Environmental Impact Associated With Arsenic Levels In Rice Grains From The Quevedo Canton, Ecuador

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Abstract
Arsenic contamination in agricultural crops poses a significant risk to human health and the environment. In this study, we analyzed the environmental impact of arsenic on corn grains from the Quevedo canton in Ecuador. Rice, as a global staple food, is a potential source of exposure to arsenic, a toxic metalloid that affects both health and agriculture. The lack of updated data in the region motivated this research. Rice samples were collected from the main distributors in the canton, as well as a control sample from crops. Using graphite furnace atomic absorption spectrometry, arsenic concentrations were determined to range from 0.12 ± 0.02 mg/kg to 0.21 ± 0.06 mg/kg, with an average of 0.17 mg/kg. Although these values comply with European Union regulations (0.25 mg/kg), one sample exceeded the national limit (0.2 mg/kg), posing a risk to food safety. Statistical analysis (ANOVA and Tukey) revealed that there are no significant differences between distributors. The analysis of the environmental impacts associated with the presence of arsenic reveals that, on average, the values obtained are negative, indicating that they do not represent severe environmental damage.

INTRODUCTION

Globally, various studies reveal that rice (Oryza sativa L) is a fundamental pillar of food security and the largest source of arsenic-containing food worldwide (Moulick, et al., 2023; Yao, et al., 2021). Rice grains (Oryza sativa L) reached a total production of 526.2 million tons globally in 2023 (FAO, 2024). This cereal is a staple food for more than 50% of the world's population; however, global production faces challenges due to the presence of toxic metals in soil and water sources, which represents a serious environmental problem that poses a danger to humanity. Transmission to the food chain is a significant global concern that may hinder the achievement of the Sustainable Development Goals (Galán, et al., 2021; Medina, et al., 2018; Moulick, et al., 2021). The absorption of arsenic by rice plants, as well as its accumulation in edible parts, contributes significantly to human exposure to this toxic element through food intake (Peng, et al., 2024; Makinoa, et al., 2016).
In Latin America, around 25 million tons of rice are produced and sold each year to meet a growing market due to population demand (Degiovanni, et al., 2010). When focusing on the reality of Latin America, in recent decades, the presence of arsenic has been recognized as a serious environmental and public health problem (Honma, et al., 2012). This presence

of toxic metals in crops is mainly attributed to illegal mining and unsustainable agricultural practices that affect the 20 countries that make up Latin America. Soil characteristics facilitate the mobilization of arsenic under anaerobic conditions, which increases the absorption of this metal (Suda & Makino, 2018; Bundschuha, et al., 2021).

Ecuador stands out as one of the largest consumers of rice in South America. However, there is little research on arsenic concentrations in rice farming systems, although high levels of this element are known to be present in certain water bodies in Ecuador (Otero, et al., 2016; Gavilanes, et al., 2019). Regulations establish that rice intended for consumption must comply with permissible arsenic limits. Failure to comply with this requirement has detrimental effects on food security and the economy of farmers, affecting the cost-benefit ratio and optimal prices. In addition, the consumption of rice with high arsenic content carries significant health risks, especially for the Ecuadorian population with celiac disease (Bundschuh, et al., 2012; Mishra, et al., 2021; Debnath, et al., 2018).

The Quevedo canton is known for its outstanding rice grain (*Oryza sativa* L.) trade, making it one of the most sought-after products in the region. The main objective of this research project was to analyze the environmental impact of arsenic on corn grains from the Quevedo canton, Ecuador.

MATERIALS AND METHODS

Sampling

Based on the food code of Latin American countries, it is recommended that food samples be analyzed in triplicate, ensuring the consistency and identity of each sample in terms of origin, product, content, location, batch number, and other relevant aspects; for this reason, sampling was carried out in triplicate.

To this end, reconnaissance visits were made to the main distributors in the Quevedo canton. Once identified, rice grain samples were collected randomly in triplicate (n=3) on a monthly basis. This approach ensures that an accurate and reliable representation of the arsenic concentrations present in the rice available in the canton is obtained.

In addition, a control sample was randomly taken in triplicate from the rice crops. The control sample is used as a reference to control the quality and accuracy of the analytical results (Achipiz, et al., 2013). Control samples play a crucial role in the interpretation of scientific and toxicological analysis results, facilitating the identification and correction of errors and ensuring accurate results (Rodriguez, et al., 2016). Ecuador's crop planting maps were used as the basis for selecting control simples.

The analysis of the collected samples was carried out using the analytical method "Standard Methods 3111B Modified," which is widely recognized for its accuracy in quantifying arsenic in food samples. This method allows for the determination of metals using atomic absorption spectrophotometry, enabling the evaluation of multiple parameters. Method 3111B improves sensitivity and accuracy for the quantification of toxic metals in samples, ensuring reliable results (Mohana, et al., 2023).

Analytical method

After collecting the rice grain samples, they were processed in a laboratory certified by the Ecuadorian Accreditation Service, ensuring compliance with the ISO/IEC 17025 standard. The objective of this process was to quantify arsenic using the graphite furnace atomic absorption spectrometry technique, in accordance with the "Standard Methods 3111B Modified" method. The use of a graphite furnace in this technique significantly improved the sensitivity and accuracy of arsenic detection, allowing for a detailed and accurate assessment of the concentrations present in the rice samples (Jiménez de Blas et al., 1996; Morand et al., 2002; Schlotthauer et al., 2024; Sandoval et al., 2024).

Instrument calibration

To quantify arsenic in rice grains, precise instrument calibration was required. Standard solutions or arsenic standards were created to establish calibration or working curves. These curves were prepared from concentrated solutions of 100 mg/L. In addition, 1% v/v HNO3 was used as a reference solution for the measurements.

Once this stage was complete, the method was programmed using Perkin Elmer® Analyst 200 atomic absorption spectrophotometer software. This program allowed the reading of the aqueous standards of the calibration curve, as well as the samples prepared from the rice grains. The precision and accuracy in the preparation of the calibration curves are crucial to ensure reliable and reproducible results in the quantification of arsenic present in the analyzed simples.

Sample treatment

To digest the solid rice grain samples and quantify the arsenic, the following detailed procedures were followed, based on standardized methods and good laboratory practices:

- Sample grinding: The rice grains were ground using a porcelain mortar until a fine powder was obtained, which ensures a larger contact surface for acid digestion.
- Precise weighing: Weigh exactly 2 g of the crushed rice grains with a high-precision analytical balance (±0.0001 g), ensuring consistency in the amount of sample used for each analysis.
- Muffle furnace calcination: Subject the samples to a temperature of 600°C in a muffle furnace for two hours. This step decomposes the organic matter and converts the arsenic into a form that can be dissolved in acid (EPA, 1996).
- Dissolution of calcined samples: Transfer the calcined samples to a beaker and dissolve them in 5 ml of a 1% v/v HNO3 solution. This acid solution facilitates the extraction of arsenic from the calcined material (ISO, 2008).
- Transfer and dilution: Transfer the resulting solution to a 10 ml volumetric flask and make up the volume with the same nitric acid solution, ensuring homogeneous dilution.
- Absorbance readings: Take absorbance readings of the solutions using an atomic absorption spectrophotometer with a graphite furnace, which offers high sensitivity and precision for arsenic detection. The operating conditions of the instrument must be pre-established and optimized for the arsenic analyte (Latimer, 2016).

These steps are essential to ensure the correct preparation of samples and accurate quantification of arsenic present in rice grains. The use of standardized techniques and certified equipment guarantees the reliability and reproducibility of the results obtained, allowing for a rigorous assessment of the arsenic content in the samples analyzed.

Sample analysis

To ensure accurate quantification of arsenic in rice grains, certain procedures were carried out, comprising the following steps:

- Preparation of the nebulizer: Before taking the reading, the nebulizer was cleaned by aspirating a 1% nitric acid solution. This cleaning ensures that there is no residual contamination that could affect the accuracy of the measurements.
- Nebulization in a graphite furnace: The analyses were performed using the graphite furnace atomic absorption spectrometry technique. This technique offers greater sensitivity and accuracy in the quantification of arsenic compared to direct flame nebulization (ISO, 2008).
- Sample aspiration: The previously prepared sample solutions will be aspirated to determine their absorbance and concentration (mg/L). This process is performed automatically using atomic absorption spectrophotometer software, using the previously established calibration curve to ensure the accuracy of the measurements (Latimer, 2016).

- Calibration range control: In situations where samples have concentrations outside the calibration range, appropriate dilutions will be made using a 1% nitric acid solution. This step ensures that all samples are analyzed within the optimal range of the instrument, providing reliable results (EPA, 1996).
- Automation and data analysis: The spectrophotometer software (Analyst 200 from Perkin Elmer®) enables data reading and analysis. Automation of the process ensures consistency and minimizes human error, relying on calibration curves to determine the exact concentrations of arsenic in rice samples.
- Validation of results: The results obtained are validated through internal quality controls and, if necessary, repetition of the analyses to confirm the reproducibility and accuracy of the data.

Estos procedimientos son fundamentales para garantizar una cuantificación precisa y confiable del arsénico en los granos de arroz, contribuyendo a la evaluación del impacto ambiental y la seguridad alimentaria en el cantón Quevedo.

Data processing

To determine whether there were significant differences ($p<0.05$) in the concentrations of arsenic from the distributors and control samples, a statistical analysis was performed, beginning with a normality test of the data obtained. If the data showed abnormalities, a non-parametric Kruskal-Wallis test was applied using INFOSTAT statistical software. If the data followed a normal distribution, an ANOVA was performed, followed by a Tukey test to identify specific differences between distributors and control samples. This is a non-parametric statistical tool used to compare three or more independent groups. It is based on the Kruskal-Wallis test, but its implementation and analysis are performed using Infostat software (Labana, et al., 2018).

Environmental impact caused by arsenic-contaminated rice grains in the Quevedo cantón

To assess the environmental impact of arsenic concentrations in rice grains sold in the Quevedo canton, the methodology proposed by Arada et al. (2017) was used, adapted to this specific context, applying the following equation.

(Environmental Impact = P_A - P_{NC})

Where:

P_A: value of the parameter determined in the rice samples

P_{NC}: value of the parameter reported in the NTE INEN; Codex Alimentarius and European Union.

To identify whether there is a risk and contamination, the maximum levels and maximum permissible limits established by national and international regulations were used as a basis: NTE INEN, Codex Alimentarius, and the European Union (Table 1).

Table 1. Maximum levels and maximum permissible limits established

Regulations	**Quantity**	**Unit**
NTE INEN	0.2	mg/kg
Codex Alimentarius	0.2	mg/kg
Unión Europea	0.25	mg/kg

When the values of the characterization parameters (in this case, arsenic concentrations) exceed the permissible limits established by regulations, a positive impact (+) represents severe environmental damage, whereas a negative impact (-) does not imply severe damage to the environment. This approach allows for the quantification and qualification of environmental impact in clear terms that are comparable with international standards, thereby facilitating decision-making for risk mitigation and the implementation of corrective measures.

Data processing

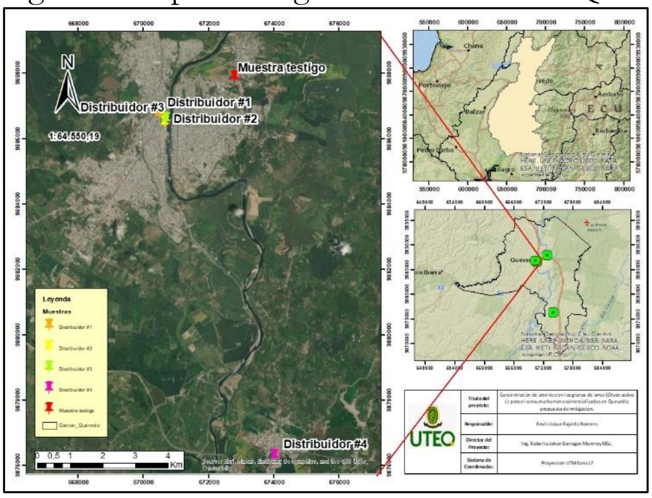
To determine whether there were significant differences ($p<0.05$) in environmental impact, a statistical analysis was performed, beginning with a normality test of the data obtained. If the data did not show a normal distribution, a non-parametric Kruskal-Wallis test was applied using INFOSTAT statistical software. If the data followed a normal distribution, an ANOVA was performed, followed by a Tukey test to identify specific differences in the impacts for each distributor.

RESULTS AND DISCUSSION

Sampling

During the technical visit to the Quevedo canton, the main rice grain distributors in the key markets in the area were surveyed with the aim of identifying the most relevant ones, taking into account the number of users. It was determined that these are: Distributor #1, distributor of market #1; Distributor #2, distributor of market #2; Distributor #3, distributor of El Río market; Distributor #4, distributor of the San Camilo organic market; and the control sample was taken from a rice crop. The location of the identified distributors is shown in Figure 1.

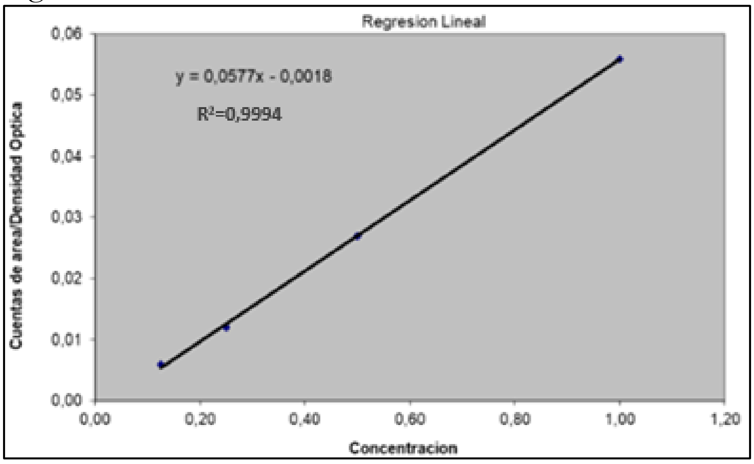
Figure 1. Map showing the location of the Quevedo sampling site



Calibration curve

For the quantification of arsenic, a linear calibration curve with the equation $y=0.0577x-0.0018$ was used, obtaining a coefficient of determination $R^2=0.9994$, as shown in Figure 2. This R^2 value indicates an excellent correlation between the experimental values and those predicted by the calibration curve, demonstrating the high accuracy of the method used. In addition, a quantification limit of 0.125 mg/kg was determined.

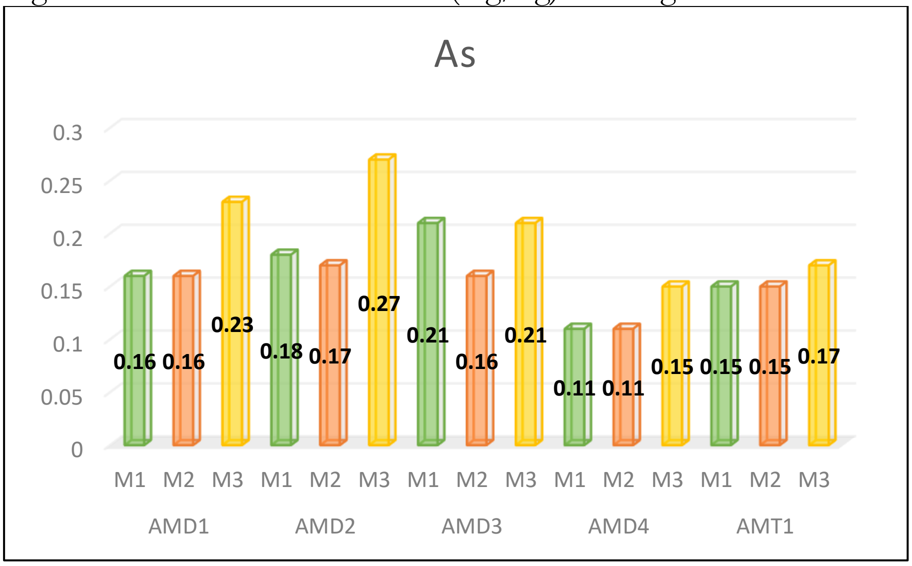
Figure 2. Calibration curve



Arsenic Concentrations

The arsenic concentrations in rice grains from the main distributors in the Quevedo markets are as follows: 0.18 ± 0.04 mg/kg (AMD1), 0.21 ± 0.06 mg/kg (AMD2), 0.19 ± 0.03 mg/kg (AMD3), 0.12 ± 0.02 mg/kg (AMD4), and 0.16 ± 0.01 mg/kg for the control sample (AMT1). Figure 3 shows an increase in the concentration of arsenic in the sample corresponding to the distributor identified with the code AMD3, with a concentration of 0.19 ± 0.03 mg/kg, while the distributor with the code AMD2 has the lowest arsenic content, with a concentration of 0.12 ± 0.02 mg/kg.

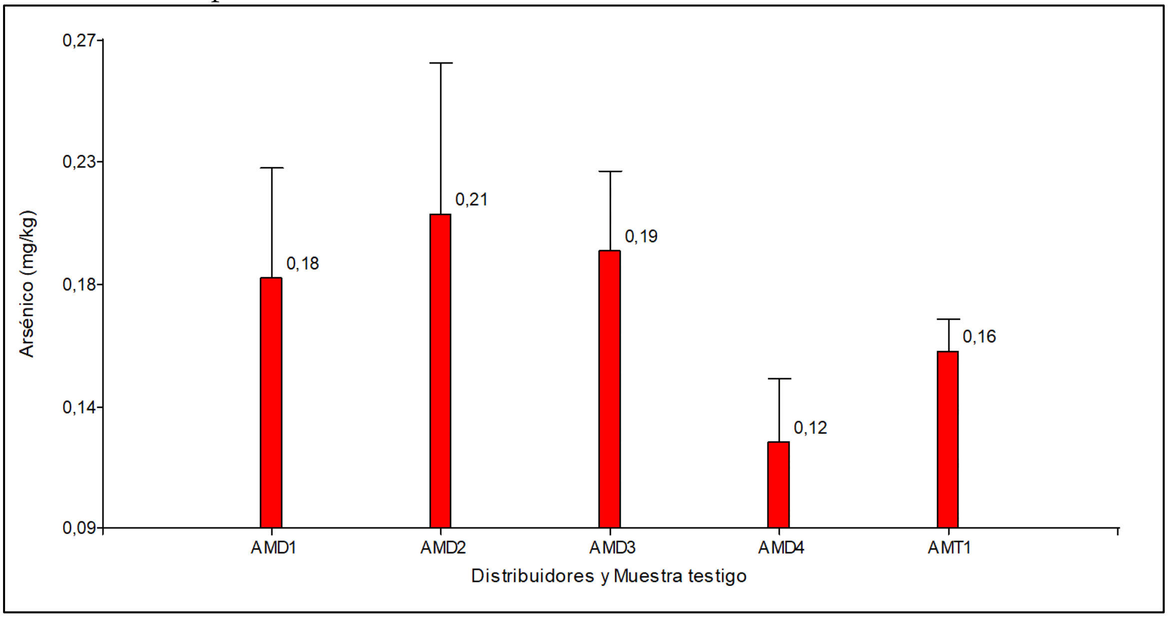
Figure 3. Arsenic concentrations (mg/kg) in rice grains from distributors in Quevedo.



Statistical analysis

According to the normality analysis using the Shapiro-Wilk test (modified), a p-value of 0.3921 was obtained. According to the decision rule ($p < 0.05$), it is concluded that the data follow a normal distribution. Consequently, a parametric analysis was performed using ANOVA, complemented by Tukey's multiple comparison test. The results indicated a p-value of 0.0949. Since the p-value is greater than 0.05, it is evident that there are no statistically significant differences in arsenic concentrations between rice distributors and the control sample, as shown in Figure 4.

Figure 4. Statistical analysis of arsenic concentrations in rice grains from distributors and the control sample



Arsenic concentrations in rice samples from the main distributors in Quevedo, as shown in Figure 2, may be influenced by various factors, including the use of agrochemicals containing heavy metals, which represent a significant source of arsenic in rice. The application of these products contributes to the bioaccumulation of heavy metals in the soil, facilitating their absorption by plants throughout their growth cycle.

Various studies have shown that the use of agrochemicals is a determining factor in the bioaccumulation of arsenic in rice. Barboza et al. (2023) highlight the need to optimize agricultural production through sustainable alternatives that reduce the use of agrochemicals such as calcium arsenate, due to the negative environmental impacts they generate. According to Dash et al. (2016), the application of agrochemicals in rice crops in wetlands, particularly herbicides, insecticides, and nitrogen fertilizers, can contribute to soil and water contamination, affecting crop quality. For their part, García et al. (2019) warn that the most commonly used agrochemicals, such as fungicides, herbicides, and insecticides, can have adverse effects on ecosystem health and food security. Along these lines, Medina et al. (2018) point out that rice has higher concentrations of arsenic species compared to other plant products. Similarly, Shofiqul et al. (2019) indicate that, although most of the arsenic accumulates in the roots and stems of the plant, a significant proportion is transferred to the grains, posing a potential risk to human consumption.

Another factor influencing the accumulation of arsenic (As) in rice crops is the quality of the water used for irrigation. According to Saldaña et al. (2018), irrigation with arsenic-contaminated water is a significant source of this metalloid's introduction into rice plants, with soil and irrigation water being the main means of transport and accumulation. Pathak et al. (2024) indicate that the mobility of arsenic in agricultural soils and its absorption by plants are determined by variables such as irrigation management and the application of chemical treatments. In this context, it has been shown that rice plants are capable of absorbing and accumulating arsenic in their roots and shoots, which increases the risk of contamination in the crop. Abhiram & Amarathunga. (2024) warn that arsenic concentrations in rice grains intended for human consumption can fluctuate and, in some cases, exceed the maximum permissible limits established by international regulations, posing a potential risk to public health.

Comparison of arsenic concentrations with national and international standards

The selected regulations, NTE INEN and Codex Alimentarius, establish a maximum permissible limit for arsenic of 0.2 mg/kg, while the European Union sets a limit of 0.25

mg/kg. Figure 9 shows that the arsenic concentrations in the samples analyzed (AMD1: 0.18 mg/kg, AMD2: 0.21 mg/kg, AMD3: 0.19 mg/kg, AMD4: 0.12 mg/kg, AMT1: 0.16 mg/kg) are below the limit established by European regulations (REGULATION (EC) No 1881/2006). However, according to national regulations (NTE INEN – CODEX 193:2013) and Latin American regulations (CODEX STAN 193-1995), sample AMD2, with a concentration of 0.21 mg/kg, exceeds the permissible limit, as shown in Figure 5.

Figure 5. Comparison of arsenic concentrations with national and international standards

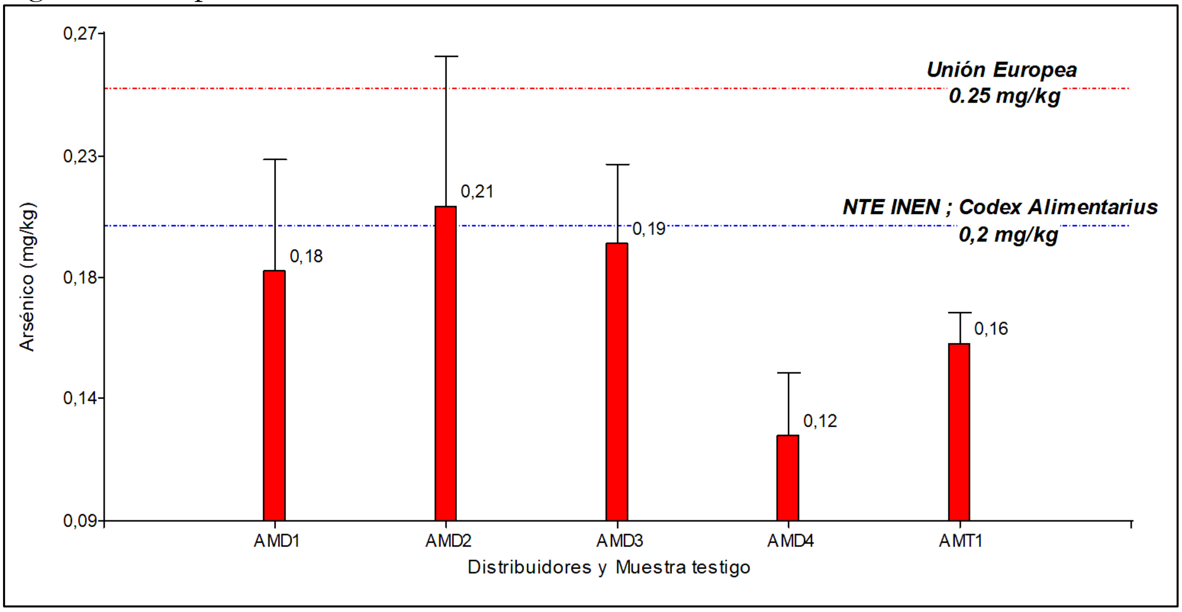
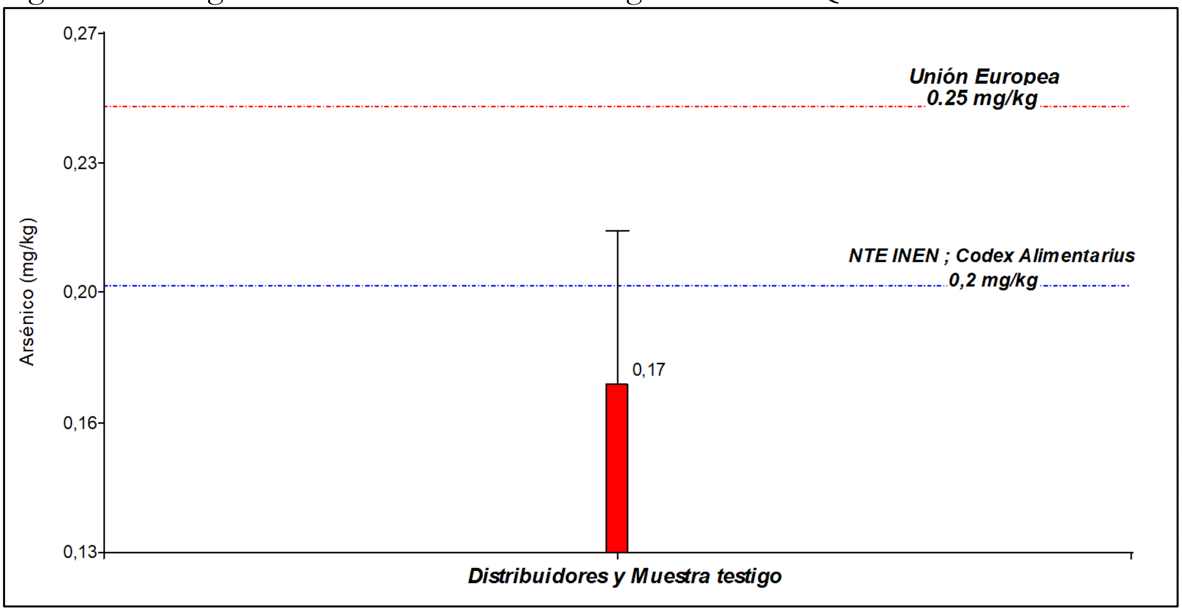


Figure 6 shows the overall average arsenic concentration in rice grains distributed in Quevedo, with a value of 0.17 mg/kg. This result is below the maximum limit of 0.2 mg/kg established by NTE INEN and Codex Alimentarius, and is significantly lower than the threshold allowed by the European Union (0.25 mg/kg). The standard deviation bar reflects the variability in the measurements, suggesting a heterogeneous distribution of the contaminant in the samples analyzed. Although the values comply with current regulations, it is crucial to implement continuous monitoring to prevent fluctuations that could exceed the permissible limits and pose a risk to food safety.

Figure 6. Average concentrations of arsenic in grains sold in Quevedo



The permissible limits for arsenic in rice vary according to international regulations established by different control agencies (Alrashdi et al., 2024). According to Kumar et al. (2025), rice productivity and quality are at risk in areas affected by arsenic (As) contamination, a problem that could intensify due to the effects of climate change. Jiménez et al. (2024) point out that the presence of heavy metals represents a global challenge, given that their origin can be associated with both anthropogenic and natural sources.

Alrashdi et al. (2024) point out that rice can be contaminated with toxic elements, including arsenic, prolonged exposure to which has been associated with various diseases, including cancer. Along these lines, Marchetti et al. (2021) determined that arsenic contamination in rice represents a public health problem, highlighting the need to continue expanding and deepening research to obtain accurate knowledge about the content of this metal in crops.

Environmental impact caused by arsenic-contaminated rice grains in the Quevedo cantón

Arsenic levels in rice samples distributed in Quevedo were evaluated based on their environmental impact, in accordance with NTE INEN and Codex Alimentarius regulations (Table 2). Environmental impact values range from -0.08 to 0.01, with sample AMD2 standing out with a positive value of 0.01, indicating significant environmental damage. Although the overall arsenic concentrations are within the limits permitted by the regulations, some high values could, if not properly managed, pose long-term risks to both public health and the natural environment.

Table 2. Environmental impact of arsenic in rice grains distributed in Quevedo through regulations (NTE INEN and Codex Alimentarius)

AM D1	**AM D2**	**AM D3**	**AM D4**	**AM T1**	**NTE INEN / Codex Alimentarius**	**Environmental impact**				
						AM D1	**AM D2**	**AM D3**	**AM D4**	**AM T1**
0.18	0.21	0.19	0.12	0.16	0.20	-0.02	0.01	-0.01	-0.08	-0.04

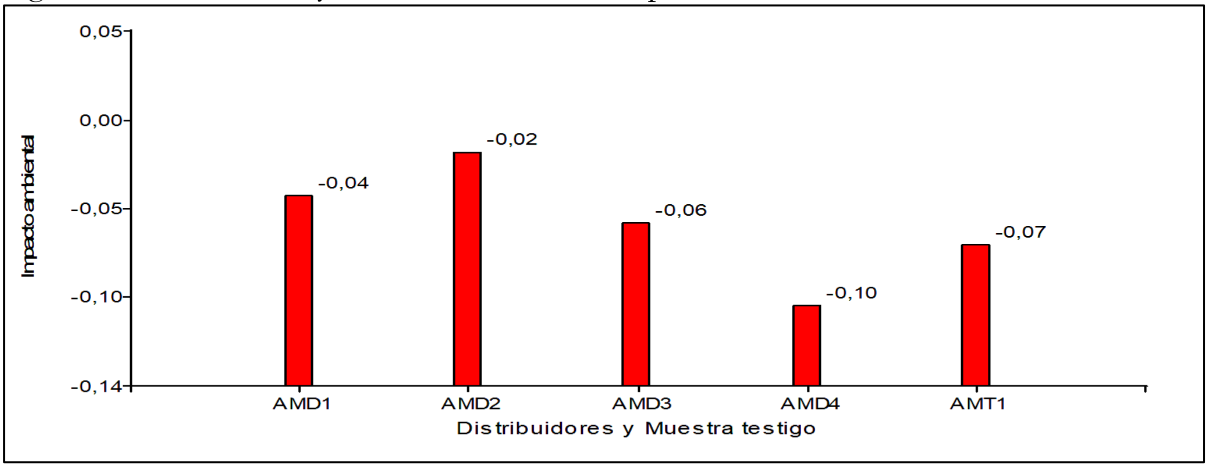
The environmental impact values range from -0.04 to -0.13, with the AMD4 sample showing the lowest compliance margin (-0.04), indicating that it does not represent severe environmental damage. However, this value highlights the importance of maintaining constant and preventive monitoring to ensure that arsenic levels do not exceed established limits, thereby minimizing environmental impact and ensuring the protection of the ecosystem.

Table 3. Environmental impact of arsenic in rice grains distributed in Quevedo through regulations (Regulation (EC) No. 1881/2006).

AM D1	**AM D2**	**AM D3**	**AM D4**	**AM T1**	**REGLAMENTO (CE) No 1881/2006**	**Impacto ambiental**				
						AM D1	**AM D2**	**AM D3**	**AM D4**	**AM T1**
0.18	0.21	0.19	0.12	0.16	0.25	-0.07	-0.04	-0.06	-0.13	-0.09

Data analysis
The normality test, performed using the modified Shapiro-Wilk test, yielded a p-value of 0.2486, indicating that the data follow a normal distribution, as this value is greater than the significance threshold of 0.05. Based on this evidence, an analysis of variance (ANOVA) was performed, followed by Tukey's multiple comparison test to evaluate the differences between the means of the groups. The p-value of 0.0180 obtained in the ANOVA confirms the existence of statistically significant differences between at least one of the distributor groups, suggesting that the environmental impact varies depending on the distributor. The Tukey test identified similarities and differences between the groups, determining that AMD4 is statistically similar to AMT1, AMD3, and AMD1 (Group A), while AMD2 is only similar to AMD1, AMD3, and AMT1 (Group B). This indicates that AMD4 has the lowest mean and is significantly different from AMD2, while the other distributors have intermediate means with no significant differences between them.

Figure 7. Statistical analysis of environmental impact data for arsenic in rice



The analysis of the impacts recorded in relation to the presence of arsenic reveals that, on average, all values obtained are below zero. However, the sample corresponding to distributor AMD2 shows a significant value of -0.02, which suggests that it does not imply severe damage to the environment, as indicated in Figure 7. According to Saeed et al. (2023), arsenic is present in water and soil systems, which facilitates its availability and potential absorption by plants. In this context, Etesami et al. (2023) highlight that rice has a significantly higher arsenic absorption capacity compared to other food crops, which increases the risk of bioaccumulation. Likewise, Kaur et al. (2022) state that the rice plant has the highest arsenic retention capacity throughout its growth cycle, which increases its concentration in harvested grains. On the other hand, Vega et al. (2023) emphasize that rice (Oryza sativa L.) is one of the most widely consumed foods worldwide and plays a fundamental role in the food industry, in addition to being a crop of high economic importance and a key pillar for the food security of many families. Along the same lines, Mondal et al. (2024) warn that the presence of arsenic in water used for irrigation poses a potential risk to rice quality, which can affect its nutritional composition and have adverse effects on its consumption.

CONCLUSIONS

This study confirms the presence of arsenic in rice grains sold in the Quevedo canton, revealing a contamination process that, although it does not exceed the maximum limits established by national and international regulations, still represents a latent environmental risk. The detection of constant concentrations of this metalloid at all sampling points suggests continuous exposure of the agricultural system to arsenic, probably derived from the intensive use of agrochemicals and contaminated water sources for irrigation. From an environmental perspective, the results of the impact analysis indicate that, on average, current concentrations do not cause severe damage; however, the persistence of these levels in the agricultural ecosystem could lead to progressive accumulation in soils and affect their quality, with direct repercussions on crop health, biogeochemical cycles, and soil biodiversity. Rice, due to its ability to absorb arsenic, acts as a bioindicator of the environmental quality of the production system, so its monitoring is key to preventing long-term cumulative effects

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