A Case Study on Minerals Interaction in the Soil and Se Enrichment in Rice (*Oryza sativa L.*) †

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Abstract: Selenium plays an important role in regulating soil–plant ecosystem functions. It is an essential element with antioxidative activity; however, its presence in plants is scarce [1,2]. Since 1930, studies have been conducted to understand the relationship between Se concentrations in soil and plant uptake [3]. Selenium content in plants is correlated with the bioavailability of the micronutrient in the soil [4]. According to [5], soils in humid climates and temperate zones hold low Se availability, which directly interferes with the Se content in food production. Nowadays, it is known that organic and inorganic forms of Se present in food are crucial for human nutrition [6]. Considering

1. Introduction

Selenium (Se) is an essential micronutrient to many species; however, its presence in plants is scarce [1,2]. Since 1930, studies have been conducted to understand the relationship between Se concentrations in soil and plant uptake [3]. Selenium content in plants is correlated with the bioavailability of the micronutrient in the soil [4]. According to [5], soils in humid climates and temperate zones hold low Se availability, which directly interferes with the Se content in food production. Nowadays, it is known that organic and inorganic forms of Se present in food are crucial for human nutrition [6]. Considering
that plants absorb from the soil, the main Se species in the form of selenate (SeO$_4^{2-}$) and selenite (SeO$_3^{2-}$), strategies for enriching the rice grain (Oryza sativa L.) with Se have been applied [7,8]. According to a nutritional perspective, in addition to Se, any crop should maximize the uptake of essential mineral elements and decrease the accumulation of contaminants in the edible parts [9]. However, there are antagonistic relationships that are important to consider, as in the case of Zn. It is an essential micronutrient for humans and animals, while in plants it is associated with the physiological processes of metabolism and growth [10]. It is important on the one hand to enrich the rice grain and on the other to ensure that the quality parameters are not negatively affected because rice quality parameters directly influence its commercial value [11].

This work aimed to correlate mineral interactions in the paddy rice field soil as well as to characterize the interactions between Se and Zn content in rice grains considering the quality parameters.

2. Materials and Methods

2.1. Experimental Fields

The experimental rice field was conducted in central Portugal in the experimental station of Rice Technological Center (COTArroz) from May to November of 2018. The Se enrichment in Ariete variety (Oryza sativa L.) was carried out by foliar spraying with solutions of sodium selenate (Na$_2$SeO$_4$—treatment A) and sodium selenite (Na$_2$SeO$_3$—treatment B) at different concentrations (50 and 75 g Se·ha$^{-1}$). Foliar pulverizations occurred at booting, anthesis and milky grain stage. No spraying was applied to control. The experimental design in the field was performed in randomized blocks and a factorial arrangement in 24 plots (3 concentrations $\times$ 2 forms selenium $\times$ 1 variety $\times$ 4 replicates) considering an area of 9.6 m$^2$ of each plot. The analysis was performed in paddy and white rice grains of Ariete variety.

2.2. Quantification of Mineral Elements in Soil, Paddy and White Rice Grains

Soil samples from the rice paddy field were collected and treated as described by [12]. Minerals content was analyzed using an XRF analyzer (model XL3t 950 He GOLDD+) under helium atmosphere [13]. At grain harvest, an acid digestion procedure was carried with a mixture of HNO$_3$–HCl (4:1) according to [14,15]. Selenium and Zinc contents were quantified by atomic absorption spectrophotometry (Perkin Elmer AAnalyst 200) according to [16].

2.3. Thousand Grain Weight and Colorimetric Parameters

After harvest, the samples were hulled and whitened as mentioned in [7]. The thousand-grain weight was carried out for each treatment in quadruplicate, according to [17]. Colorimetric parameters were performed in harvested rice grains in quadruplicates using a spectrophotometric colorimeter (Agrosta, European Union) according to [18].

2.4. Statistical Analysis

Data were statistically analyzed using a One-Way Analysis of Variance ($p \leq 0.05$), to assess differences and then Tukey’s test was performed for mean comparison. A 95% confidence level were adopted for all tests.

3. Results

3.1. Characterization of Rice Field

Considering the importance and the contribution of soil to the enrichment of Se in the rice grains, rice paddy soils were analyzed. The results showed a pH range of 5.86 with electrical soil conductivity of 0.223 dS/m and 1.32 of organic matter. Soil analysis showed significantly different levels of Fe, Ca, K, P, S, Mg and high levels of Pb and As, while Se remained below 1 ppm (Figure 1).
3.2. Analysis of Selenium and Zinc Contents

Selenium accumulation in paddy rice grains increased in both treatments (Table 1). Regarding the control, it was in the treatment with sodium selenite that the increase was more significant, from 22.1 ppm (control) up to 58.0 ppm. In the same treatment but in the white rice grains the contents increased from 29.9 ppm to 77.9 ppm. Selenium spraying resulted in higher Se contents compared to the control; however, it promoted the progressive decrease in the Zn contents in white rice grains (i.e., the contents decreased from 16.6 to 9.01 ppm).

Table 1. Average values (ppm) ± standard deviation (n = 4) of Se and Zn in the paddy and white rice grains of *Oryza sativa* L., variety Ariete at harvesting. Letters a and b indicate significant differences among treatments (p ≤ 0.05).

| Treatments (g Se·ha⁻¹) | Paddy | White Rice |
|-------------------------|-------|------------|
| Se Zn                   |       |            |
| Control                 | 22.1 ± 0.01 ab | 10.4 ± 4.02 a | 29.9 ± 7.20 b | 16.6 ± 0.75 a |
| Na₂SeO₄ 50              | 27.4 ± 0.10 b | 3.89 ± 0.76 a | 31.7 ± 3.15 b | 8.63 ± 0.19 b |
| 75                      | 47.6 ± 0.02 ab| 10.3 ± 2.77 a| 35.6 ± 2.39 b| 7.59 ± 0.99 ab|
| Na₂SeO₃ 50              | 53.7 ± 2.27 a| 8.17 ± 2.05 a| 37.1 ± 2.43 b| 8.87 ± 0.80 ab|
| 75                      | 58.0 ± 1.96 a| 11.5 ± 1.23 a| 77.9 ± 1.97 a| 9.01 ± 1.28 ab|

3.3. Grain Weight and Colorimetric Analysis

The grain weight did not show significant differences in paddy rice grains regarding the different forms of Se applied (Figure 2). However, in white rice grains, the sodium
selenate enrichment showed a little bit of an increase in weight in both treatments (50 and 75 g Se·ha$^{-1}$).

Figure 2. Average (g) ± standard deviation ($n = 4$) of 1000-grain weight of paddy and white rice grains of *Oryza sativa* L. variety Ariete at harvesting. Letters a and b represent sodium selenate and sodium selenite treatments, respectively. Letters a and b indicate significant differences among treatments ($p \leq 0.05$).

In paddy (Figure 3a) and white rice grains (Figure 3b), regarding the control, no significant differences can be observed. Both grains showed two peaks at 550 and 650 nm which corresponds to green to yellow and yellow to red transitions. These peaks are more pronounced in white grains because they are associated with industrial processing.

Figure 3. Average colorimetric parameters ± standard deviation ($n = 4$) of paddy (a) and white rice grains (b) of *Oryza sativa* L., variety Ariete at harvesting. Letter a indicates the absence of significant differences among treatments ($p \leq 0.05$).

4. Discussion

Trace elements in the soil such as Zn, Cd, Pd, Cu, As and others are absorbed and transported to tissues at an aboveground level [19]. The results show that the pH ranged from 5.5 to 6.5, which indicates that we are in the presence of suitable soil for crops management. In the soil samples, the levels of Fe, Ca, K, P, S, Mg, Pb, As and Se were quantified (Figure 1). Studies have reported the role of Se in combating heavy metal stress in plants [20]. The interaction of elements in the soil–plant system will affect their bioavailable content in the soil and the growth of crops [10]. By formation of immobilized compounds by plants, Se can reduce the uptake of these metals, thus exhibiting a strongly antagonistic effect [19]. The reduction in heavy metal uptake can be explained because there is a reduced synthesis of heavy metal enzymes triggered by increased glutathione peroxidase synthesis [21]. Previously, studies reported Se application in rice plants [7]. The enrichment of the rice crop with Se must respect the needs of the plant to enrich the edible portions [17]. However, the success of grain enrichment depends on the characteristics of
the variety, the form of Se applied and the concentration of the solutions [22]. Our study showed that for the Ariete variety, both forms of Se applied promoted the enrichment; however, better results were obtained in the treatment with selenite (Table 1). As previously found, foliar application of sodium selenate is less effective than sodium selenite [23]. These results are associated with the mobility of selenite (which is very mobile and easily absorbed by the plants) [24]. The foliar spraying promoted the accumulation of Se; however, the Zn values decreased in white grains (Table 1) as pointed by other authors [25]. Other studies suggest that Zn is metabolized and assimilated in different pathways [26]. The literature reports that selenate application promotes the accumulation of Zn, Fe and Ca [27]. However, in our study, selenate application showed no significant changes in paddy rice and increased Zn content in white grains (Table 1). In addition to the study of plant–soil interactions and grain mineral contents (such as antagonistic and synergistic interactions), it is important that quality parameters such as grain weight and colorimetric parameters are not affected by grain enrichment. Indeed, independent of each treatment the biggest variations in grain weight were not detected (Figure 2). In studies about the enrichment of rice in selenite, the authors pointed to the production of higher brown grains [22]. For each type of grain, the colorimetric parameters did not reveal significant differences which indicated that the implemented itinerary affected the visual quality of the grains. The differences between paddy and white rice grains are probably associated with industrial processes such as dehusking and whitening (Figure 3).

5. Conclusions

The enrichment of the rice grains with Se at concentrations ranging between 50–75 g Se·ha$^{-1}$ did not present any symptoms of toxicity. The increment of Se influences the concentration of the element Zn, particularly in white rice grains. These interactions did not significantly affect the grain weight or the colorimetric parameters. Accordingly, it is concluded that the applied itinerary showed an antagonistic relation of Se with Zn. Additionally, regarding the interactions between soil minerals and interactions of micronutrients in the grain, it was possible to enrich rice grains with Se without compromising the quality parameters.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/IECPS2021-11953/s1.

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