



Reducing conditions on barium absorption in rice plants cultured in BaSO₄-enriched soil

Marcio Osvaldo Lima Magalhães^{1*}, Nelson Moura Brasil do Amaral Sobrinho¹, Everaldo Zonta¹, Alfredo Tolón Becerra², Xavier Bolívar Lastra-Bravo² and Izabella Bezerra Coutinho¹

¹Departamento de Solos, Universidade Federal Rural do Rio de Janeiro, BR-465, km 7, 23890-000, Seropédica, Rio de Janeiro, Brazil. ²Rural Engineering Department, University of Almería, Almería, Spain. *Author for correspondence. E-mail: marciomagalhaes@gmail.com

ABSTRACT. To evaluate the possible solubilization of barium sulfate in soils under reducing conditions and its effects on barium bioavailability, an *Oryza sativa* pot trial was established. Increasing barium doses and two redox potential conditions were evaluated. The geochemical fractionation data demonstrated that reducing conditions led to an increase in the levels of more labile forms of barium and a reduction in more stable forms. Furthermore, higher doses of barium were found to have a negative impact on grain production. The highest levels of barium accumulation in the leaves, roots, and grains were observed with the highest barium dose under reducing conditions. These results demonstrate that reducing conditions increased barium bioavailability and absorption by rice plants.

Keywords: contamination, barite, *Oryza sativa*.

Efeito do potencial redox na absorção de bário por plantas de arroz cultivadas em solos enriquecidos com BaSO₄

RESUMO. Com o objetivo de avaliar a possível solubilização do sulfato de bário em solos sob condições redutoras e aumento da biodisponibilidade do bário, instalou-se ensaio em vasos com *Oryza sativa*. Avaliaram-se doses de bário e duas condições de potencial redox. Os resultados do fracionamento geoquímico demonstraram que a condição de redução favoreceu o aumento nos teores de bário nas formas de maior labilidade e diminuição nas formas de maior estabilidade. A produção de grãos foi influenciada, de forma negativa, pela aplicação da maior dose de bário. Os teores mais elevados e acúmulo de bário nas folhas, raízes, e grãos foram encontrados na maior dose e na condição de redução. Esses resultados evidenciaram que a condição de redução proporcionou maior biodisponibilidade desse elemento.

Palavras-chave: contaminação, baritina, *Oryza sativa*.

Introduction

Barium is present in small quantities in igneous rocks such as feldspars and micas. The primary source, however, is the mineral barite (BaSO₄), which is widely used in the petroleum industry as a drilling fluid component due to its high density (4.2 g cm⁻³) (FAM et al., 2003). Barite (BaSO₄) often is added as a weighting agent to drilling muds to counteract pressure in the geologic formations being drilled, preventing a blowout (NEFF, 2008). During the drilling of oil wells for oil prospecting and production, the drilling fluid is mixed with ground rock, thus releasing its component substances (POZEBON et al., 2005). Consequently, these component substances greatly influence the concentration of barium and other substances in oil well residues (MELTON et al., 2000).

Soils in flood areas exhibit alterations in elemental composition and microbial metabolism

that trigger a series of physical, chemical, and biological transformations. These changes subsequently produce soil characteristics that are profoundly distinct from the initial conditions (SEYBOLD et al., 2002). These new chemical environments are ecologically relevant because the change redox states affecting the mobility and bioavailability of elements present in the soil.

The barium contained in barite is relatively immobile, and its low water solubility (2.47 mg L⁻¹ at 25°C) reduces its bioavailability. However, the solubility of barium sulfate can be improved under highly reducing environments (MAGALHÃES et al., 2011a; MONNIN et al., 2001), reflecting the fact that sulfate reduction occurs at Eh values of -250 mV (KHANAL; HUANG, 2003). Previous studies have shown that barite can serve as a sulfate source for the respiration of anaerobic bacteria (BALDI et al., 1996). When these wastes are

disposed into poorly drained soil, the release of the most toxic form of barium, Ba^{+2} , into the environment (USEPA, 2005) may contaminate bodies of water and introduce the element into the food chain (MAGALHÃES et al., 2011b).

Because barium is present in most soils, low, non-toxic levels of barium, approximately 4 to 50 $mg\ kg^{-1}$, are commonly found in plants (CHAUDHRY et al., 1977). Nogueira et al. (2010), for example, found no signs of barium toxicity in corn plants with barium concentrations ranging from 90 to 106 $mg\ kg^{-1}$. In a hydroponic trial conducted with soy plants, however, Suwa et al. (2008) observed signs of toxicity, namely, high concentrations of barium in the leaves (4,970 $mg\ kg^{-1}$) and reductions in dry mass, following treatment with 5 mM barium.

The aim of the present study was to test the effects of oxidizing and reducing conditions on the bioavailability of barium and its absorption by rice plants (*Oryza sativa*).

Material and methods

The soil samples used were collected from an Oxisol, at a depth of 0-20 cm, in the State of Rio de Janeiro, Brazil. The soil characteristics were as follows: barium: 223 $mg\ kg^{-1}$ (ISO, 1995), pH in H_2O : 5.8; sand: 272 $g\ kg^{-1}$; silt: 132 $g\ kg^{-1}$; clay: 596 $g\ kg^{-1}$; Corg.: 10,7 $g\ kg^{-1}$ and a $CEC_{(pH\ 7.0)}$: 97.0 $mmol_c\ dm^{-3}$ (EMBRAPA, 1997).

Using barium sulfate ($BaSO_4$) as a source, barium doses were applied according to the values proposed by the 420 CONAMA Resolution (BRASIL, 2009). The treatments were as follows: soil without barium application (control); 100 $mg\ barium\ kg^{-1}$ of dry soil (dose 1); 300 $mg\ barium\ kg^{-1}$ of dry soil (dose 2); and 3,000 $mg\ barium\ kg^{-1}$ of dry soil (dose 3).

The pots were filled with 5 dm^3 of soil, and the soil was homogenized after the barium doses were added. The moisture conditions were 70% of field capacity (oxidizing conditions) and saturation (reducing conditions). To maintain the reducing conditions, a 7 cm layer of water was applied to the soil surface. During the incubation period, drainage was impeded for all treatments, and the pots were covered to prevent water loss by evaporation. A total of 32 experimental units were prepared in a factorial design (4 x 2) with four barium levels, two moisture levels, and four replicates.

During the incubation period, pH and Eh values were determined 2 hours after flooding on days 2, 4, and 6. Following the first week of incubation, the assessment was performed on a weekly basis for the

saturated soil until stabilization of the redox potential required for the reduction of sulfate was obtained (i.e., Eh values of -250 mV). The Eh values of the soil under oxidizing and reducing conditions were directly measured using a specific electrode. Combined ORP analyzer electrodes were used for measuring Eh, and half-cell pH analyzer electrodes were used for measuring pH with the pH/Ion 450M[®] Analyzer. Thirty days after a redox potential value of -250 mV was obtained, rice seedlings (*Oryza sativa* var. Bico Ganga) were transplanted to the pots. The choice for rice was due to the fact that it is a culture that adapts to both dryland and flooding conditions.

Following the incubation period, the barium was geochemically fractionated for all experimental treatments according to the method recommended by the European Communities Bureau of Reference (BCR) and adopted by Sahuquillo et al. (1999). The geochemical fractions were as follows: the acid-soluble fraction, extracted with 0.11 $mol\ L^{-1}$ acetic acid (F1); the fraction bound to Fe and Mn oxides, extracted with 0.1 $mol\ L^{-1}$ hydroxylamine hydrochloride (F2); the fraction bound to organic matter, extracted with 8.8 $mol\ L^{-1}$ hydrogen peroxide and 1.0 $mol\ L^{-1}$ ammonium acetate (F3); and the residual fraction, which represents the aqua regia extracts from all other fractions (F4).

Ten days after germination, seedlings homogeneous in size and vigor were selected, and two plants were transplanted into each pot. A parceled fertilization method was used, with 80 $kg\ N\ ha^{-1}$, 40 $kg\ P\ ha^{-1}$ (single dose), and 40 $kg\ K\ ha^{-1}$ applied at the time of planting. After 40 days, surface fertilization was performed by applying 40 $kg\ N\ ha^{-1}$ and 40 $kg\ K\ ha^{-1}$. The plants were collected at the end of the experiment, after approximately 4 months of growth, corresponding to the growth cycle of the cultivar. The collected plants were separated into shoots, roots, and grains and then rinsed in deionized water. The plant samples were oven-dried at 70°C until a constant weight was obtained. The digestion material was obtained by grinding the shoots, roots, and grains in a Willey-type mill using a 2 mm mesh. Nitroperchloric digestion was used to determine the barium concentrations, at a ratio of 6:1, according to the method described by Tedesco et al. (1995). The total barium content in the shoots, roots, and grains were calculated using the determined concentration and the amount of dry matter produced.

The levels of barium in the soil and plant extracts were quantified using a plasma emission spectrometer (ICP-OES; Perkin Elmer, model OPTIMA 3000), with Detection Limit = 0.036 $mg\ kg^{-1}$

and Quantification Limit = 0.36 mg kg^{-1} for barium. To validate the determination of the pseudo total content of barium in the soil and plants, the following reference materials were used: NIST SRM 2709a (San Joaquin soil) and SRM 1573a (tomato leaves), which had barium concentrations of $979 \pm 28 \text{ mg kg}^{-1}$ (95% recovery) and 63 mg kg^{-1} (93% recovery), respectively. These values are within the range classified as normal by the National Institute of Standards and Technology (NIST) for soil and plant samples. The oxidation-reduction variations were assessed by analysis of variance with F-test ($p < 0.05$), and the mean values of soil redox potential conditions compared by Tukey test ($p < 0.05$). Analyses were performed using the SAS/STAT 9.2[®] software (SAS Institute Inc., Cary, NC, USA). An error bar was also used to highlight possible differences among barium contents for the same redox potential condition.

Results and discussion

Figure 1A shows that the soil Eh values at 70% field capacity ranged from ± 350 to 450 mV , which is within the range for oxidized soil ($800\text{-}300 \text{ mV}$) (CAMARGO et al., 2001). The pH values also remained constant, ranging from 5.8 to 6.0. When saturation conditions in the soil were combined with prolonged flooding (Figure 1B), a reduction in Eh values and subsequent stabilization of highly reducing conditions below -250 mV were observed, indicative of highly reducing conditions. According to the literature (KHANAL; HUANG, 2003; JONES; INGLE JR., 2005; MAGALHÃES et al., 2011b), the reduction of sulfate to sulfide by sulfate-reducing bacteria (SRB) in the soil may occur at this Eh value. At the onset of flooding, Eh values of -250 mV and pH values below 6 were observed. As saturation continued, Eh values decreased, and pH values increased until stabilizing at an approximately neutral value.

The observed increase in pH is characteristic of soils under flooding conditions and reflects the accumulation of protons (GONÇALVES et al., 2008; LIMA et al., 2005; VEPRASKAS; FAULKNER, 2001). As described by Seybold et al. (2002), Eh and pH levels reflect the activity of protons and electrons in the soil because the excess of one causes a deficit in the other. According to Camargo et al. (1999), the increase in pH after submergence depends not only on the ratio of OH^- and H^+ consumption but also on the ratio of H^+ and electron consumption. The change in pH necessarily depends on two conditions: a well-developed reduction process and a sufficient amount of reduced Fe (SEYBOLD et al., 2002; PONNAMPERUMA, 1978). The measured Eh and

pH values in the present study indicate that the incubation period was sufficient to promote these conditions and thus favored the reduction of oxidized soil components, particularly sulfate.

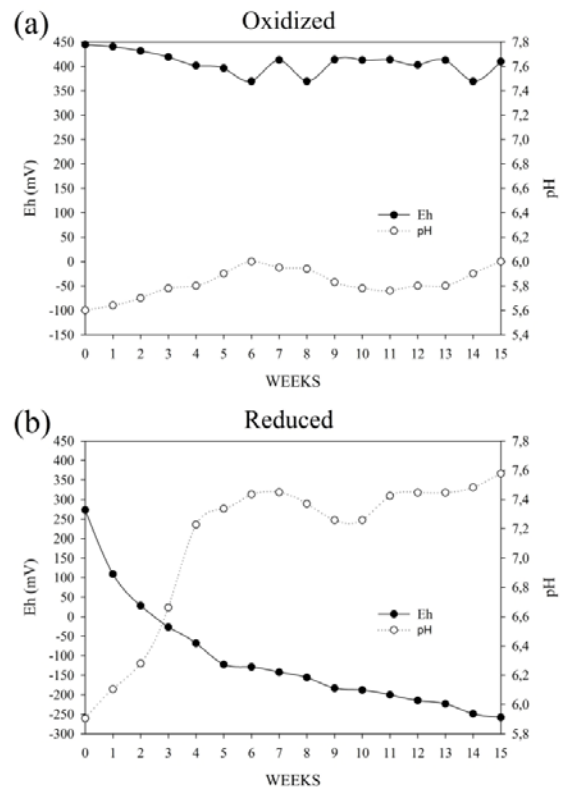


Figure 1. Redox potential values (Eh) for two condition (oxidized and reduced) and the relationship between Eh and pH after weeks of flooding.

Figure 2 shows the mean barium distributions in the different geochemical fractions obtained by BCR scheme. Shows that under reducing conditions in the soil (-250 mV), the barium concentration in the acid soluble fraction (F1) increased significantly. The increases observed for the different treatments under reducing conditions were as follows: 11 mg kg^{-1} for the control, 25 mg kg^{-1} for dose 1, 87 mg kg^{-1} for dose 2, and 135 mg kg^{-1} for dose 3. Higher treatment doses yielded greater increases in the barium concentration of the F1 fraction. This fraction contains barium in solution that is electrostatically adsorbed on the surface of the soil colloids (exchangeable) and precipitated in the form of carbonates (FILGUEIRAS et al., 2004; MARIN et al., 1997).

The increased barium concentration in the F1 fraction under saturated conditions was accompanied by decreased barium concentrations in the oxide-bound (F2) and residual (F4) fractions. The binding of heavy metals with oxides does not guarantee

surface immobilization because these elements can be released by oxide reduction in this fraction, resulting in a negative impact on the soil biota (CHLOPECKA, 1996; RODRIGUEZ et al., 2009). No significant differences were observed for the barium concentration in the organic matter fraction (F3). These results demonstrate the low affinity of barium for organic matter, because this complex is considered limited by some authors (BODEK et al., 1988; DANG et al., 2002). Used geochemical fractionation and observed that only 1% of the total barium was present in the fraction bound to organic matter (SMEDA; ZYRNICKI, 2002). The results of the geochemical fractionation in the present study demonstrate that reducing conditions increased barium concentrations in the most labile fraction (F1) and reduced the amount of barium associated with more stable fractions (F2 and F4). The increase observed in F1, which was promoted by increased BaSO_4 solubility, may result in increased barium bioavailability (ALBERTA ENVIRONMENT, 2009; MAGALHÃES et al., 2011b).

For both of the redox potential conditions, no significant differences were observed in the shoot, root, and total dry matter production of control plants and rice plants treated with varying barium doses (Figure 3). However, differences in grain mass were observed in plants that received the highest barium dose and plants without BaSO_4 application (control). Relative to the control, the highest barium dose resulted in decreases of approximately 18% and 38% in grain yield under oxidizing and reducing conditions, respectively. The findings of the present study therefore indicate that the highest barium dose ($3,000 \text{ mg kg}^{-1}$) negatively affected grain yield. In the literature, there is limited information about the influence of barium on plant metabolism. However, in a study that utilized *Glycine max* in a nutrient solution, Suwa et al. (2008) reported similar results: high barium doses affected plant development, particularly yield, demonstrating the phytotoxic effect of this element. Llugany et al. (2000) observed phytotoxicity symptoms in *Phaseolus vulgaris* plants even at low barium concentrations.

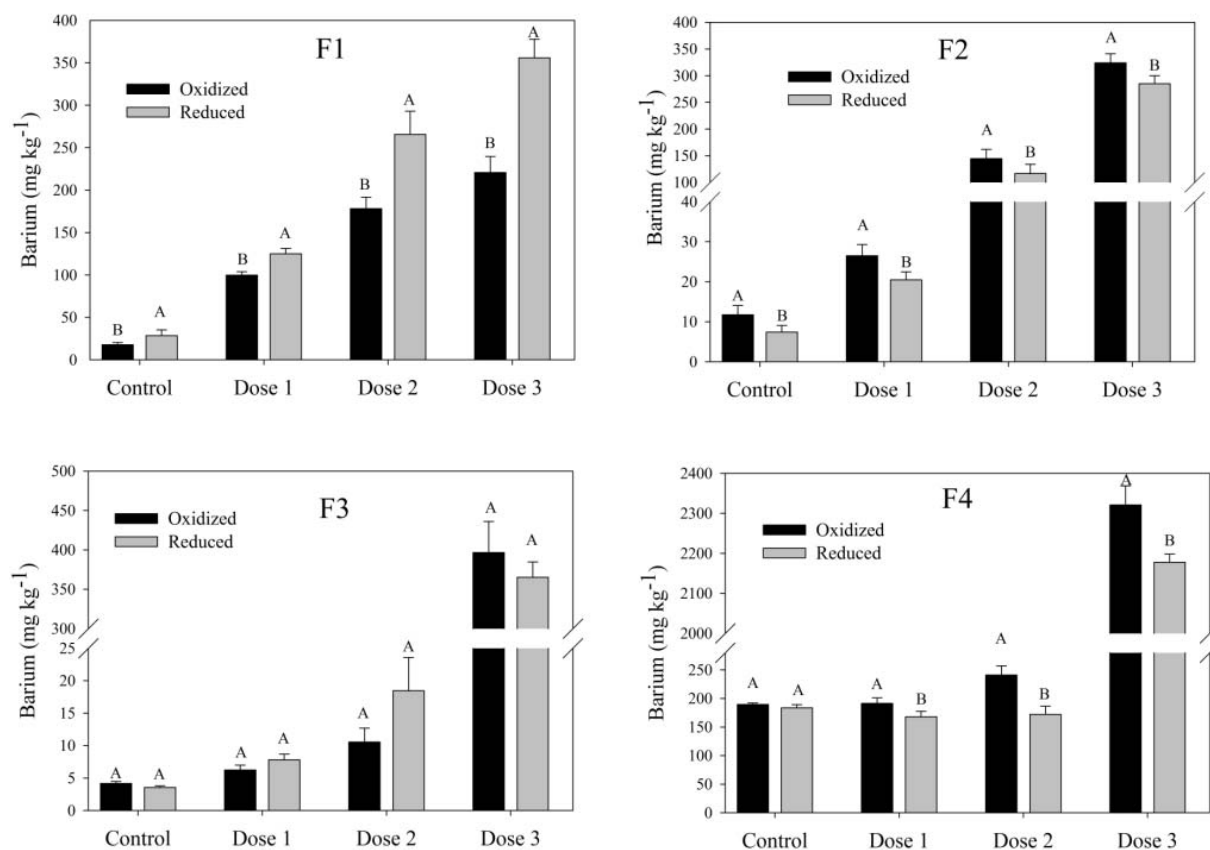


Figure 2. Barium distribution in different geochemical fractions as a function of dose and redox potential (oxidized and reduced). F1: soluble acid fraction; F2: fraction bound to iron and manganese oxide; F3: fraction bound to organic matter and sulfides; F4: residual fraction. Letters (for each barium content) indicate a significant difference ($p < 0.05$). Control: no barium sulfate application; Dose 1: 100 mg kg^{-1} ; Dose 2: 300 mg kg^{-1} ; Dose 3: $3,000 \text{ mg kg}^{-1}$.

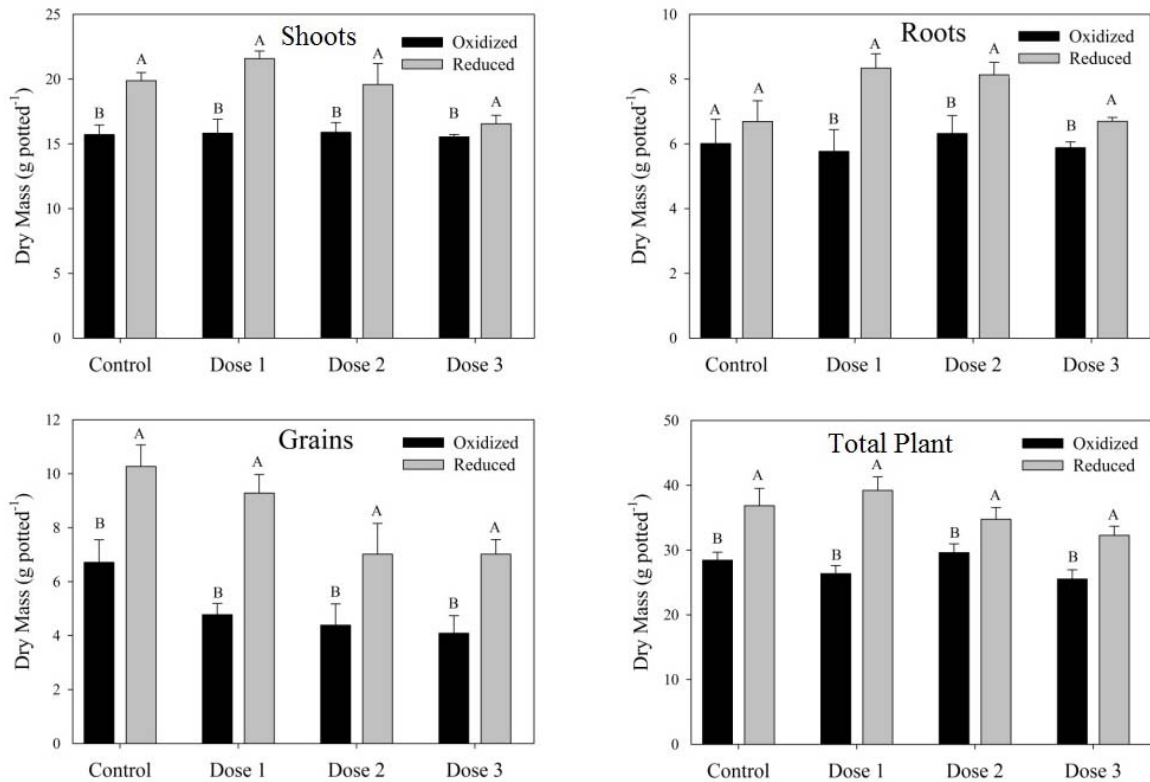


Figure 3. Dry mass production of rice plants as a function of barium dose and redox potential (oxidized and reduced). Letters (for each barium content) indicate a significant difference ($p < 0.05$). Control: no barium sulfate application; Dose 1: 100 mg kg⁻¹; Dose 2: 300 mg kg⁻¹; Dose 3: 3,000 mg kg⁻¹.

In the present study, the biomass of rice plants was significantly different under the two soil redox conditions, with a greater biomass observed in reduced soils than in oxidized soils. Although reducing conditions yielded greater grain mass at all doses, this increase was lowest at the highest dose, and significant differences were observed between doses.

There is no reference data describing the toxicity of barium to rice plants grown in nutrient solution. Although there are no reports of the effects caused by the toxicity of barium, they may be associated to the deficiency of other elements due to competition, for instance, competition with calcium for root absorption, due to its similarity (NOGUEIRA et al., 2010).

According to the data obtained, higher moisture levels (saturation) resulted in higher dry matter production for all of the evaluated parameters. Thus, saturation positively influenced the development of plants. Several studies have shown that the highest rice yields are obtained under flood conditions. For example, Patel et al. (2010) observed a mean reduction of 27% in plant yield when plants were cultivated under oxidizing conditions compared to flooded cultivation (reducing conditions).

Among the different doses treatments, no significant differences in barium content were observed in the shoots of rice plants cultivated in oxidized soil (Figure 4), and the mean concentration was 180 mg kg⁻¹. However, there were differences in barium absorption by rice plants under reducing conditions, with the lowest concentrations observed in the control (150 mg kg⁻¹) and the highest concentrations (620 mg kg⁻¹, approximately 4 times higher) observed in plants that received the highest barium dose (dose 3). The effects of doses 1 and 2 were not significantly different. A comparison of the barium content on plant shoots under different redox potential revealed no significant differences in the control (background levels of barium). For plants treated with BaSO₄, however, reducing conditions resulted in the highest barium concentrations. At the highest dose, reducing conditions resulted in a 3-fold increase in the barium content of plant shoots. Absorption in plant roots was also dependent on the dose under both soil redox conditions. The following barium concentrations were measured in plants cultivated in oxidized soil: 61 mg kg⁻¹ for the control, 222 mg kg⁻¹ for dose 1, 508 mg kg⁻¹ for dose 2, and 826 mg kg⁻¹ for dose 3. There was a 13-fold increase in the barium concentration in plants that received the highest dose compared to the control. Furthermore, the significant

differences observed in reduced soil were greater than those in oxidized soil. Under reducing conditions, there was a 36-fold difference between the control and the highest dose. Analysis of the barium content in the grains revealed higher concentrations in plants cultured under reducing conditions compared to oxidizing conditions, especially at higher doses.

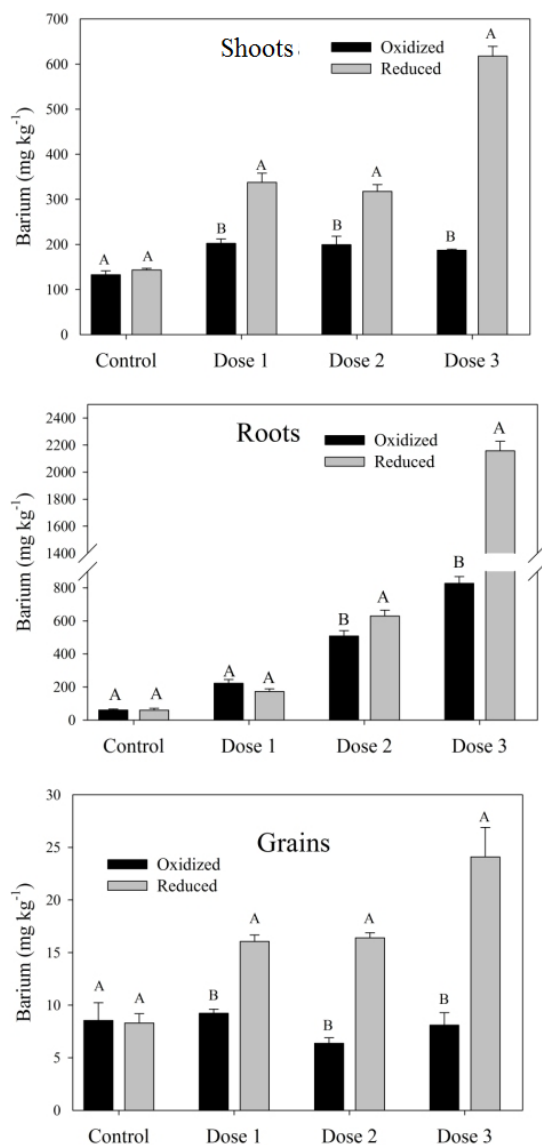


Figure 4. Barium concentration in leaves, roots, and grains of rice plants as a function of barium dose and redox potential (oxidized and reduced). Letters (for each barium content) indicate a significant difference ($p < 0.05$). Control: no barium sulfate application; Dose 1: 100 mg kg⁻¹; Dose 2: 300 mg kg⁻¹; Dose 3: 3,000 mg kg⁻¹.

The levels of barium that can be considered normal or toxic for plants are not well established (SUWA et al., 2008). According to Nogueira et al. (2010), barium is commonly found in plant tissues but not at levels that can be considered toxic, and the

values of barium absorption they observed in *Zea mays* plants ranged from 90 to 106 mg kg⁻¹. These levels were not found to influence plant development or produce toxicity symptoms. In a *Glycine max* hydroponic trial, Suwa et al. (2008) observed high concentrations of barium in the leaves (4,970 mg kg⁻¹) following a treatment dose of 5 mM barium. These levels led to decreased dry mass production, which is one indicator of phytotoxicity.

Another trend observed in the present study was increased translocation of barium from the roots to the leaves under low dosage concentrations. In contrast, higher barium concentrations in the soil (doses 2 and 3) decreased translocation, resulting in greater barium immobilization in the roots. The ability of plants to immobilize metal in the roots is one of the mechanisms some plant species have evolved to tolerate heavy metals present in the soil (MAGALHÃES et al., 2011a; SANTOS et al., 2007).

The first barrier against the entering of heavy metals, especially regarding root level, is the immobilization of heavy metals in the cell wall and by extracellular carbohydrates, such as mucilage and callose (FRITZ, 2007; KARTEL et al., 1999), avoiding the presence of free ions in root tissues and, consequently, the translocation of ions to shoots, thereby reducing phytotoxicity. Pectins and histidine stand out for immobilizing heavy metals in the cell wall (LEITA et al., 1996).

Among the doses treatments, no significant differences were observed with respect to the amount of barium accumulated in the shoots and grains under oxidizing conditions (Figure 5). Under reducing conditions, however, plants cultured at the highest dose exhibited greater accumulation relative to the control. In the roots, there was a significant difference between the control and the dose treatments for both redox potential. An assessment of the total barium accumulated in the roots under oxidizing conditions revealed that the only significant difference was between the highest dose and the control. Under reducing conditions, the effect for the highest dose was significantly different from all other dosage treatments and the control. For natural concentrations of barium in the soil (control), there was no significant difference in barium accumulation as a function of redox conditions (oxidized and reduced). For the dose treatments, however, reducing conditions resulted in higher barium accumulation, except in the roots, where a significant difference was only observed at the highest dose. The accumulation increase in plants grown under reducing conditions was approximately 3-fold for the shoots, roots, filled grains, and accumulated total at the highest dose. Except in the control, differences were observed in the amount of

accumulated barium between the two soil redox conditions, with greater accumulation observed under reducing conditions.

These findings demonstrate that highly reducing conditions improve barium sulfate solubility. As demonstrated by the geochemical fractionation (Figure 2), barium bioavailability increased, enabling absorption and accumulation of this element in plants.

It is worth noting that the increase in barium accumulation in the grains was approximately 300%, this increases the probability of introducing barium in to the food chain because rice grains are a staple food in many countries.

According to the United Nations Food and Agriculture Organization, the consumption of rice around the world amounts to an average 84.8 kg person⁻¹ year⁻¹, which is equivalent to an average daily consumption per person of approximately 230 g. The maximum daily ingestion of barium per kg of body mass suggested by the United States Environmental Protection Agency (USEPA, 2005) is 0.2 mg kg⁻¹ bw day⁻¹. Based on this information, a person weighing 70 kg may ingest a maximum of 14 mg of barium per day. If this person consumes an average of 230 g day⁻¹ of rice grains produced under the most critical conditions presented in this study (extremely reduced soil with the highest amount of barium), this person would ingest a total of 5.5 mg of barium, or

approximately 40% of the maximal value of barium. This value may be considered high because barium is found in many food groups and in water (USEPA 2005; YSART et al., 1999). It is also important to compare the values obtained in this study with the values measured in plants grown in soil with natural barium concentrations (control). Under such conditions, the daily ingestion of barium from rice would be 1.8 mg, or 13% of the reference dose.

Pearson correlation analysis was performed for the barium extracted in the acid soluble fraction (F1) and the barium absorbed and accumulated in different plant parts for the two redox potential conditions (Table 1). High and significant correlations were observed for all variables, except for barium concentration and accumulation in the grains under oxidizing conditions. The correlation of the barium concentration in F1 with barium concentration in the leaves under reducing conditions was greater ($r = 0.87$) than the correlation under oxidizing conditions ($r = 0.54$). A similar pattern was observed in the roots, with the highest correlation always under reducing conditions. There was no correlation between the barium concentration in F1 and the concentration and accumulation of barium in the grains under oxidizing conditions. However, a high correlation ($r = 0.86$) was observed for these parameters under reducing conditions.

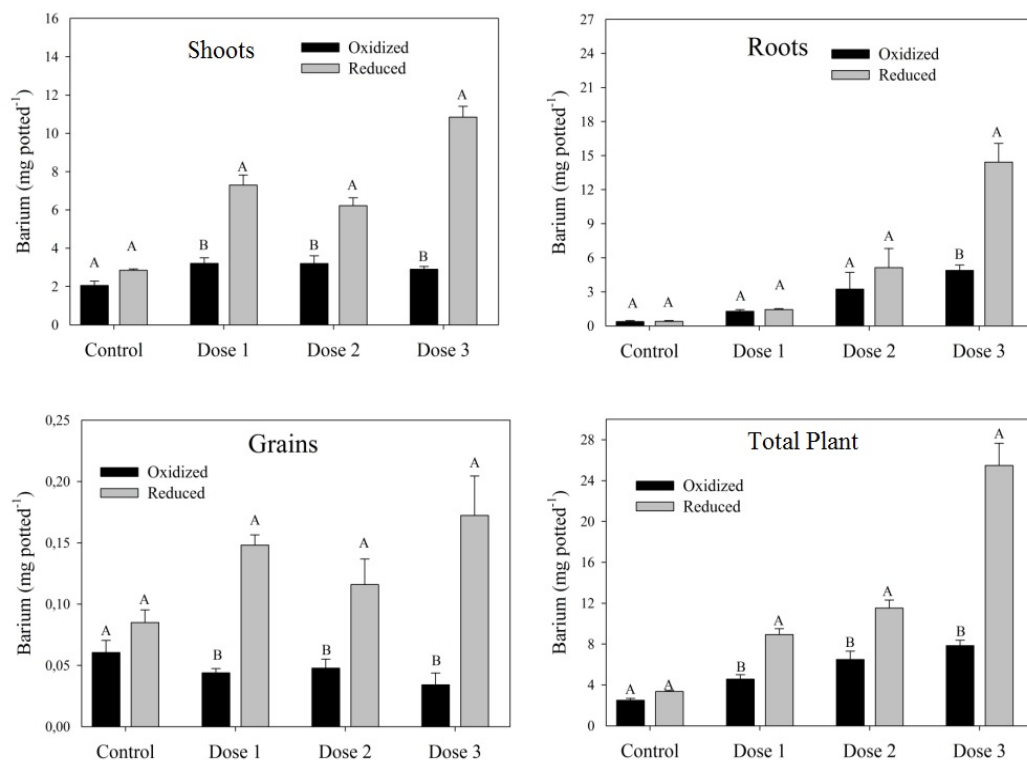


Figure 5. Barium uptake in leaves, roots, grains, and whole rice plants as a function of barium dose and redox potential (oxidized and reduced). Letters (for each barium content) indicate a significant difference ($p < 0.05$). Control: no barium sulfate application; Dose 1: 100 mg kg⁻¹; Dose 2: 300 mg kg⁻¹; Dose 3: 3,000 mg kg⁻¹.

In general, higher correlations were observed under reducing conditions than under oxidizing conditions. These results are consistent with the higher levels of barium found in the F1 fraction under reducing conditions, which promoted the absorption and accumulation of barium in the plants.

Table 1. Pearson correlation coefficients for the barium extracted in the acid soluble fraction (F1) and the barium absorbed and accumulated in different plant parts, as a function of the redox potential.

Correlation		Oxidized	Reduced
Concentration	Shoot	0,54*	0,87**
	Root	0,73**	0,87**
	Grain	-0,23	0,86**
Accumulated	Shoot	0,51*	0,83**
	Root	0,81**	0,88**
	Grain	-0,34	0,51*
	Total Plant	0,89**	0,89**

**significant at 1%; *significant at 5%.

Conclusion

Reducing conditions led to increased levels of barium in the most labile fraction.

The highest dose of barium resulted in a decrease in grain yield.

Saturation promoted the absorption and accumulation of barium in plants, increasing the risk of the introduction of this element into the food chain.

The highest correlation between the soluble acid fraction and the barium accumulation in plants was observed under reducing conditions.

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