at the beginning of each set of samples by analyzing a rice sample spiked with the pesticide mixture and comparing the results with a control graph. Results within the range of the mean recovery ± 2x RSD from the validation method is accepted (EC, 2019).

3.3 Industrial scale process

All 250 samples were processed in triplicate (Supplementary Data 2). Reduction of concentrations of pesticides in husking and polishing stages, and total reduction of the process is shown in Table 2. In order to compare reductions, all information was expressed regarding paddy rice, and thus it was possible to make an assessment of pesticides which suffered a reduction.

Reduction range of the initial pesticide content in the husking stage was 26.8–33.4%. Azoxystrobin shows the lowest reduction percentage, considering the average value of 32.0%, and kresoxim-methyl shows a higher reduction with a value of 32.3%. In all cases, average values represent approximately a third of the initial value of pesticides in paddy rice, therefore, two-thirds of the initial content would remain in brown rice. In the polishing stage, total reduction range, expressed in terms of percentage, is 43.1–67.8%, and it represents the lower reduction of azoxystrobin, with an average value of 50.0%. On the contrary, penconazole shows the higher reduction percentage, with a value of 62.2%. Considering both stages, it is observed that the polishing stage reduces 59.4% of the content of pesticide residue found in brown rice, considering an average reduction value of all pesticides. However, the husking stage only reduces 32.2%, an average value of the six analytes, of pesticide residue content in paddy rice. Considering the total reduction of the process, from paddy rice to polished rice, a range between 66.1% and 74.7% was obtained. Lowest reduction was shown in azoxystrobin with a 66.1% value and the highest belonged to penconazole with a 74.7% value. Kaushik et al., (2009) achieved a reduction of approximately 95% for malathion, in wheat, until flour was obtained.

Holland et al. (1994) mentioned that the milling of grains substantially eliminates the pesticide residues Most residues are present in the outer layers of grain and, therefore, levels in the bran are consistently higher than in the polished grain, even for those pesticides that can enter the grain by translocation. The percentage reduction in residue concentration during rice processing has been demonstrated. The husk elimination step allowed 70 – 93% reduction of bioresmethrin, carbaryl, deltamethrin, fenitrotion, d-phenothrin, methacrifos, parathion and pirimiphos-methyl. They found only 2 – 8% of the initial concentration in polished rice.

It is noticed that in all pesticides under examination, the highest percentage of reduction is shown in the polishing stage, that is to say, when rice bran layer is removed. The bran fraction contained 2.5 times more

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concentration of pesticides than polished rice. Dors et al. (2011) analyzed bran rice fraction obtained from the milling process and reached the conclusion that concentration of tebuconazole, clomazone, carbofuran and bispyribac-sodium was 8.0, 2.3, 2.2 and 1.6 times higher than polished rice, respectively. Balinova et al. (2006) studied the dissipation and distribution of chlorpyrifos-methyl and pirimiphos-methyl in wheat grain and its derivatives. They found that the higher quantity of these pesticides were located in the wheat bran, and thus it showed 3.6-4.5 times more of chlorpyrifos-methyl and 1.6-4.7, of pirimiphos-methyl than the whole grain after the milling process. Mahugija et al. (2017), found organochlorine pesticide (DDT, DDD, DDE, endosulfan, aldrin and dieldrin), and organophosphorous and pyrethroid pesticides (chlorpyrifos, pirimiphos methyl, fenitrothion and cypermethrin), in maize grain and flour. They observed that during the milling process, in order to obtain white flour (polished), the content of pesticides is reduced due to the fact that they remain in the bran fractions. The same observation was reached by Sgarbiero et al. (2003), while they analyzed the pirimiphos-methyl behavior in corn grains and processed products as, for example, popcorn. They mentioned that bran had approximately 70% more pirimiphos-methyl than polished corn grain, because of its higher oil content.

Rice bran contains 14.5-17.0% fat, while the husk has only 0.4–0.6% and polished rice, 0.3–0.6% (Callejo González, 2002). It is possible that those nonpolar pesticides with a high octanol-water partition coefficient prefer to adhere to rice bran, high in fat. The octanol / water coefficients and the percentage of deltamethrin, penconazole, kresoxim - methyl, cyproconazole, epoxiconazole and azoxystrobin, that were eliminated with the bran samples, were 4.60 and 41.8%, 3.72 and 42.1%, 3.40 and 40.3%, 3.09 and 41.2%, 3.30 and 42.0%, 2.50 and 33.8%, respectively. It can be seen than azoxystrobin with Kow of 2.50 is the pesticides which initial concentration was reduced less in the bran (33.8%).

From a commercial point of view, it is important to consider the maximum Residue Limits (MRL) stablished by the European Commission (EC, 2005) and Codex Alimentarius (Codex Alimentarius, 2013), for exportation, and by SENASA (SENASA, 2010) for national consumption (Table 3). In the case of kresoxim-methyl, 34 samples of paddy rice exceed the maximum residue level established by the European Union, and one sample exceeds the maximum residue level established by SENASA. If only the average value obtained from the 50 analyzed samples is considered, whose value is 20.3 ppb, only the MRL provided by the European Union would be exceeded. If the average value obtained from the 50 polished rice samples, which is 5.53 ppb, is taken into account, the European Union MRL would not be exceeded; however, it is important to highlight that 6 of the 50 samples have values that exceed the 10 ppb limit. In the case of brown rice, 27 samples exceed this maximum limit and average value of the 50 samples is 13.7 ppb. This suggests that more attention should be focused on this cereal, due to the current

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brown rice consumption. Another aspect that should be considered is pesticide content in rice bran as it is used for animal consumption. While performing the same analysis for epoxiconazole, SENASA established an MRL of 10 ppb. The average value of the initial content of this pesticide in paddy rice is 46.9 ppb. However, the 50 paddy rice samples contain a concentration of epoxiconazole above this limit, and 5 exceed the E.U. limit of 100 ppb. In the case of brown rice, the average value of the 50 samples is 31.8 ppb, 49 of them exceeding the limit established by SENASA and one the E.U. limit.

Although the process to obtain polished rice from paddy rice reduces the initial content of pesticides, it is not enough in the case of epoxiconazole as from the 50 polished rice samples analyzed, 18 exceed the MRL established by SENASA, with an average value of 12.1 ppb. Concentrations obtained after the analysis, for brown rice as well as for polished rice, exceed the maximum residue limits allowed. The LMR established for azoxystrobin in Brazil is 100 ppb, fifty times lower than E.U. one (Pareja et al., 2011). This information is important because Brazil is one of the main exportation destinies of Argentinian rice.

3.4. Laboratory scale process

The laboratory mill was used to compare the reduction percentage of pesticide content in the global process and husking and polishing stages, with the industrial process. Besides, fractions of the milling by-products, husk and rice bran were obtained, verifying that, as in the industrial process, they represent 20% and 10% of the whole grain, respectively (Supplementary Data 3).

Pilot scale results obtained after the processing of the samples, extraction of pesticides and data analysis (Supplementary Data 4), were compared with those got from industrial scale. Since there was not normal distribution of the results, we applied two non-parametric tests, Mann–Whitney and Kolmogorov Smirnov, to perform the comparisons. The p-values were higher than 0.05, so medians and distribution did not present statistically significant differences with a confidence level of 95%.

3.5. Estimation of the exposure and risk assessment

Firstly, the process factors related to brown rice and polished rice production were determined. The PFs related to brown rice production were 0.68, 0.69, 0.67, 0.67, 0.68 and 0.69; while they were 0.36, 0.26, 0.23, 0.25, 0.30 and 0.25 in polished rice, for azoxystrobin, cyproconazole, deltamethrin, epoxiconazole, kresoxim-methyl and penconazole, respectively.

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The information found about the consumption of rice and the body weight (Bw) of people from different ages and gender in Argentina are summarized in Table 4. In this study, to simulate the worst conditions, the higher intakes and lower Bw of children from 2 – 5 years old, men and women, were considered for calculation. Polished rice intakes were 61.6, 65.5 and 78.6 g/day, for children, men and women, respectively. Brown rice intakes were 21.0 g/day for children and men, and 57.4 g/day for women. Regarding to body weight, they were 12.7, 60.4 and 50.2 kg, for children, men and women, respectively.

Table 5 summarized the ADI, EDI and HQ values for the studied pesticides in brown and polished rice, related to men, women and children consumption. The exposure for children is higher than for adults because of the intake per kg of body weight.

Among the EDI values, it could be seen than they were below 0.83%, 2.34% and 3.70% of ADI, for men, women and children, respectively. The highest percentage of the ADI value was obtained for epoxiconazole, which resulted in 0.83% and 0.71% for men, 1.19% and 2.34% for women, and 3.70% and 3.39% for children, in polished and brown rice, respectively. It was followed by deltamethrin with 0.53% for children in both types of rice, 0.12% and 0.11% for men, and 0.17% and 0.37% for women, in polished and brown rice, respectively. The results were lower than 0.05%, 0.14%, and 0.22%, for the rest of the analyzed pesticides, for men, women and children, respectively. Łozowicka et al. (2020) studied deltamethrin in apples, pulp of apples and peel of apples, with values of 1.36% and 7.40%, 0.73% and 3.97%, and 5.44% and 29.57%, for adults and infants, respectively. Lemos et al. (2016) determined the long-term risk assessment of vegetables intake in the Basque Country, with HQ of 0.007%, 0.02% and 0.001% for azoxystrobin, cyproconazole and kresoxim-methyl, respectively. These results indicate that the exposure to pesticides from vegetable intake is not relevant. Butinof et al. (2014) proposed two indexes to describe pesticide exposure for applicators in vegetables fields from Córdoba Province, Argentina, but they did not study the risk assessment related to food intake.

Regarding the HQ, it was lower than 1 in all cases. These results show a very low potential risk for human health in terms of residue ingestion.

A most detailed study by gender and age could be carried out, but it is not justified because considering the worst situation, the rice intake alone does not represent a health risk.

4. Conclusions

The techniques validated for each matrix allowed the analysis of the entire polished rice production process and to know the reduction percentage by stage.

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Polished rice production process eliminates between 66.1% and 74.7% of the initial content of deltamethrin, penconazole, kresoxim-methyl, cyproconazole, epoxiconazole and azoxystrobin in husk rice. The higher reduction percentage is obtained by eliminating the rice bran, where most of the pesticides are found in the study.

It is important to highlight that for brown rice consumption the process is not enough, because residue levels of kresoxim-methyl and epoxiconazole exceed the MRL established by national and international legislation. Therefore, it would be necessary to apply a minimum polishing process to brown rice, to eliminate small layers of bran in order to reduce its contamination.

On the other hand, better agricultural practices should be followed to reduce the residue content of these pesticides in husk rice, principally epoxiconazole, with the aim of minimizing the final concentration after rice processing, and avoiding the maximum residue limitss are exceeded.

HQ for analyzed pesticides in brown and polished rice, for men, women and children, demonstrates that rice intake does not represent a health risk for consumers, but it should be taken into account for calculation of cumulative exposure and risk assessment, considering the total diet.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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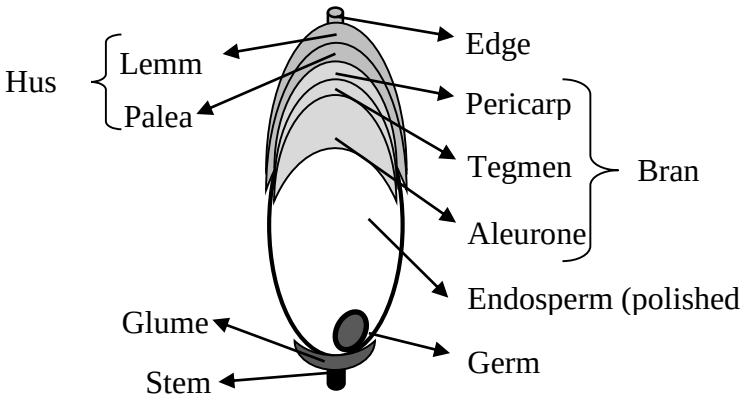
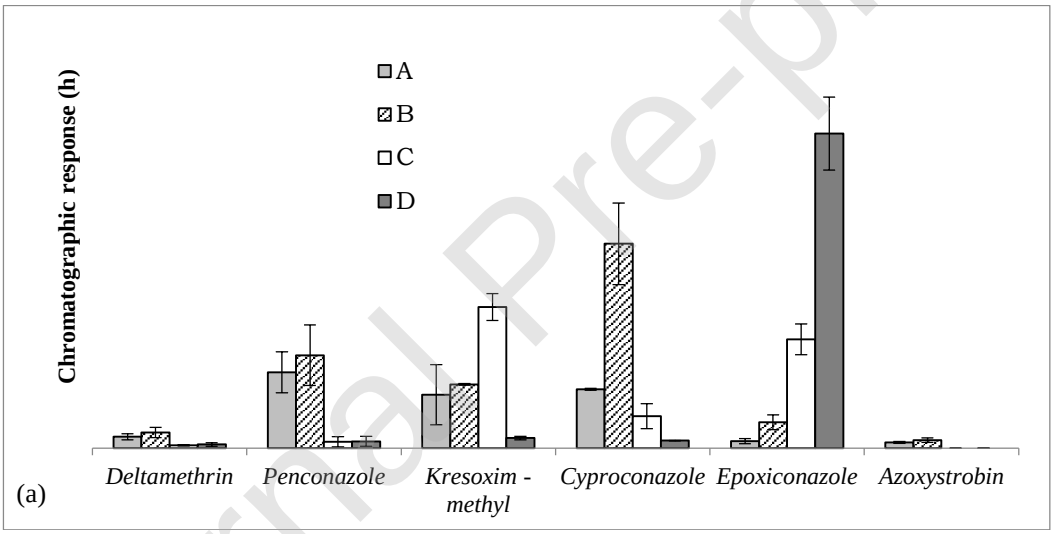


Fig. 1. Rice grain constituent parts



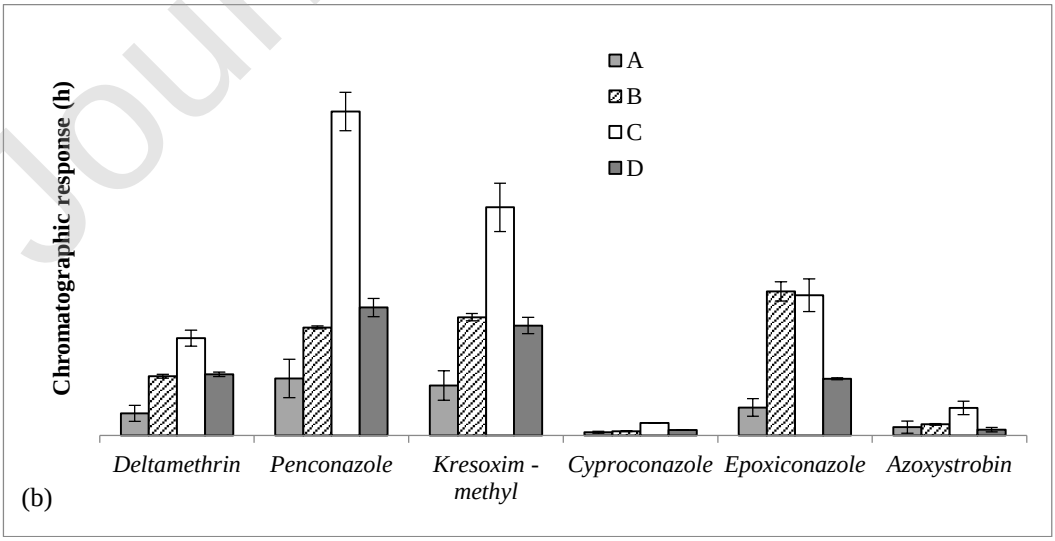


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Fig. 2. Comparison of four pesticides extraction procedures for (a) bran, and (b) husk. A: 5 g sample, 10 mL water and 10 mL AcN; B: 10 g sample, 10 mL water and 10 mL AcN; C: 10 g sample, 17 mL water and 10 mL AcN; D: 5 g sample, 10 mL water and 5 mL AcN.

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Table 1. LOD and LOQ (µg/kg), precision (%RSD) and % recovery for studied pesticides in husk rice, husk, brown rice, and bran.

Pesticides	*Husk rice*			*Husk*			*Brown rice*			*Bran*		
	LOD-LOQ µg/kg	RSD (%)	Recovery (%)	LOD-LOQ µg/kg	RSD (%)	Recovery (%)	LOD-LOQ µg/kg	RSD (%)	Recovery (%)	LOD-LOQ µg/kg	RSD (%)	Recovery (%)
Deltamethrin	0.26-0.85	3.2-8.2	97.3-101.0	0.31-0.92	2.9-7.0	99.8-100.1	0.28-0.88	3.5-6.3	87.9-92.4	0.30-0.90	2.3-8.7	83.1-95.4
Penconazole	0.24-0.77	3.7-7.1	89.7-99.6	0.27-0.82	4.0-9.2	88.5-100.1	0.26-0.79	3.1-7.7	91.3-99.4	0.25-0.81	2.6-6.8	84.7-100.2
Kresoxim methyl	0.23-0.74	3.0-7.4	81.7-97.4	0.26-0.79	2.8-8.1	92.8-101.9	0.25-0.77	3.4-9.1	83.1-99.7	0.25-0.78	4.2-8.9	87.0-95.5
Cyproconazole	0.27-0.89	1.7-6.3	90.6-98.9	0.28-0.89	2.4-7.2	88.3-90.0	0.28-0.90	3.5-8.6	97.6-102.0	0.29-0.92	4.3-9.3	85.5-100.3
Epoxiconazole	0.23-0.73	5.7-9.6	87.5-98.0	0.28-0.78	4.2-8.9	88.3-99.9	0.25-0.75	3.0-7.4	83.5-100.3	0.26-0.77	2.7-8.5	89.9-100.7
Azoxystrobin	0.28-0.91	2.8-9.9	89.1-99.9	0.33-0.96	3.2-8.7	87.7-93.2	0.29-0.92	3.0-9.1	80.0-85.5	0.31-0.95	4.6-9.8	84.9-98.0

Table 2. Pesticide reduction percentage during shelling and polishing steps, and total reduction during rice processing (n=3).

Pesticides	*Shelling stage HR. – BR (%)*	*Mean (%)*	*Polishing stage BR – PR (%)*	*Mean (%)*	*Total process reduction HR. – PR (%)*	*Mean (%)*
Deltamethrin	30.30 – 33.33	**32.26**	54.82 – 67.38	**61.57**	69.96 – 78.60	**74.19**
Penconazole	26.83 – 33.33	**32.11**	53.66 – 67.80	**62.15**	71.43 – 78.05	**74.66**
Kresoxim - methyl	30.28 – 33.34	**32.30**	53.79 – 64.21	**60.01**	69.00 – 76.05	**72.99**
Cyproconazole	29.16 – 33.41	**32.21**	54.06 – 67.56	**60.76**	69.02 – 77.70	**73.48**
Epoxiconazole	30.28 – 33.33	**32.02**	55.04 – 66.36	**61.87**	70.00 – 77.89	**74.12**
Azoxystrobin	29.47 – 33.36	**31.99**	43.10 – 57.45	**50.05**	62.00 – 69.99	**66.11**

HR: Rice Husk; **BR**: Brown Rice; **PR**: Polished Rice

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Table 3. Maximum Residue Limits (MRL) of studied pesticides for different legislations.

Pesticides	MRL (mg/kg) European Union	MRL (mg/kg) Codex Alimentarius	MRL (mg/kg) SENASA
Deltamethrin	1.00	2.00	1.00
Penconazole	0.05	-	-
Kresoxim - methyl	0.01	-	0.05
Cyproconazole	0.10	-	-
Epoxiconazole	0.10	-	0.01
Azoxystrobin	5.00	5.00	1.00

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Table 4. Argentinean Rice intake (g/day) and Body weight (kg) divided by gender and age

Reference	Men		Women		Children			
Polished Rice Intake								
	18-24 years	25-50 years	18-24 years	25-50 years	10-49 years	6-23 months	2-5 years	10 years
Pacin et al. (1998. 1999)	13.4±46.2	9.9±26.9	8.2±23.3	8.2±21.4	-	-	-	-
WHO (2003)				65.5*				
ENNyS (2005)	-	-	-	-	45.1±33.5	26.3±24.0	35.8±25.3	-
Anino (2017)				30*				
Brown Rice Intake								
WHO (2003)				21.0*				
ENNyS (2005)	-	-	-	-	35.5±21.9	16.0±7.9	-	-
Body Weight								
	Men		Women		Children			
	18-24 years	25-50 years	18-24 years	25-50 years	10-49 years	6-23 months	2-5 years	10 years
Pacin et al. (1998. 1999)	70.3±9.9	73.9±10.3	58.9±8.7	62.5±9.9	-	-	-	-
Del Pino (2005)	65	-	54	-	-	-	-	32
Lejarraga et al. (2009)	-	-	-	-	-	9.6±1.1	15.3±2.6	31.6±0.1
Maggioni et al. (2018)	-	-	60	-	-	-	15.4	-

* Mean values without age or gender distinction

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Table 5. Exposure and hazard quotients (HQ) for pesticides in brown and polished rice for the consumer group of men, women and children (from 2 – 5 years old)

Pesticides	ADI	Men				Women				Children			
		Polished Rice		Brown Rice		Polished Rice		Brown Rice		Polished Rice		Brown Rice	
		EDI	HQ	EDI	HQ	EDI	HQ	EDI	HQ	EDI	HQ	EDI	HQ
Azoxystrobin	0.18	2.0E-05	1.1E-04	1.2E-05	6.6E-05	2.8E-05	1.6E-04	3.9E-05	2.2E-04	8.7E-05	4.9E-04	5.6E-05	3.1E-04
Cyproconazole	0.02	9.8E-06	4.9E-04	8.3E-06	4.2E-04	1.4E-05	7.0E-04	2.7E-05	1.4E-03	4.4E-05	2.2E-03	4.0E-05	2.0E-03
Deltamethrin	0.01	1.2E-05	1.2E-03	1.1E-05	1.1E-03	1.7E-05	1.7E-03	3.7E-05	3.7E-03	5.3E-05	5.3E-03	5.3E-05	5.3E-03
Epoxiconazole	0.008	6.6E-05	8.3E-03	5.7E-05	7.1E-03	9.6E-05	1.2E-02	1.9E-04	2.3E-02	3.0E-04	3.7E-02	2.7E-04	3.4E-02
Kresoxim-methyl	0.3	1.6E-05	5.4E-05	1.2E-05	3.9E-05	2.3E-05	7.8E-05	3.9E-05	1.3E-04	7.3E-05	2.4E-04	5.6E-05	1.9E-04
Penconazole	0.03	8.7E-06	2.9E-04	7.6E-06	2.5E-04	1.3E-05	4.2E-04	2.5E-05	8.4E-04	3.9E-05	1.3E-03	3.6E-05	1.2E-03

EDI (mg/kg Bw day). ADI (mg/kg Bw day).

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