SCIENTIFIC CULTURE
www.sci-cult.com

SCIENTIFIC CULTURE, Vol. 11, No. 4, (2025), pp. 3264-3271
Open Access. Online & Print

DOI: 10.5281/zenodo.19054735

PROCESS-DRIVEN BIOAVAILABILITY OF CADMIUM IN ACIDIC PADDY SOILS AND ITS TRANSFER TO RICE GRAIN: IMPLICATIONS FOR FOOD SAFETY CONTROL

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Received: 25/09/2025
Accepted: 15/11/2025

ABSTRACT

Cadmium contamination in rice production systems represents a critical challenge for food safety and process sustainability, particularly in regions characterized by acidic soils. From a chemical engineering perspective, cadmium transfer from soil to grain can be understood as a chemically driven transport process controlled by soil pH, metal speciation, and competitive ion interactions. This study evaluated cadmium accumulation in rice cultivated and commercialized in the El Zulia region (Norte de Santander, Colombia) by analyzing its distribution across soil, paddy rice, and polished grain matrices. A composite sampling strategy was applied to representative mechanized rice farms and commercial rice products. Cadmium concentrations were determined by atomic absorption spectrometry, while key soil parameters governing metal mobility, including pH, iron, and manganese content, were characterized. Results revealed cadmium concentrations of up to 0.84 mg•kg⁻¹ in polished rice, exceeding the Codex Alimentarius maximum limit (0.4 mg•kg⁻¹) by more than 100%. Commercial rice samples also surpassed international regulatory thresholds, demonstrating that industrial processing steps such as dehusking and polishing are insufficient to mitigate contamination when cadmium originates at the production stage. The soil exhibited a strongly acidic pH (3.49) and elevated cadmium levels, conditions that promote the predominance of soluble Cd^{2+} species and suppress immobilization mechanisms. Despite high iron availability, no effective antagonistic control of cadmium uptake was observed, indicating that metal competition strategies collapse under extreme acidity. These findings confirm that cadmium contamination in rice is the result of a systemic process imbalance rather than isolated agronomic factors. The study highlights soil pH as the dominant control variable governing cadmium bioavailability and transfer. Effective mitigation therefore requires upstream process control strategies, such as chemical neutralization or immobilization at the soil level, rather than reliance on downstream post-harvest treatments. This process-oriented interpretation provides a technical basis for designing sustainable cadmium mitigation strategies in acidic rice production systems.

KEYWORDS: Cadmium; Rice Production; Soil Acidity; Metal Bioavailability; Process Control; Food Safety.

1. INTRODUCTION

Rice (Oryza sativa L.) is a strategic staple crop that sustains more than half of the global population and plays a central role in food security across tropical and subtropical regions. However, the increasing incidence of heavy metal contamination in rice-based systems has raised critical concerns regarding both food safety and process sustainability. Among these contaminants, cadmium (Cd) represents one of the most problematic trace elements due to its high mobility, persistence, and toxicity, as well as its efficient transfer from soil matrices to edible plant tissues (Rai et al., 2019; Suhani et al., 2021).

From a chemical engineering perspective, cadmium contamination in rice cultivation can be understood as a multiphase transport problem governed by soil chemistry, mass transfer mechanisms, and competitive ion interactions within the soil–root–grain continuum. Cadmium is a non-essential metal that exists predominantly as Cd^{2+} under acidic conditions, where its solubility and bioavailability are maximized. This physicochemical behavior facilitates its uptake by rice roots through non-specific divalent cation transporters, followed by translocation and accumulation in the grain, thereby bypassing conventional post-harvest mitigation steps such as milling and polishing (Bayona-Penagos, 2020; Murugan et al., 2019). Soil pH and redox potential constitute the primary control variables regulating cadmium mobility in paddy systems. Acidic soils, which are common in several rice-producing regions of Latin America, promote desorption of Cd from soil colloids and suppress its immobilization by iron and manganese oxides.

Although iron is often considered a natural antagonist capable of limiting Cd bioavailability through competitive adsorption and co-precipitation mechanisms, its protective role becomes marginal under strongly acidic conditions, where both metals remain in soluble forms and compete ineffectively for binding sites (Al-Wabel et al., 2015; Yang et al., 2018). Consequently, the soil effectively behaves as an open reactive medium, continuously supplying bioavailable cadmium to the crop throughout the growing cycle.

International regulatory frameworks, such as the Codex Alimentarius, have established maximum permissible limits for cadmium in polished rice (0.4 $mg \cdot kg^{-1}$) to protect consumers and facilitate safe international trade (Codex Alimentarius Commission, 1995). Nevertheless, recent studies conducted in Asia and Latin America demonstrate that rice cultivated in acidic or metal-enriched soils frequently exceeds these thresholds, even after industrial processing, revealing a systemic failure of downstream control strategies (Gao et al., 2022; Yang et al., 2019). This underscores the necessity of addressing cadmium contamination at the process-origin level, rather than relying on post-harvest remediation. While cadmium contamination in rice has been widely documented in Asia, emerging evidence indicates that South American production systems, including Colombia, exhibit physicochemical conditions that favor future risk escalation.

In Colombia, mechanized rice production represents a cornerstone of national food supply, with annual yields exceeding three million tons (DANE, 2023). The department of Norte de Santander, particularly the municipality of El Zulia, constitutes a key production zone characterized by intensive cultivation practices and acidic alluvial soils. Despite its agronomic importance, there is a notable lack of process-oriented studies evaluating cadmium transfer dynamics in this region, especially those integrating soil physicochemical parameters with grain-level contamination and regulatory compliance.

Therefore, the objective of this study was to evaluate cadmium accumulation in rice cultivated and commercialized in the El Zulia region by analyzing its distribution across soil and grain matrices under acidic conditions. By framing cadmium uptake as a chemically driven transport process, this work aims to identify the key controlling variables responsible for system failure and to provide a technical basis for the design of effective mitigation and control strategies aligned with food safety requirements and chemical engineering principles.

2. MATERIALS AND METHODOLOGY

2.1. Study area and System Description

The study was conducted in the municipality of El Zulia, Norte de Santander, Colombia, a strategic rice-producing region located within the irrigation district of the Zulia River. From a process engineering standpoint, the evaluated system was conceptualized as a soil–root–grain reactive continuum, in which cadmium transfer is governed by physicochemical equilibria, mass transport, and competitive ion interactions under flooded paddy conditions.

Three representative mechanized rice farms were selected within the study area based on their agronomic similarity, irrigation source, and continuous rice cultivation history. The soils are predominantly alluvial, with a documented tendency toward strong acidity, a condition known to enhance cadmium solubility and transport (Yang et al., 2018). The selected farms were treated as parallel units, within the same process domain, enabling a diagnostic evaluation of cadmium behavior at the regional scale.

2.2. Sampling Strategy and Experimental Design

A composite sampling design was employed to minimize intra-field spatial variability and to characterize the average process behavior of cadmium transfer within the system. This approach is consistent with diagnostic studies aimed at identifying dominant transport mechanisms rather than site-specific heterogeneities (Ramírez et al., 2023).

For each farm, soil and plant material were collected following a zig-zag sampling pattern. Multiple subsamples ($n \geq 10$) were manually homogenized to generate one representative composite sample per matrix. The evaluated matrices included: (i) agricultural soil, (ii) rice grain with husk (paddy), and (iii) polished rice grain.

In parallel, commercial rice samples were obtained from local distribution outlets in the metropolitan area of Cúcuta. Two high-consumption brands were selected, and composite samples were prepared by homogenizing rice obtained from different production batches available at the point of sale. This procedure allowed evaluation of cadmium persistence after industrial processing and market distribution.

2.3. Sample Preparation and Pretreatment

All samples were handled following strict contamination control protocols. Soil samples were air-dried at room temperature, gently disaggregated, and sieved through a 2 mm mesh. Plant samples were oven-dried at 60 °C to constant weight and milled to obtain a homogeneous powder.

For total cadmium determination, samples were subjected to acid digestion using a microwave-assisted protocol to ensure complete matrix decomposition. Approximately 0.5 g of dried sample was digested with concentrated nitric acid (HNO_3, analytical grade), following standardized procedures for trace metal analysis in agricultural matrices (Skoog et al., 2018; Rodríguez Giraldo et al., 2024).

2.4. Analytical determination of Cadmium and Soil parameters

Cadmium quantification was performed using atomic absorption spectrometry (AAS), selected for its robustness, sensitivity, and widespread validation for metal determination in food and soil samples. Soil cadmium was determined using graphite furnace AAS, while grain samples were analyzed using flame AAS, depending on concentration ranges and matrix effects.

Soil pH was measured potentiometrically in a 1:1 soil-to-water suspension, as pH represents the principal control variable governing cadmium solubility and speciation in flooded soils. Additionally, iron (Fe) and manganese (Mn) concentrations were determined by flame AAS to evaluate their potential antagonistic role in cadmium uptake through competitive ion interactions.

All measurements were conducted in triplicate to ensure analytical precision. Instrument calibration was performed using certified reference standards, and quality control included procedural blanks and replicate analyses.

2.5. Data Analysis and Regulatory Comparison

Results were expressed as mean values ± standard deviation of the analytical replicates. Given the diagnostic nature of the study, statistical analysis focused on comparative evaluation rather than inferential modeling.

Cadmium concentrations in rice were directly compared against international regulatory thresholds, including the Codex Alimentarius maximum limit of 0.4 $mg \cdot kg^{-1}$ for polished rice and the more restrictive European Union limit of 0.2 $mg \cdot kg^{-1}$ (Codex Alimentarius Commission, 1995; European Commission, 2021). Exceedance ratios were calculated to quantify the magnitude of regulatory non-compliance and to assess the effectiveness of downstream processing as a mitigation step.

This methodological framework enabled the identification of critical control failures within the soil–plant–food chain and provided a process-based basis for interpreting cadmium accumulation in rice under acidic conditions.

3. RESULTS AND DISCUSSION

3.1. Cadmium Accumulation in Rice and Regulatory Exceedance

The analytical results revealed a systemic accumulation of cadmium in rice cultivated in the El Zulia region, with concentrations that significantly exceed international food safety thresholds. The mean cadmium concentration in cultivated polished rice reached 0.84 $mg \cdot kg^{-1}$, while rice paddy samples exhibited 0.73 $mg \cdot kg^{-1}$. Both values surpass the Codex Alimentarius maximum limit of 0.4 $mg \cdot kg^{-1}$ by more than 100%, indicating a failure of the production system to control cadmium transfer at the source (Figure 1).

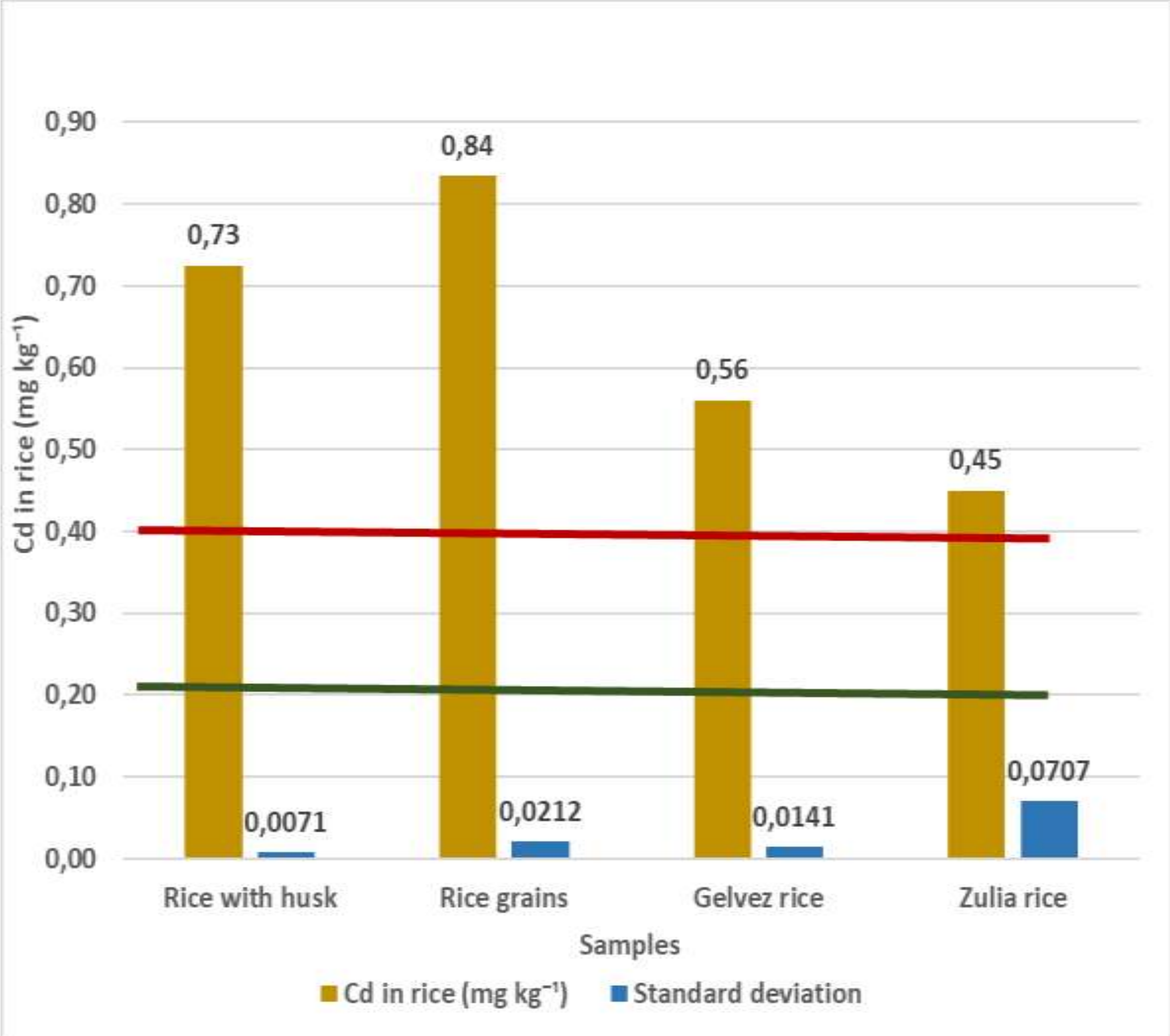

Figure 1: Cadmium concentration in rice matrices relative to international regulatory thresholds. Bars represent mean cadmium concentrations (± SD, n = 3) measured in paddy rice, cultivated polished rice, and commercial polished rice samples from the El Zulia region. Dashed horizontal lines indicate the maximum limits established by the Codex Alimentarius (0.4 mg•kg⁻¹) and the European Union (0.2 mg•kg⁻¹). Results demonstrate systematic regulatory exceedance in both cultivated and commercial rice, indicating that post-harvest processing does not effectively mitigate cadmium contamination when uptake occurs at the production stage.

Commercially available polished rice showed cadmium concentrations ranging from 0.45 to 0.56 $mg \cdot kg^{-1}$, confirming that industrial processing steps such as dehusking and polishing are insufficient to mitigate contamination when the raw material is heavily enriched. From a process engineering standpoint, this demonstrates that polishing acts only as a partial mass removal step, incapable of altering the chemical speciation or internal distribution of cadmium already incorporated into the endosperm.

Comparable exceedance levels have been reported in highly contaminated rice-producing regions in Asia, particularly in the Yangtze River basin, where similar soil acidity and long-term fertilization practices result in chronic cadmium bioaccumulation (Gao et al., 2022; Yang et al., 2019). These findings reinforce the interpretation that cadmium contamination in El Zulia is not an isolated phenomenon but rather the outcome of a structural process imbalance within the soil–plant system.

3.2. Soil Acidity as the Dominant Control Variable

The soil matrix exhibited a strongly acidic pH of 3.49, coupled with a total cadmium concentration of 8.86 $mg \cdot kg^{-1}$, values well above background levels for agricultural soils (Figure 2). At such low pH, cadmium predominantly exists as free Cd^{2+} ions, maximizing its solubility and transport potential. This condition fundamentally alters the soil from a buffering medium into a continuous source of bioavailable cadmium, effectively feeding the uptake process throughout the rice growth cycle.

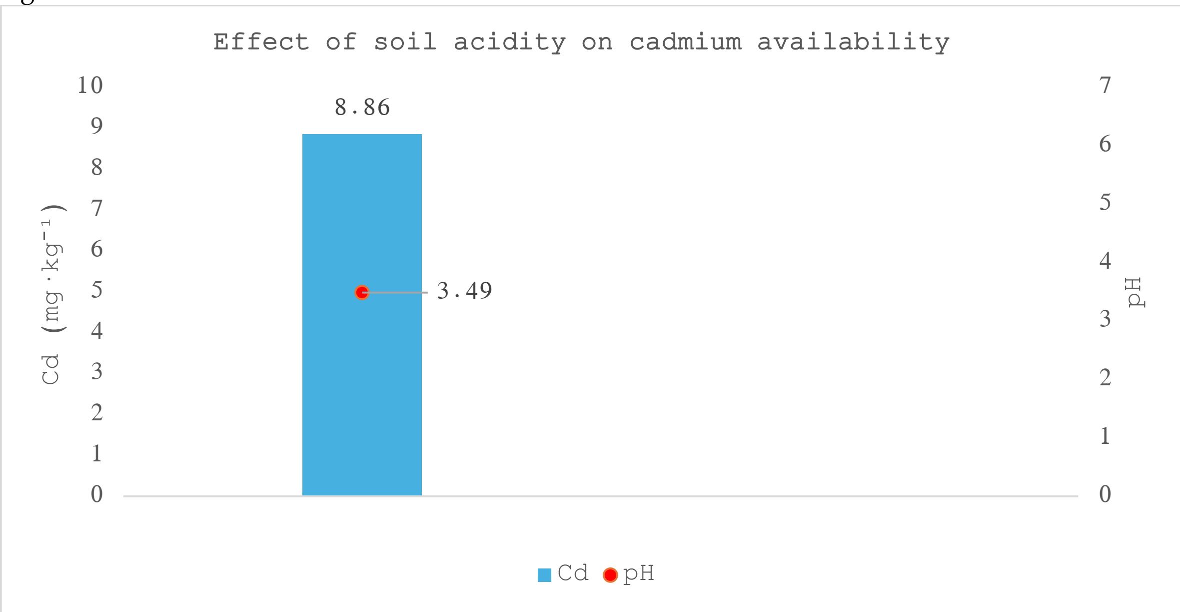

Figure 2: Effect of Soil acidity on Cadmium availability in paddy Soils. The bar represents total Cadmium concentration in the composite soil sample, while the line indicates soil pH. The strongly acidic condition (pH = 3.49) promotes the predominance of soluble Cd^{2+} species, enhancing metal mobility and uptake by rice plants. Shaded area highlights the pH range (< 5.0) associated with increased cadmium bioavailability in flooded rice systems.

From a chemical equilibrium perspective, acidic conditions suppress cadmium adsorption onto clay minerals and organic matter while inhibiting co-precipitation with iron and manganese oxides (Figure 3). As a result, the soil operates as an open reactive system, where cadmium mobility is governed primarily by proton activity rather than sorptive capacity. This explains the strong correspondence observed between soil cadmium levels and grain contamination.

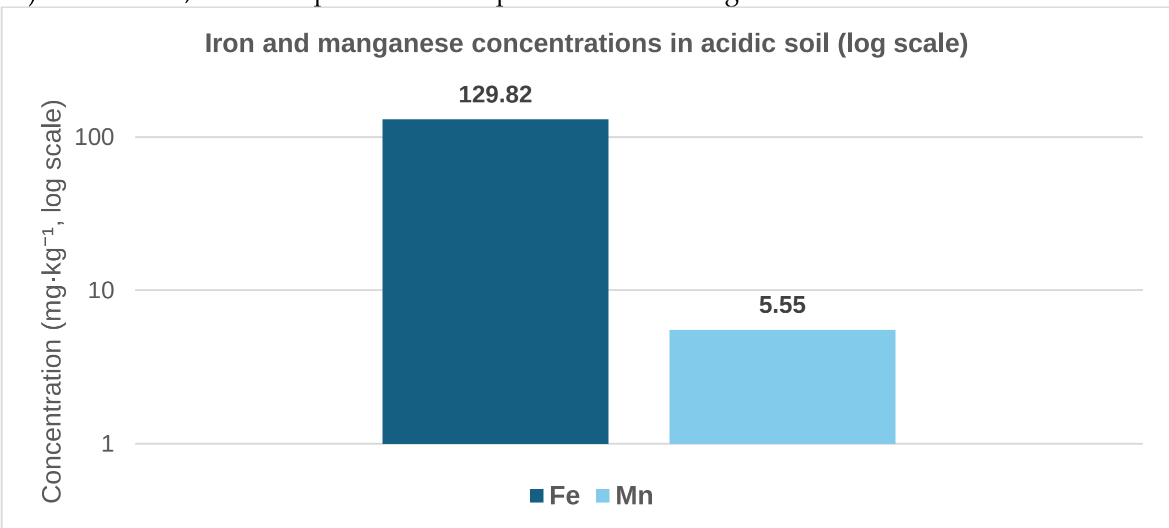

Figure 3: Iron and manganese concentrations in agricultural soil and their limited antagonistic role under acidic conditions. Bars represent mean concentrations (± SD, n = 3) of Fe and Mn determined by atomic absorption spectrometry. Despite elevated iron levels, cadmium immobilization is ineffective at low pH, while low manganese availability further reduces competitive ion buffering in the rhizosphere, facilitating cadmium uptake.

The magnitude of cadmium transfer observed in this study aligns with previous reports indicating exponential increases in plant uptake when soil pH drops below 5.0 (Bayona-Penagos, 2020; Murugan et al., 2019). Thus, pH emerges not merely as a contributing factor but as the primary process control variable dictating system behavior.

3.3. Ineffectiveness of Iron-mediated Antagonism under Acidic conditions

Despite the relatively high iron concentration measured in the soil (129.82 mg•kg^{-1}), no effective antagonistic effect on cadmium uptake was observed (Table 1). Under neutral or mildly acidic conditions, iron oxides can immobilize cadmium through adsorption or co-precipitation mechanisms. However, at the extreme acidity recorded in El Zulia, iron remains largely in soluble or weakly sorbed forms, drastically reducing its capacity to sequester cadmium.

Table 1: Physicochemical characteristics of paddy soil from the El Zulia region and their process implications.

Parameter	Value	Unit	Process implication
pH	3.49	–	High Cd^{2+} solubility
Total Cd	8.86	mg·kg^{-1}	High source term
Fe	129.8	mg·kg^{-1}	Ineffective antagonist at low pH
Mn	5.5	mg·kg^{-1}	Low competitive buffering

This behavior highlights a critical limitation in relying on natural antagonists as passive mitigation agents. Although iron and cadmium compete for similar transport pathways at the root interface, the overwhelming availability of Cd^{2+} ions under acidic conditions negates this competition. Similar observations have been reported by Al-Wabel et al. (2015), who demonstrated that iron-rich soils fail to restrict cadmium uptake when pH-driven solubilization dominates system kinetics.

From an engineering perspective, this indicates that antagonistic control strategies are conditional, and their effectiveness collapses outside a narrow operational pH window. Consequently, mitigation efforts based solely on metal competition are inherently unstable in acidic paddy systems.

3.4. Process Implications for Food safety and System Control

The persistence of cadmium above regulatory thresholds in polished rice can be further explained by the intrinsic transport mechanisms operating within the rice plant. Cadmium uptake occurs primarily through non-specific divalent cation transporters at the root interface, followed by xylem-mediated translocation and internal allocation within the grain endosperm (Uraguchi and Fujiwara, 2012; Ueno et al., 2010). Once incorporated into internal grain tissues, cadmium becomes largely inaccessible to physical separation processes, which explains the limited effectiveness of dehusking and polishing as mitigation steps. This behavior highlights that cadmium contamination is structurally embedded within the soil–plant system and cannot be resolved through downstream processing alone. Moreover, although metal competition has been proposed as a potential control mechanism, its effectiveness is strongly conditioned by soil chemistry, particularly pH, which governs both transporter selectivity and metal speciation (Clemens et al., 2013). Under strongly acidic conditions, such as those observed in the present study, these control pathways collapse, reinforcing the need for upstream chemical process regulation rather than reliance on post-harvest interventions (Figure 4).

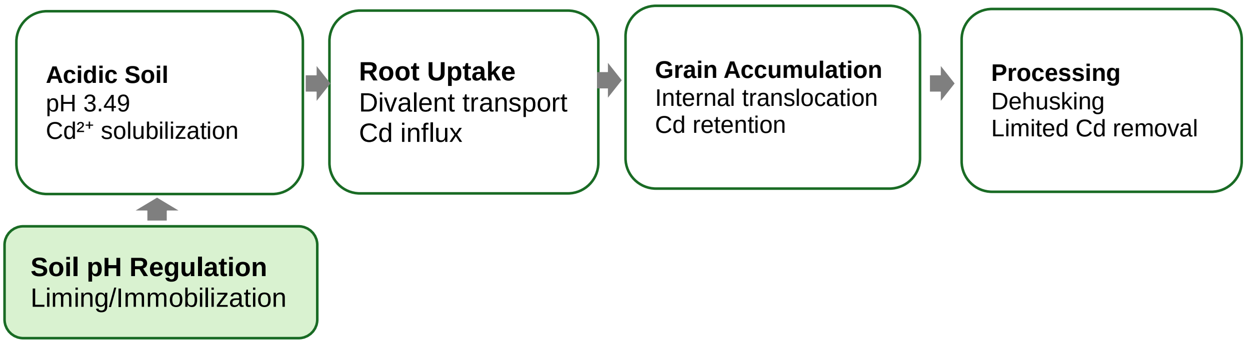

Figure 4: Simplified process-based model of cadmium transfer in acidic rice systems. Soil acidity (pH 3.49) enhances Cd^{2+} solubilization, facilitating root uptake and internal grain accumulation. Post-harvest processing provides limited cadmium removal, emphasizing the importance of upstream soil pH regulation and immobilization strategies.

This finding underscores the necessity of upstream process intervention, particularly soil pH management, as a prerequisite for effective cadmium control. From a process design standpoint, soil amendment strategies such as liming, alkaline biochar incorporation, or chemically engineered adsorbents should be viewed as process control units, analogous to neutralization or immobilization steps in conventional chemical reactors.

Failure to regulate these upstream variables results in a cascading system failure, where regulatory non-compliance becomes inevitable regardless of post-harvest interventions. Therefore, cadmium contamination in rice must be addressed as a process design and control problem, rather than a purely environmental or agronomic issue.

4. CONCLUSIONS

This study demonstrates that cadmium contamination in rice cultivated in the El Zulia region constitutes a systemic process failure driven primarily by soil chemical conditions rather than by isolated agronomic practices. The detection of cadmium concentrations up to 0.84 $mg \cdot kg^{-1}$ in polished rice—exceeding international regulatory limits by more than 100%—confirms that the soil–plant–grain continuum operates as an efficient transfer pathway under strongly acidic conditions.

Soil acidity emerged as the dominant control variable governing cadmium mobility and uptake. At a pH of 3.49, the soil behaves as an open reactive medium in which cadmium persists predominantly in its soluble Cd^{2+} form, overwhelming natural immobilization mechanisms. Under these conditions, the presence of elevated iron concentrations in the soil was insufficient to exert a protective antagonistic effect, demonstrating that metal competition strategies are ineffective outside a limited operational pH window.

The results further reveal that downstream mitigation through industrial processing, such as dehusking and polishing, does not provide adequate reduction of cadmium concentrations when contamination originates at the production stage. Once cadmium is incorporated into the internal grain matrix, physical separation processes fail to restore regulatory compliance, rendering post-harvest interventions structurally ineffective.

From a chemical engineering perspective, these findings highlight the necessity of upstream process control as the only viable strategy to mitigate cadmium transfer in rice production systems. Soil pH regulation through liming, alkaline amendments, or engineered sorbents should be conceptualized as essential control units within the production process, analogous to neutralization or immobilization steps in conventional chemical reactors. Without such interventions, compliance with food safety standards becomes unattainable regardless of downstream processing intensity.

Overall, this work reframes cadmium contamination in rice as a process design and control challenge, rather than solely an environmental or agronomic issue. The proposed process-oriented interpretation provides a technical foundation for the development of integrated mitigation strategies capable of reducing cadmium bioavailability, ensuring food safety, and enhancing the sustainability of rice production systems in acidic environments.

Acknowledgments: The authors acknowledge the Quality Control and Diagnostic Laboratory at Universidad de Pamplona for infrastructural support.

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