



## Proceeding Paper

# A Case Study on Minerals Interaction in the Soil and Se Enrichment in Rice (*Oryza sativa* L.) <sup>+</sup>

Ana Coelho Marques <sup>1,2,\*</sup>, Diana Daccak <sup>1,2</sup>, Inês Carmo Luís <sup>1,2</sup>, Ana Rita F. Coelho <sup>1,2</sup>, Cláudia Campos Pessoa <sup>1,2</sup>, Paula Scotti Campos <sup>2,3</sup>, Manuela Simões <sup>1,2</sup>, Ana Sofia Almeida <sup>2,4</sup>, Maria F. Pessoa <sup>1,2</sup>, Fernando H. Reboredo <sup>1,2</sup>, Carlos Galhano <sup>1,2</sup>, José C. Ramalho <sup>2,5</sup>, Paula Marques <sup>6</sup>, Maria Manuela Silva <sup>2,7</sup>, Paulo Legoinha <sup>1,2</sup>, Karliana Oliveira <sup>2</sup>, Isabel Pais <sup>2,3</sup> and Fernando C. Lidon <sup>1,2</sup>

- <sup>1</sup> Earth Sciences Department, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal
- <sup>2</sup> GeoBioTec Research Center, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal
- <sup>3</sup> Instituto Nacional de Investigação Agrária e Veterinária, I.P. (INIAV), Avenida da República, Quinta do Marquês, 2780-157 Oeiras, Portugal
- <sup>4</sup> Instituto Nacional de Investigação Agrária e Veterinária, I.P. (INIAV), Estrada de Gil Vaz 6, 7351-901 Elvas, Portugal
- <sup>5</sup> PlantStress & Biodiversity Lab., Centro de Estudos Florestais (CEF), Instituto Superior Agronomia (ISA), Universidade de Lisboa (ULisboa), Quinta do Marquês, Av. República, 2784-505 Oeiras and Tapada da Ajuda, 1349-017 Lisboa, Portugal
- <sup>6</sup> Centro Operativo e Tecnológico do Arroz (COTARROZ), 2120-014 Salvaterra de Magos, Portugal
- <sup>7</sup> Escola Superior de Educação Almeida Garrett (ESEAG-COFAC), Avenida do Campo Grande 376, 1749-024 Lisboa, Portugal
- \* Correspondence: amc.marques@campus.fct.unl.pt; Tel.: +351-212-948-573
- + Presented at the 2nd International Electronic Conference on Plant Sciences—10th Anniversary of Journal Plants, 1–15 December 2021; Available online: https://iecps2021.sciforum.net/.

**Abstract:** Selenium plays an important role in regulating soil-plant ecosystem functions. Is an essential element with antioxidative activity however its presence in plants is scarce. In this context, a technical itinerary was implemented in the rice variety (Ariete) through foliar pulverization with two selenium concentrations (50 and 75 g Se·ha<sup>-1</sup>) of sodium selenate (Na<sub>2</sub>SeO<sub>4</sub>) and sodium selenite (Na<sub>2</sub>SeO<sub>3</sub>). Regarding the interaction of Se with other nutrients namely Zn the contents were analyzed in paddy and white grains. It was found that in the white grains there was an antagonistic relationship with the element Zn: an increase of Se in the grain, 29.9 to 77.9 g Se·ha<sup>-1</sup>, and a decrease of Zn content from 16.6 to 9.01 g Se·ha<sup>-1</sup>.

Keywords: rice; soil; selenium; zinc

Published: 30 November 2021

Citation: Marques, A.C.; Daccak, D.;

Luís, I.C.; Coelho, A.R.F.; Pessoa, C.C.; Campos, P.S.; Simões, M.;

Reboredo, F.H.; et al. A Case Study

on Minerals Interaction in the Soil

and Se Enrichment in Rice (Oryza

x. https://doi.org/10.3390/xxxxx

sativa L.). Biol. Life Sci. Forum 2021, 1,

Academic Editor: Dimitris Bouranis

Almeida, A.S.; Pessoa, M.F.;

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/license s/by/4.0/). 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 crucial for human nutrition [6]. Considering that plants absorb from the soil, the main Se species in the form of selenate (SeO<sub>4<sup>2-</sup></sub>) and selenite (SeO<sub>3<sup>2-</sup></sub>), 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 it is important

to consider as in the case of Zn. 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 of Portugal in the experimental station of Rice Technological Center (COTArroz) during 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<sub>2</sub>SeO<sub>4</sub>—treatment A) and sodium selenite (Na<sub>2</sub>SeO<sub>3</sub>—treatment B) at different concentrations (50 and 75 g Se·ha<sup>-1</sup>). 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 × 2 forms selenium × 1 variety × 4 replicates) considering an area of 9.6 m<sup>2</sup> 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, a acid digestion procedure was carried with a mixture of HNO<sub>3</sub>–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 mentionned in [7]. The thousand grain weight was carried out for each treatments in quadriplicate, according to [17]. Colorimetric parametrs 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 ( $p \le 0.05$ ), to assess differences and then a Tukey's for mean comparation was performed. 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 analysed. The results shows that pH range 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).



**Figure 1.** Soil analysis at 0–30 cm deep. Average values (% or ppm) ± standard deviation (n = 16) of Fe, Ca, K, P, S, Mg, Pb, As and Se contents in the soil samples of rice paddy field trial. Letters a, b and c indicate significant differences among different elements on each graph ( $p \le 0.05$ ).

## 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, promote the progressive decrease of the Zn contents in white rice grains (i.e., the contents decrease from 16.6 to 9.01 ppm).

**Table 1.** Average values (ppm)  $\pm$  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 ( $p \le 0.05$ ).

Treatments (g Se·ha <sup>-1</sup> )	Paddy		White Rice	
	Se	Zn	Se	Zn
Control	22.1 ± 0.01 ab	$10.4 \pm 4.02$ a	29.9 ± 7.20 b	16.6 ± 0.75 a
	Na2SeO4			
50	$27.4 \pm 0.10$ b	3.89 ± 0.76 a	31.7 ± 3.15 b	8.63 ± 0.19 b
75	$47.6 \pm 0.02$ ab	10.3 ± 2.77 a	35.6 ± 2.39 b	7.59 ± 0.99 ab
	Na <sub>2</sub> SeO <sub>3</sub>			
50	53.7 ± 2.27 a	8.17 ± 2.05 a	37.1 ± 2.43 b	$8.87 \pm 0.80$ 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 showed significant differences in paddy rice grains regarding the different forms of Se applied (Figure 2). However, in white rice grains, the sodium selenate enrichement showed a little bit increase of weight in both treatments (50 and 75 g Se·ha<sup>-1</sup>).





In paddy (Figure 3a) and white rice grains (Figure 3b), regarding to the control, are not 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 it is associated with industrial processing.



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

## 4. Discussion

Trace elements in the soil such as Zn, Cd, Pd, Cu, As, and others are absorbed and transported to tissues aboveground level [19]. The results show that pH range 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 are 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 bioavailability 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, a form of Se applied, and the concentration of the solutions [22]. Our study showed that for 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 that foliar application of sodium selenate is less effective than sodium selenite [23]. These results to be 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]. Literature report 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 grain weight biggest variations were not detected (Figure 2). In studies about the enrichment of rice in selenite, the authors pointed 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<sup>-1</sup> did not present any symptoms of toxicity. The increment of Se influences the concentration of the element Zn particularly in the 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. Also, 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.

Author Contributions: Conceptualization, A.C.M. and F.C.L.; methodology, A.C.M., D.D., I.C.L., A.R.F.C. and C.C.P.; formal analysis, A.C.M., D.D., I.C.L., A.R.F.C. and C.C.P.; investigation, A.C.M., D.D., I.C.L., A.R.F.C. and C.C.P.; resources, M.F.P., F.H.R., C.G., J.C.R., P.M., M.M.S., P.L., K.O. and I.P.; writing—original draft preparation, A.C.M.; writing—review and editing, A.C.M. and F.C.L.; supervision, P.S.C., M.S. and A.S.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by PDR2020, grant number 101-030671.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: Authors thanks to Paula Marques, Cátia Silva (COTArroz) and Orivárzea (Orizicultores do Ribatejo, S.A.) for technical assistance. We also thanks to the Research centers (GeoBioTec) UIDB/04035/2020 and (CEF) UIDB/00239/2020 for support facilities.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

## References

- Garcia-Bañuelos, M.L.; Hermosillo-Cereceres, M.A.; Sanchez, E. The importance of selenium biofortification in food crops. *Curr. Nutr. Food Sci.* 2011, 7, 181–190. https://doi.org/10.2174/157340111797264796.
- Schiavon, M.; Pilon-Smits, E. The fascinating facets of plant selenium accumulation—Biochemistry, physiology, evolution and ecology. *New Phytol.* 2016, 213, 1582–1596. https://doi.org/10.1111/nph.14378.
- 3. Fordyce, F.M. Selenium deficiency and toxicity in the environment. In *Essentials of Medical Geology*; Springer: Dordrecht, The Netherland, 2013; pp. 375–416. https://doi.org/10.1007/978-94-007-4375-5\_16.
- 4. White, P.J. Selenium accumulation by plants. Ann. Bot. 2016, 117, 217–235. https://doi.org/10.1093/aob/mcv180.
- Reis, A.; El-Ramady, H.; Santos, E.F.; Gratão, P.L.; Schomburg, L. Overview of selenium deficiency and toxicity worldwide: Affected areas, selenium-related health issues, and case studies. In *Selenium in Plants*; Plant Ecophysiology; Springer: Cham, Switzerland, 2017; Volume 11, pp. 209–230. https://doi.org/10.1007/978-3-319-56249-0\_13.
- 6. Lopes, G.; Ávila, F.; Guilherme, L. Selenium behavior in the soil, water, plants and its implication for human health. A review. *Curr Sci Int.* **2021**. https://doi.org/10.36632/csi/2020.9.2.17.

- Lidon, F.; Oliveira, K.; Ribeiro, M.; Pelica, J.; Pataco, I.; Ramalho, J.; Leitão, A.; Almeida, A.; Campos, P.; Ribeiro-Barros, A.; et al. Selenium biofortification of rice grains and implications on macronutrients quality. J. Cereal Sci. 2018, 81, 22–29. https://doi.org/10.1016/j.jcs.2018.03.010.
- Li, Y.; Liu, K.; Chen, F. Effect of selenium enrichment on the quality of germinated brown rice during storage. *Food Chem.* 2016, 207, 20–26. https://doi.org/10.1016/j.foodchem.2016.03.080.
- 9. Zhou, X.; Yang, J.; Kronzucker, H.; Shi, W. Selenium Biofortification and Interaction with Other Elements in Plants: A Review. *Front. Plant Sci.* 2020, *11*, 586421. https://doi.org/10.3389/fpls.2020.586421.
- 10. Xue, M.; Wang, D.; Zhou, F.; Du, Z.; Zhai, H.; Wang, M.; Dinh, Q.; Tran, T.; Li, H.; Yan, Y.; et al. Effects of selenium combined with zinc amendment on zinc fractions and bioavailability in calcareous soil. *Ecotoxicol. Environ. Safe.* **2021**, *190*, 1–14. https://doi.org/10.21203/rs.3.rs-705742/v1.
- 11. Burestan, N.; Afkari Sayyah, A.; Taghinezhad, E. Prediction of some quality properties of rice and its flour by near-infrared spectroscopy (NIRS) analysis. *Food Sci. Nutr.* **2020**, *9*, 1099–1105. https://doi.org/10.1002/fsn3.2086.
- Pessoa, C.; Lidon, F.; Coelho, A.; Caleiro, J.; Marques, A.; Luís, I.; Kullberg, J.; Legoinha, P.; Brito, M.; Ramalho, J.; et al. Calcium biofortification of Rocha pears, tissues accumulation and physicochemical implications in fresh and heat-treated fruits. *Sci Hortic.* 2021, 277, 109834. https://doi.org/10.1016/j.scienta.2020.109834.
- Pelica, J.; Barbosa, S.; Lidon, F.; Pessoa, M.; Reboredo, F.; Calvão, T. The paradigm of high concentration of metals of natural or anthropogenic origin in soils—The case of Neves-Corvo mine area (southern Portugal). J. Geochem. Explor. 2018, 186, 12–23. https://doi.org/10.1093/jxb/erh192.
- 14. Carrondo, M.; Reboredo, F.; Ganho, R.; Santos Oliveira, J.F. Heavy metal analysis of sediments in Tejo estuary, Portugal, using a rapid flameless atomic absorption procedure. *Talanta* **1984**, *31*, 561–564. https://doi.org/10.1016/0039-9140(84)80141-1.
- 15. Reboredo, F.H.S.; Ribeiro, C.A.G. Vertical distribution of Al, Cu, Fe and Zn in soil salt marshes of the Sado estuary, Portugal. *Int. J. Environ. Stud.* **1984**, *23*, 249–253. https://doi.org/10.1080/00207238408710160.
- Pessoa, C.C.; Coelho, A.R.; Luís, I.C.; Marques, A.C.; Daccak, D.; Simões, M.; Reboredo, R.; Silva, M.M.; Pessoa, M.F.; Galhano, C.; et al. A technological workflow for Ca enrichment in Rocha pears: Implication in quality. In Proceedings of the 1st International Conference on Water Energy Food and Sustainability (ICoWEFS 2021), Leiria, Portugal, 10–12 May 2021; Galvão, J., Brito, P., Santos, F.d., Craveiro, F., Almeida, H., Vasco, J., Neves, L., Gomes, R., Mourato, S., Ribeiro, V., Eds.; Springer Nature: Cham, Switzerland, 2021. https://doi.org/10.1007/978-3-030-75315-3\_21.
- Luís, I.; Lidon, F.; Pessoa, C.; Marques, A.; Coelho, A.; Simões, M.; Patanita, M.; Dôres, J.; Ramalho, J.; Silva, M.; et al. Zinc Enrichment in Two Contrasting Genotypes of *Triticum aestivum* L. Grains: Interactions between Edaphic Conditions and Foliar Fertilizers. *Plants* 2021, 10, 204. https://doi.org/10.3390/plants10020204.
- Ramalho, J.C.; Pais, I.P.; Leitão, A.E.; Guerra, M.; Reboredo, F.H.; Máguas, C.M.; Carvalho, M.L.; Scotti-Campos, P.; Ribeiro-Barros, A.I.; Lidon, F.J.C. Can elevated air [CO<sub>2</sub>] conditions mitigate the predicted warming impact on the quality of coffee bean? *Front. Plant Sci.* 2018, *9*, 287. https://doi.org/10.1016/j.envexpbot.2014.05.005.
- Yang, H.; Yang, X.; Ning, Z.; Kwon, S.; Li, M.; Tack, F.; Kwon, E.; Rinklebe, J.; Yin, R. The beneficial and hazardous effects of selenium on the health of the soil-plant-human system: An overview. *J Hazard Mater.* 2021, 422, 126876. https://doi.org/10.1016/j.jhazmat.2021.126876.
- Feng, R.; Wang, L.; Yang, J.; Zhao, P.; Zhu, Y.; Li, Y.; Yu, Y.; Liu, H.; Rensing, C.; Wu, Z.; et al. Underlying mechanisms responsible for restriction of uptake and translocation of heavy metals (metalloids) by selenium via root application in plants. *J. Hazard. Mater.* 2021, 402, 123570. https://doi.org/10.1016/j.jhazmat.2020.123570.
- 21. Hasanuzzaman, M.; Bhuyan, M.; Raza, A.; Hawrylak-Nowak, B.; Matraszek-Gawron, R.; Mahmud, J.; Nahar, K.; Fujita, M. Selenium in plants: Boon or bane? *Environ. Exp. Bot.* **2020**, *178*, 104170. https://doi.org/10.1016/j. envexpbot.2020.104170.
- Wang, Y.D.; Wang, X.; Wong, Y.S. Generation of selenium-enriched rice with enhanced grain yield, selenium content and bioavailability through fertilisation with selenite. *Food Chem.* 2013, 141, 2385–2393. https://doi.org/10.1016/j.foodchem.2013.05.095.
- Deng, X.; Liu, K.; Li, M.; Zhang, W.; Zhao, X.; Zhao, Z.; Liu, X. Difference of selenium uptake and distribution in the plant and selenium form in the grains of rice with foliar spray of selenite or selenate at different stages. *Field Crop. Res.* 2017, 211, 165–171. https://doi.org/10.1016/j.fcr.2017.06.008.
- 24. Lyons, G.; Genc, Y.; Stangoulis, J.; Palmer, L.; Graham, R. Selenium distribution in wheat grain, and the effect of postharvest processing on wheat selenium content. *Biol. Trace Elem. Res.* 2005, *103*, 155–168. https://doi.org/10.1385/BTER:103:2:155.
- Mangueze, A.; Pessoa, M.; Silva, M.; Ndayiragije, A.; Magaia, H.; Cossa, V.; Reboredo, F.; Carvalho, M.; Santos, J.; Guerra, M. Simultaneous zinc and selenium biofortification in rice accumulation, localization and implications on the overall mineral content of the flour. J. Cereal Sci. 2018, 82, 34–41. https://doi.org/10.1016/j.jcs.2018.05.005.
- Sors, T.; Ellis, D.; Salt, D. Selenium uptake, translocation assimilation and metabolic fate in plants. *Photosynth. Res.* 2005, *86*, 373–389. https://doi.org/10.1007/s11120-005-5222-9.
- Fargasova, A.; Pastierova, J.; Svetkova, K. Effect of Se-metal pair combinations (Cd, Zn, Cu, Pb) on photosynthetic pigments production and metal accumulation in *Synapis alba* L. seedlings. *Plant Soil Environ.* 2006, *52*, 8–15. https://doi.org/10.17221/3340-PSE.