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Agricultural use of Samarco's spilled mud assessed by rice cultivation: A promising residue use?

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HIGHLIGHTS

- Low content of toxic elements in rice grains cultivated with mud.
- Soil containing mud-50% intensely damaged the plants.
- Simple soil amendment helped on rice growth in the mud.
- Possible use of the mud for agricultural practices.

GRAPHICAL ABSTRACT

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ABSTRACT

Mining activity is one of the main responsible for accumulation of potentially toxic elements in the environment. These contaminants are absorbed by plants served as food that could be a risk to human health, such rice. Rice is a staple food with known accumulation of toxic elements. The recent collapse of a mining dam operated by Samarco Mining Company spilled around 50 million m^3 of Fe-mining waste in the environment, including rivers and farming areas. In the present study, concentrations of As, Cd, Hg, Pb, Co, Zn, Mn, Cu, Fe, Al, Se, and Sr were determined in soils, roots and grains of rice plants cultivated in soil containing Samarco's residual mud (0, 16, 34 and 50%). Further, rice plant agronomic parameters (chlorophyll, carotenoids, grain yield, mass, height) were assessed. Rice cultivated at Samarco's residual mud produced grains with low levels of As, Cd and Pb. However, the excess of mud (50%) during the rice cultivation reduced roots' growth and grains yield. Chlorophyll (*a* and *b*) and carotenoids contents were significantly lower in all mud cultivations, mainly mud-50%. Our findings suggest that plant alterations induced by the mud were associated to the deficiency of nutrients and the physical properties of the mud. Soil fertilization by organic matter and top soil provided conditions for plant development.

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Soil amendment
Agronomic parameters

Therefore, considering the experimental conditions here used, we showed that is possible the use of the affected land for agriculture and reforestation after soil amendment.

1. Introduction

On November 5, 2015, the biggest socio-environmental disaster involving iron mining occurred in Brazil. The Fundão dam, operated by Samarco, a mining company located at the town of Mariana (State of Minas Gerais), collapsed, spilling 50 million m^3 of residual-mud over Bento Rodrigues sub-district. This accident caused the partial destruction of this district and uncountable socioeconomic and environmental damages to the entire river basin (Santarém, Gualaxo do Norte, Do Carmo and Doce rivers). The disaster left 17 dead, more than 600 homeless people and interrupted the water supply services in 35 cities in the state of Minas Gerais and 3 cities in the state of Espírito Santo (SEDRU, 2016). Moreover, the mud spilled by Samarco's dam traveled over 600 km of watercourse until reach the Atlantic Ocean and destroyed approximately 1.5 ha of farming lands (Dos Santos et al., 2006).

Mining is one of the main responsible for the accumulation of chemical elements in the environment. Dust, waste and disposal of contaminated water are generated during the mining activities. In addition, accidental disruption of tailings dams can easily contaminate the environment by pollutants dispersions, destabilizing soils and water supplies (rivers and aquifers) over long distances (Lei et al., 2010). Assuming that mud may have toxic elements, the soil contamination is an environmental concern once it could accumulate in crops, magnifying in the food chain, causing ecosystem unbalance and several human health problems (Dos Santos et al., 2006).

Considering the most studied chemical elements in toxicology (As, Cd, Hg and Pb), the effect of accumulation is more important mainly when cultivation of plant destined to human consumption (Dos Santos et al., 2006). In this context, rice, a cereal consumed by approximately 50% of the world population, presents known ability of accumulation for As, Cd, Pb and Hg (Argumedo-García et al., 2013; Liu et al., 2003; Norton et al., 2014; Rahman et al., 2008; Segura et al., 2016a; Yang et al., 2006). A previous study have shown that Cd concentrations in rice cultivated at areas close to mine sites were significantly higher than those from distant areas (Ok et al., 2011). Regarding As, it's well known that rice can accumulate As^{3+} and As^{5+}, the most toxic As-forms found in food, in the grains (Abedin et al., 2002; Ma et al., 2008; Raab et al., 2005). Mercury present in the paddy soils can be methylated by soil microorganisms and then accumulate in the grains as methyl-Hg, the most toxic form of Hg (Zhao et al., 2016). Furthermore, Norton et al. (2014) found elevated Pb-levels in rice grains collected from known contaminated/mine impacted regions in China.

With this background, the present study aimed to evaluate the use of mud for cultivation, using as model rice, an important plant used for human diet with ability for accumulation of toxic elements. For this purpose, we grown rice in soils containing increased levels of the spilled mud for evaluation of the accumulation of chemical elements and agronomic characteristics of the plants.

2. Materials and methods

2.1. Reagents and materials

High purity water (resistivity 18.2 MΩ cm) was used throughout the experiments (Master All Gehaka, Brazil). Nitric acid (HNO_3, 65%, Synth Brazil) was previously sub-distilled (DST-100 Savillex, USA). All plastic bottles and glassware have been washed with Extran® and acid bath (15% v/v HNO_3) during 24 h. After that, all materials have been rinsed 5 times with ultra-pure water and then, it was dried in a class 100 laminar flow hood (Filterflux, Brazil). Solutions and standards were stored in cleaned plastic bottles. The materials used for *in vitro* culture were autoclaved and the experiments were conducted in a class 100 laminar flow hood (Filterflux, São Paulo, Brazil). A microwave oven Ethos Easy (Milestone, Italy) was used for sample digestion. An inductively coupled plasma mass spectrometer (ICP-MS Agilent 7900, Hachioji, Japan) was used for determination of all analytes.

2.2. Mud sampling and rice cultivar

Samarco's mud was collected on November 28th, 2015 at the margin of Santarém River, at Bento Rodrigues (Mariana, State of Minas Gerais, Brazil). The mud was collected in plastic bags at the coordinates S/W 20°14′11.37"/43°25′20.02″, altitude of 2312 m, south of Bento Rodrigues. Detailed information with regard to mud sampling is presented elsewhere (Segura et al., 2016b). Rice (*Oryza sativa* L.) cultivar BR IRGA 409, from the Rice Institute of Rio Grande do Sul (Brazil), was using during whole experiments due to its high yielding and widely cultivation in Brazil.

2.3. In vitro culture

Previously, rice seedlings were *in vitro* cultivated for screening of the possible effects associated to the mud. Firstly, the seed husks were removed. Seeds were washed in 20 mL of distilled water containing 50 μL of Tween 20 during 1 min, incubated with 70% ethanol for 1min, sterilized in 2.5% NaClO for 20 min and then washed 5 times with sterile distilled water. Seeds were soaked for 2 days at room temperature for pre-germination. Then, the germinated seeds were sown in 15 ml sterile-glass tubes using poor (water, w) or rich (Murashige & Skoog, MS) growth medium, as follows:

Water (w) control group, N = 5: agar;
Group 3.0 g Soil − w (N = 5): top soil + agar;
Group 3.0 g Mud − w (N = 5): mud + agar;
Group 7.5 g Soil − w (N = 5): top soil + agar;
Group 7.5 g Mud − w (N = 5): mud + agar;
Murashige & Skoog (MS) control group, N = 5: MS + agar;
Group 3.0 g Soil − MS (N = 5): MS + top soil + agar;
Group 3.0 g Mud − MS (N = 5): MS + mud + agar;
Group 7.5 g Soil − MS (N = 5): MS + top soil + agar;
Group 7.5 g Mud − MS (N = 5): MS + mud + agar.

Mud or top soil were weighed separately in each glass-tube and autoclaved prior to use. For water, agar or MS medium, 6 g/L of Phytagel (Sigma-Aldrich, USA) was used to increase the physical stability of the growth medium. When using MS basal salt mixture (4.3 g), the pH was adjusted to 5.7. Seedlings were grown for 15 days in a growth room at 27 ± 2 °C, 16 h:8 h (light: dark) photoperiod. Finally, shoots and roots length were measured. Further, we determined the photosynthetic pigments. The chlorophyll and carotenoid determinations were performed with 40 mg of leaf tissue, which were homogenised and kept for 2 days in the dark with 1.5 mL of DMSO (Merck, USA). The supernatant was removed and chlorophyll *a* (Chl *a*), chlorophyll *b* (Chl *b*), carotenoid (CAR) and total chlorophyll (total Chl) contents were quantified using microplate (model SpectraMax M5; Molecular Devices, USA) according to Lichtenthaler and Buschmann (2001). After that, we proceeded to the investigation with adult plants at greenhouse.

2.4. Rice cultivation to complete maturity of grains

First, seeds of rice were pre-germinated by water immersion during 24–48 h. After that, the seedlings were grown during 15 days in plug-tray. Then, two seedlings with approximately 15 cm were transferred to individual 3 L-impermeable plastic pots. Table 1 describes the soil composition used for each group. The cultivation occurred from December 2015, to May 2016 under flooded (soil immersion under 3–4 cm of water) and greenhouse (temperature 25-35 °C, 30–60% humidity) controlled conditions. After maturation of grains, soil from each pot was collected (~100 g). The plants were removed from the soil and washed with abundant tap water. Before the harvesting, plant height was recorded using the meter scale. Panicle, shoots and roots were separated with scissors. Soil, roots, shoots and panicles were dried at 65 °C until constant weight. Dried biomasses of roots, shoots and panicles were determined for the measurement of plant growth. The plant parts were individually placed in plastic bags and stored until analysis.

2.5. Soil characteristics: texture, pH, organic matter, cationic exchange capacity and content of the nutrients K, P, Ca and mg)

All the tests were performed in the soils used for rice cultivation until complete maturation of the grains. Texture (silt and sand), pH, organic matter and cationic exchange capacity were evaluated following the methodology of EMBRAPA (2011), where we can find all detailed information with regard to the analyses.

Potassium, P, Ca and Mg were measured using the method described by Raij et al., 2001. The sample was placed in water with the ion exchange resin for extraction of the analytes. The determination of Ca^{2+}, Mg^{2+} were performed complexometric method using EDTA. Potassium was determined by Flame Atomic Absorption Spectrophotometer (Contra300 Analytik Jena, Germany). Phosphorus was determined by spectrophotometer (model UV-M51; Bel Photonics).

2.6. Sample preparation and determination of elements by ICP-MS

The treatment of samples was based on Batista et al. (2014). Briefly, 200 mg of milled samples (soils, roots and grains, all dried) were pre-digested (48 h) using 1.5 mL of sub-distilled HNO_3. Then, the samples were heated (90 °C) during 30 min using a microwave oven. After that, the volume was made up to 30 mL with deionized water and analyzed by ICP-MS for determination of Mn, Fe, Zn, Al, Sr, Cu, Co, Se, As, Cd, Hg and Pb. Stock solutions (Perkin Elmer, USA) containing the elements 10 mg L^{-1} and internal standard Rh 10 μg L^{-1} were also used. Reference materials from Institute for Reference Materials and Measurements (IRMM BCR670 Aquatic Plant and ERMCC141 Loam Soil), from the National Research Council of Canada (NRC TORT-3 Lobster Hepatopancreas) and, from the Certified Reference Material Agro of Brazil (CRMAgro AR01/2015 Rice Flour) were used throughout the analysis for method accuracy.

2.7. Chemical element translocation in the plant (transfer factor)

The transfer factors (TFs) of soil/roots, soil/shoots and soil/grains for As, Fe, Cu, Mn, Zn, Cd and Pb were calculated by dividing the element concentration in the destination (roots, or shoots or grains) by the concentration in the source (soils) (Raab et al., 2005).

2.8. Determination of photosynthetic pigments in adult plants

The chlorophylls and carotenoids determinations in adult plants were performed as previously described (Lichtenthaler and Buschmann, 2001).

2.9. Electronic microscopy

Standardized points of the dried roots of plants cultivated up to complete maturation of grains were evaluated using a scanning electronic microscope with energy dispersive X-ray spectroscopy (SEM-EDS, ProX, Phenom World, Netherlands). The microscope was set at 15 KeV and EDS (energy dispersive spectroscopy) was obtained for all images (mapping scan) and for specific points (spots) in the samples.

2.10. Statistics

Analysis of variance (ANOVA) were performed with GraphPad Prism 5.01 (GraphPad Software, CA, USA). Means were considered statistically different if $P < 0.05$ in Tukey's post-test.

3. Results and discussion

3.1. Screening of mud effect on rice seedlings

Initially, we investigated the influence of increasing mud concentration on rice seedlings development in an *in vitro* study for evaluation of growth and concentration of chlorophyll and carotenoids (Fig. S1 and S2). Previous studies have revealed that the mud is deficient in nutrients and has particles smaller than those from background soils (SEDRU, 2016; Segura et al., 2016b). The experiment was conducted during 15 days with: i) medium containing water + agar (thus eliminating the physical challenge of growth in a compact soil) or; ii) agar + Murashige and Skoog Basal Salt Mixture (MS) (complementation of the growth medium with macro-micronutrients) containing mud or soil, hereafter referred as mud + water, mud + MS, soil + water and soil + MS. The results of this first experiment showed that plants cultivated in mud supplemented or not with MS presented shorter roots than plants cultivated in background soils. However, the shoots grown in mud + MS was similar to those plants grown in background soils while samples with mud + agar showed the smallest height. The chlorophylls results of the group mud + MS presented lower levels than samples of soil + MS. Moreover, the samples cultivated only with mud had the lowest concentration of chlorophyll *a* and *b* and carotenoids (Fig. S2B). The nutritional supplementation with MS contributed to the growth of shoots of plants nonetheless, it was

Table 1
Experimental design for rice cultivation to complete maturity by using different quantities of Samarco's mud. Mud, top soil, sand and organic matter are in kg.

Groups	N	Mud[b]	Top soil[c]	Sand	Organic matter
Control	4	0	1	1	1
16%[a]	4	0.5	0.5	1	1
34%[a]	4	1	0	1	1
50%[a]	4	1.5	0	1.5	0

[a] Final percentage of mud into the pot.
[b] Mud spilled from Samarco's dam.
[c] a typical eutroferric red latosol.

not enough to promote the growing of roots and to induce the production of chlorophylls and carotenoids at similar levels of controls. Therefore, we decided to investigate the development of rice plants cultivated in pots containing mud up to complete maturation of the grains.

3.2. Soils

3.2.1. Concentration of chemical elements in soils by ICP-MS

The addition of mud in successive concentrations in the soils significantly reduced ($P < 0.05$) the levels of Mn, Fe, As, Pb and Cu when compared to controls. For Cd, Al, Se, Sr, Co and Zn this effect was pronounced only in samples cultivated with mud/sand 50/50% (Fig. 1A).

The highest mean concentrations were found for Fe, Mn and Al in soils. Higher concentrations of these elements in controls were expected once the soils were made mixing typical eutroferric red latosol, sand and organic matter. Eutroferric red latosol is derived from basalt and presents high levels of Fe, Al and Mn (CETESB, 2015; CETESB, 2001; Caires, 2009; Ker, 1997). Brazilian Fe-deposits are formed by hematite, goethite and magnetite, in which the main elements are Fe, Al and Mn, respectively, explaining the presence of these elements in the mud. Further, Al and Mn are not desirable in the steelmaking process, being separated and deposited at the dams (Gomes, 2009; Henriques, 2012). Mud concentrations of Fe found in the mud were the non-extractable fractions of the mining process. Additionally, the increasing of mud lead to decreased the levels of Fe in the cultivation soils (Fig. 1A), also occurring to the other elements, in agreement with Wills and Finch (2015). They find that other elements show typically low concentrations in Fe ore.

According to SEDRU (2016), the mineral composition of the mud is quartz, hematite, magnesite and ilmenite. At less extent, goethite, kaolinite and gibbsite. Gomes et al. (2011), Nascimento (2014), Silva et al. (2006) and Wolff (2009) characterized the iron ore tailings of Minas Gerais' mines. In consonance with those previous studies, our results found that the basic constitution of mud are Fe, Si, Al and Mn oxides.

Controls, mud-16% and mud-34% presented concentrations of Cu higher than 63 mg kg^{-1}, which is above the limit of the Canadian Environmental Soil Quality Guidelines (CCME, 2001). Considering the other elements, the concentrations of Cu are lower than CCME recommendations and below the recommended limit of the Brazilian Regulations (CONAMA, 2009). The concentrations of the elements in the group mud-50% are similar to the levels described in our previous study (Segura et al., 2016b).

3.2.2. Soils characteristics: texture, pH, organic matter, CEC, P, K, Ca and mg

The results of soils characteristics used for rice cultivation for all groups are described in Table 2. Sand is the major component of soils, followed by clay and silt. Groups control and mud-16% were classified as clay soils. On the other hand, the groups mud-32% and 50% presented typical sandy clay and sandy soils, respectively. Sand has quartz as the main fraction. This component is not interesting for plant nutrition (except for Si), also showing no capacity to adsorb or store nutrients necessary for plant development (Mengel et al., 2001; Raij et al., 2001).

The slightly acidic pH values were very close between groups. Therefore, it had little influence on the variations of plant development occurred during rice cultivation. Increasing pH can influence the dissociation of functional groups present in soil organic matter (carboxyl, phenolic, alcoholic and carbonyl), thereby increasing the affinity of cationic analytes. Oppositely, at low pH, cationic analytes compete with H^+ for the functional groups

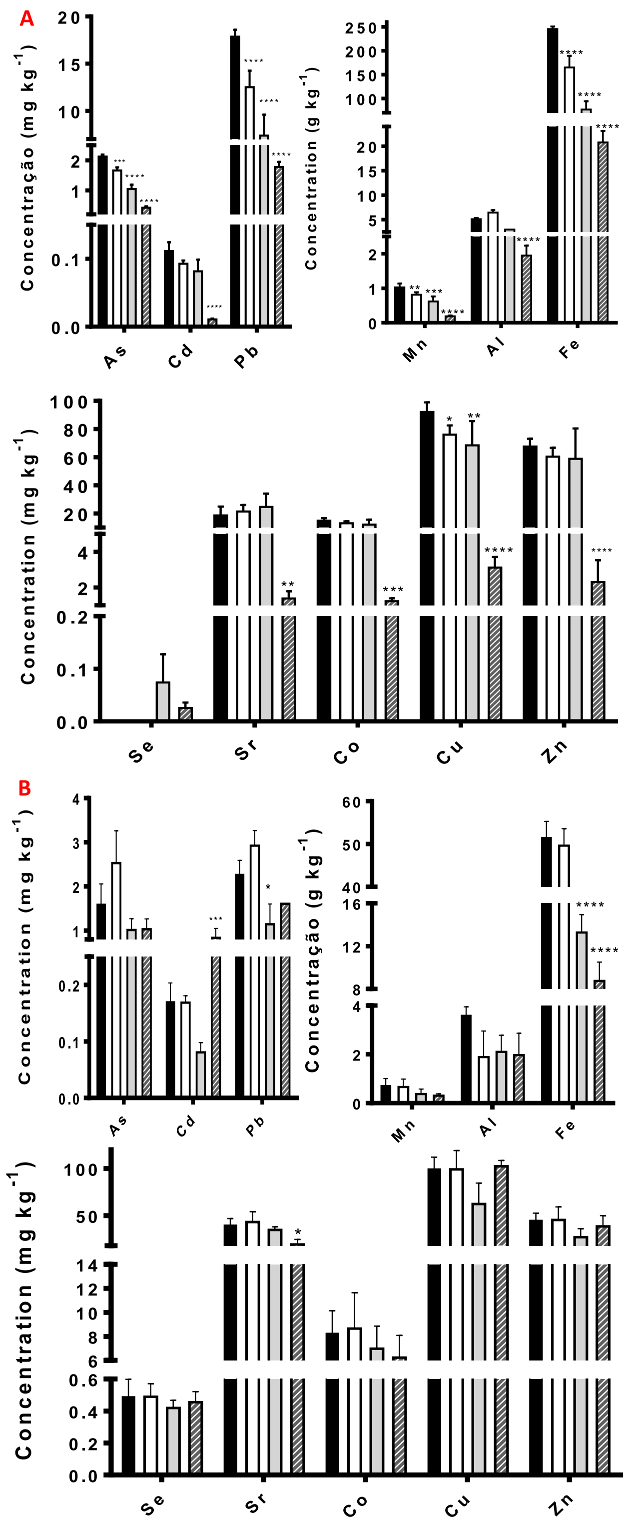

Fig. 1. Concentration of elements in soils **(A)** and roots **(B)** after rice cultivation until the complete maturity of grains. Black: controls; White, Gray and Dashed gray are 16%; 34% and 50% of mud added for cultivation, respectively (refer to Table 1). *: statistical differences between control and others groups ($P < 0.05$). Soil Se in controls and mud-16% were below the limit of quantification.

Table 2
Summary of soil properties used for rice cultivation up to complete maturation of the grains.

Groups	pH	OM g dm^{-3}	P mg dm^{-3}	K[a]	Ca[a]	Mg[a]	CEC[a]	Sand (g kg^{-1})			Clay (g kg^{-1})	Silt (g kg^{-1})	Class.
								coarse	fine	total			
Control	5.9–6.1	44 ± 10	40 ± 8	7.4 ± 1.3	75 ± 5	22 ± 4	126	253	179	423	369	199	Clay
16%	5.9–6.2	53 ± 7	47 ± 8	8.5 ± 2.2	90 ± 9	26 ± 3	149	310	149	459	383	158	Clay
34%	6.1–6.2	60 ± 9	64 ± 5	11.8 ± 1.7	104 ± 8	30 ± 4	168	417	179	596	249	155	Sandy clay
50%	6.3–6.4	12 ± 3	13 ± 2	1.0 ± 0.2	16 ± 1	3 ± 0.5	30	292	417	709	47	244	Sand

OM: organic matter; CEC: cationic exchange capacity; Class.: classification.
[a] Mmolc dm^{-3}.

(Adriano, 2001; Balcke et al., 2002 and Weigand and Totsche, 1998).

The determination of organic matter in the soils revealed very low values for mud-50% (Table 2). This result corroborates with SEDRU (2016). In general, organic matter presents humic compounds that have a negative charge surface able to adsorb cationic analytes by electrostatic attraction. The amount of cationic analytes that can be retained by these surfaces in exchangeable conditions is termed as cationic exchange capacity (CEC) (EMBRAPA, 2010; Raij et al., 2001). In addition, the CEC and the concentrations of P, K, Ca and Mg showed the lowest results for the group mud-50%. The elements P, K, Ca and Mg are macronutrients essential for plant development. Soils containing high CEC, adequate concentrations of these analytes and organic matter are fertile because they have the capacity to release nutrients, favoring the maintenance of fertility for an extended period. In addition, the mineralization of organic matter incorporates to the soil carbon and nitrogen and, at

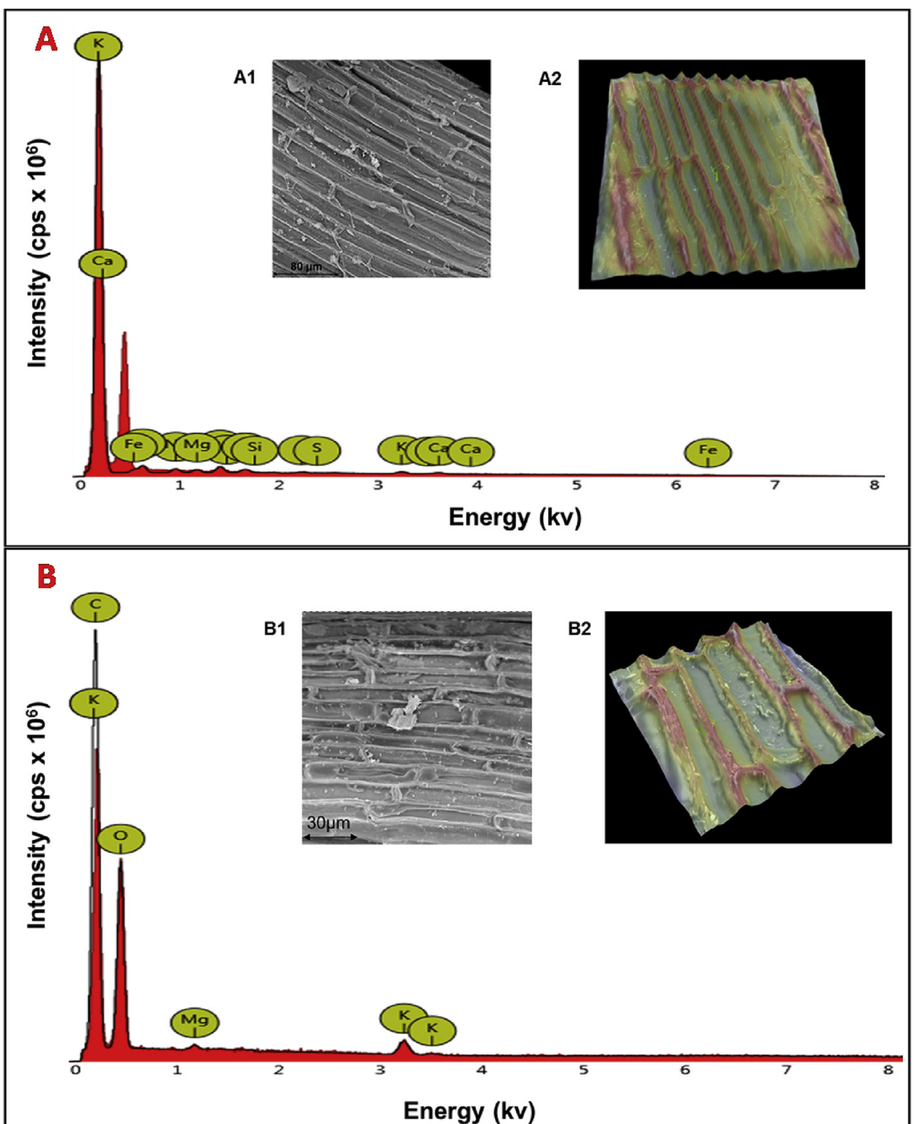

Fig. 2. Scanning electronic microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) of rice roots cultivated with and without spilled mud. **A)** Controls (A1 image of control root; A2 3D image of controls), **B)** mud-50% (B1 image of root cultivated in mud-50%; B2 3D image of mud-50% samples).

less extent, P and S (Kuzyakov and Cheng, 2001). Organic matter is an natural fertilizer that provide conditions to improve the biophysical soil properties such as porosity, density (reduction) and presence of microorganisms. Therefore, soil fertility in the group mud-50% is lower than others groups, being corrected by simple addition of organic matter and typical eutroferric latosol.

3.3. Roots

The concentrations of chemical elements in rice roots are shown in Fig. 1B. The groups presented statistically decreased concentrations ($P < 0.05$) for Fe and Al (mud-34% and mud-50%), Pb (mud-34%) and Sr (mud-50%). Only Cd in the group containing 50% of mud showed a significantly higher concentrations than the controls ($P < 0.001$). The lack of organic matter enhances the availability of Cd. Organic matter has thiol groups which bind Cd, influence its availability (Baird and Cann, 2011; Gusiatin and Kulikowska, 2016; Kaur and Crimi, 2014; Lee et al., 2009; Sampanpanish and Pongpaladisai, 2012).

Despite the bioaccumulation of a high concentration of Cd in roots of the group 50%, this study showed that Cd, As and Pb concentrations ranged 0.08–0.8, 1.0–2.5 and 1.6–2.9 mg kg^{-1}, respectively. These values were lower than those found by White and Brown (2010) to be toxic to plants (5–10 mg kg^{-1} for Cd and 10–20 mg kg^{-1} for As and Pb). This result suggest that concentrations of Cd, As and Pb in roots were not enough to affect rice growth.

Notwithstanding the low levels of the elements found in the mud (Fig. 1A), the concentrations of Mn, As, Zn, Cu, Co and Se in roots cultivated with mud did not exhibit significant differences compared to controls. However, we observed a deficiency on roots growing, as discussed below. Chopin and Alloway (2007) studied an area surrounding a Cu-mining/smelting at Tharsis, Ríotinto and Huelva, in Huelva Province of South-Western of Spain. They concluded that high trace element concentrations in soils were not correlated to elevated trace element concentrations in vegetation. Further, they concluded that areas with less organic matter exhibited higher concentration of metals that was associated to the mobility of elements. Humic acids and compounds with high molecular weight, frequently present in organic matter, contains can form metal-complexes through their –COOH terminations. These complexes can be insoluble and decrease the mobility of potentially toxic metal ions (Adriano, 2001; Baird and Cann, 2011; Schmitt et al., 2002). Thus, the presence of organic matter and the high CEC are responsible for retain metals in soil. Our results showed that the in group mud-50% the amount of organic matter and CEC were much lower than in the other groups. This fact explained the highest mobility of the elements and transfer factor from soil to roots (section 3.5) in the group mud-50%.

The roots of controls and mud-50% were analyzed by scanning electronic microscopy with EDS (SEM-EDS). The images showed a higher concentration and variety of elements in the roots of controls. These results agreed with our previously findings by ICP-MS. The abundances of elements in controls provided by SEM-EDS were 20.1; 16.9; 13.1; 12.7; 12.3; 10.7; 10.3; 4.11 for Al, Fe, K, Na, Si, Ca, Mg and S, respectively. For mud-50%, the abundances were 49.7; 48.9; 1.16; 0.28 for O, C, K, Mg respectively (Fig. 2). Images of the roots morphology (roughness) showed shorter, deeper, and thicker cell-walls of roots grown in mud-50% (Fig. 2A1, 2A2, 2B1 and 2B2).

3.4. Grains

The concentrations of chemical elements in grains of controls were find in the decreasing order: Zn > Mn > Fe > Al > Cu > Sr > Se > Co > Cd > As > Pb (Fig. 3). For

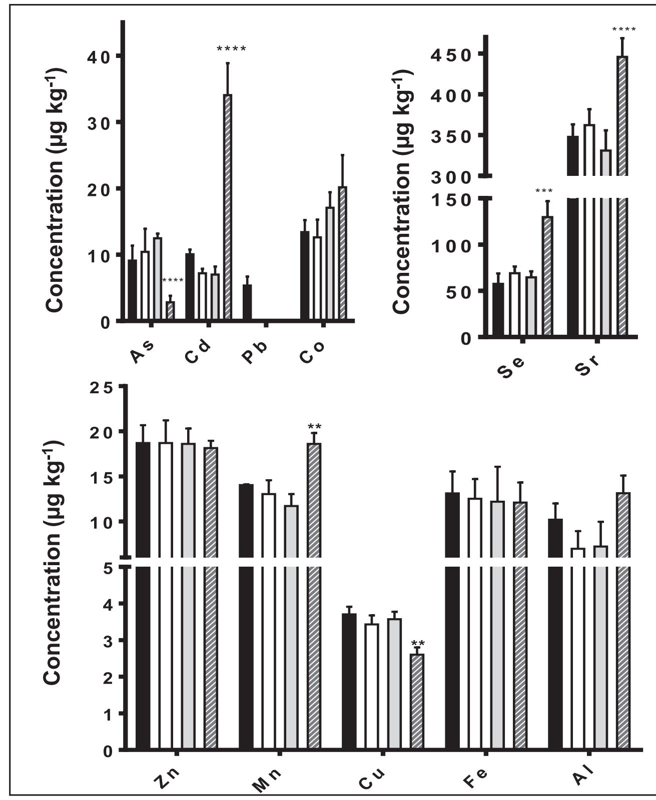

Fig. 3. Concentration of elements in grains after rice cultivated until the complete maturity. Controls: soil without mud; 16, 34 and 50 are percentages of mud added in soils for cultivation. *: statistical differences between control and other groups ($P < 0.05$). Lead was below detection limits on exposed groups (16, 34 and 50%).

sample cultivated with mud-50% the deceasing-order changes to Mn > Zn > Fe > Al > Cu > Sr > Se > Cd > Co > As > Pb. The group of mud-50% accumulated higher concentrations of Se, Sr, Cd and Mn,

Table 3
Comparison of the chemical elements concentrations (in mg kg^{-1}) between rice grains cultivated in Samarco's mud and the literature (rice and other cereals).

Elements	This study	Other studies	
		Rice from market	Other cereals[e]
Mn	14.0–18.6	5.4–146.4[a] 5.2–43.5[b] 9.4–9.6[f]	27–50
Zn	18.1–18.7	11.4–62.6[a]	18–33
Fe	12.1–13.1	10–15[c] 12.9–14.3[d] 7.2–7.9[f]	–
Al	10.1–13.1	6.10–23.4[b]	30–70
Cu	2.6–3.7	1.2–5.6[a] 0.7–2.7[b] 2.5–3.1[f]	0.3–13
Sr	0.34–0.45	–	1.5–2.5
Se	0.06–0.13	0.02–0.06[a] 0.03–0.24[b] 0.03–0.04[f]	0.1–0.8
Co	0.01–0.02	0.03–0.07[a] 0.07–0.13[b]	0.05–0.30

[a] - Batista et al. (2010).
[b] - Antoine et al. (2012).
[c] - Cakmak and Welch (2009).
[d] - Pinheiro et al. (2014).
[e] - Kabata-Pendias and Mukherjee (2007).
[f] -Joy et al. (2017).

and lower concentrations of As and Cu than the controls (Fig. 3).

Selenium is an essential element for humans and animals however has not been proven to be essential for plants (Li et al., 2008). Under flooded soil conditions, the reductive dissolution of iron oxides and hydroxides may release the adsorbed metals/metalloids into the soil solution phase (Li et al., 2010). This condition associated to the high elements' mobility in the group mud-50% may have favored the translocation of Se to the grains.

The cultivation of rice under flooded conditions creates a reducing environment that maintains the Mn as Mn^{2+}. Once the oxidation potential of Fe^{+2} is higher than Mn^{+2}, the oxygen is translocate through the spaces from the leaves into roots and even be excreted into the rhizosphere surface of rice roots and oxidizes the Fe^{+2} and maintains Mn^{+2} available (Kirk, 2003; Mengel et al., 2001; Zhang et al., 1998). The higher mobility of these elements in the group mud-50% facilitated the uptake of Mn up to the grains.

Although Cu was found at high concentrations in soils and roots, its levels in the grains were similar in all groups (Fig. 3). This is expected once Cu is known to binding in roots' cell walls, preventing metal translocation to the aerial parts of the plants (Lu et al., 2017).

Cadmium is well-known by its high toxicity and mobility compared to other potentially toxic metals (Zhao et al., 2009, 2010). In this study, the group mud-50% presented similar concentrations for Cd and As in roots. However, in the grains, Cd-levels were 12-fold higher than As. According to Batista et al. (2014) and Mou et al. (2016), As and Cd are retained in by roots' phytochelatins. In the group mud-50%, the As levels in the grains were lower than Cd, suggesting that phytochelatins expressed by this rice cultivar for As sequestration are different from those ones for Cd.

For a precise conclusion regarding the content of toxic and essential elements within the grains, we compared our findings with the literature (Tables 3 and 4). The concentrations of Mn, Zn, Fe, Al, Cu and Se agreed with the literature. For Sr and Co our study presented lower levels than previous studies (Table 3). For As, Cd and Pb we compared with the maximum levels of regulating agencies (Anvisa, *Codex Alimentarius* and European Commission, Table 4). The concentration of As and Pb were lower than previous studies. On the other hand, it was verified a higher concentration of Cd in our samples when compared to commercialized rice. However, As, Cd and Pb concentrations were below the maximum limits.

Considering the conditions of cultivation of this present study, the results have showed that Samarco's residual mud used for rice cultivation produced grains with low levels for As, Cd and Pb. In addition, Hg levels were below the limit of detection. Therefore, after soil fertilization and amendment, we should consider the use

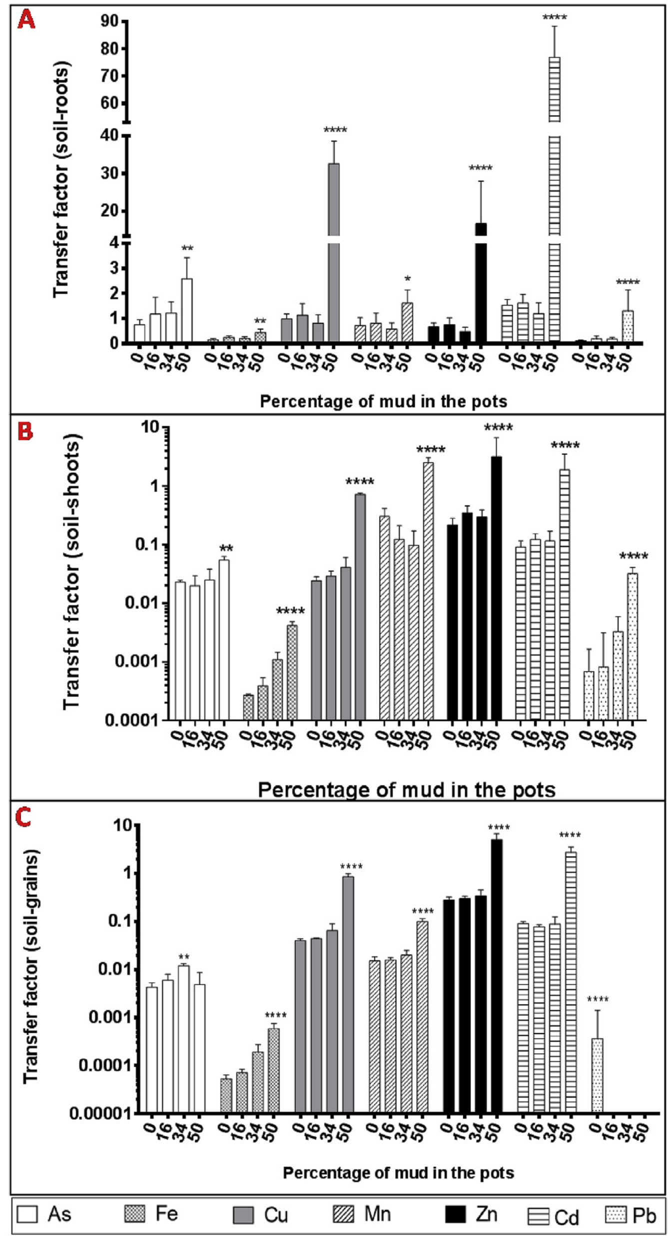

Fig. 4. Transfer factor for As, Fe, Cu, Mn, Zn, Cd and Pb between soil→shoots and soil→grains of plants exposed to increased percentage of mud. *: statistically different from control soil (P < 0.05).

Table 4
Comparison of As, Cd and Pb concentrations find in rice grains cultivated in Samarco's mud with the values found in other studies and maximum limits recommended by regulation agencies.

Elements	This study (μg kg^{-1})	Other Studies				
		Commercialized rice (μg kg^{-1})	Rice grown in contaminated area (μg kg^{-1})	Maximum limit (μg kg^{-1})		
				ANVISA (2013)	*Codex Alimentarius* (CAC, 2016)	European Commission (EC, 2014)
As	2.8–12.5	58.8–216.9[a] 110–487[b]	212–774[d]	200[e]	200[e]	–
Cd	10.1–34.1	6.0–20.2[a]	100–980[d]	400	400	200
Pb	5.3 ± 1.2	40[c]	100–334[d]	200	–	200

[a] - Batista et al. (2010).
[b] - Antoine et al., 2012.
[c] - Lima et al. (2015).
[d] - Kwon et al. (2017).
[e] Maximum limit for Inorganic As.

of the affected area for agriculture, posing a good alternative to reduce the socio-environmental damages.

3.5. Transfer factor

The transfer factor (TF) soil-roots were higher than TF soil-shoots and TF soil-grains (except for Mn, Fig. 4). Previous studies have reported that chemical elements have higher accumulation in roots than aerial parts (Grotto et al., 2015; Liu et al., 2007; Satpathy et al., 2014). This fact can be explained by the compartmentalization and translocation processes in the vascular system of plants (Kim et al., 2003). According to our results (Fig. 4), TF soil-roots showed that the mobility of elements in the mud occurred in the following order Cd > Cu > Zn > As > Mn. The TF soil-roots for Pb and Fe were very low (Pb > Fe).

The low levels of organic matter and CEC probably increased the mobility of Cd, Zn and Cu (Kabata-Pendias and Sadurski, 2004). The low TF observed for Pb was associated with its interaction with oxides of Fe, Mn and Al. Although the Fe concentrations in soil and mud were the highest among all the other elements, the TF values (soil-roots and soil-shoots) of Fe were the lowest. This fact is probably associated with the iron plate. In order to decrease Fe absorption, the plant oxidizes part of Fe^{2+} to Fe^{3+} then, Fe^{3+} precipitates as FeO(OH) in soil and root, forming iron plates (Fageria et al., 1981; Holzschuh et al., 2010). Li et al. (2016) found that Fe-plaque in rice roots decrease the absorption of Pb by the plant. In the present study Fe concentrations in roots ranged from 8.7 ± 1.8 to 51.5 ± 3.7 g kg^{-1}. Toxic Fe levels to rice, where Fe-plaque is observed, normally range from 0.5 to 1.6 g kg^{-1} (Ishizuca, 1961; De and Mandal, 1957). Therefore, it is possible that the Fe observed in the roots was not absorbed but deposited outside the surface of the roots, forming the iron plaque. In addition, no significant differences were observed in the concentration of Fe among various groups (control and treatments). This suggest that Fe-homeostasis was adequate for plant growth.

Transfer factors soil-shoots in mud presented the following order: Zn > Mn > Cd > Cu > As > Pb > Fe. This result is in accordance with the previous studies reported for Zn and Cd (Satpathy et al., 2014). They found that TFs roots-shoots were higher than other metals in paddy plants nearby the impacted area Kalpakkam (Tamil Nadu), India. Transfer factors soil-grains in the mud showed the following order Zn > Cd > Cu > Mn > As > Fe > Pb. These results are

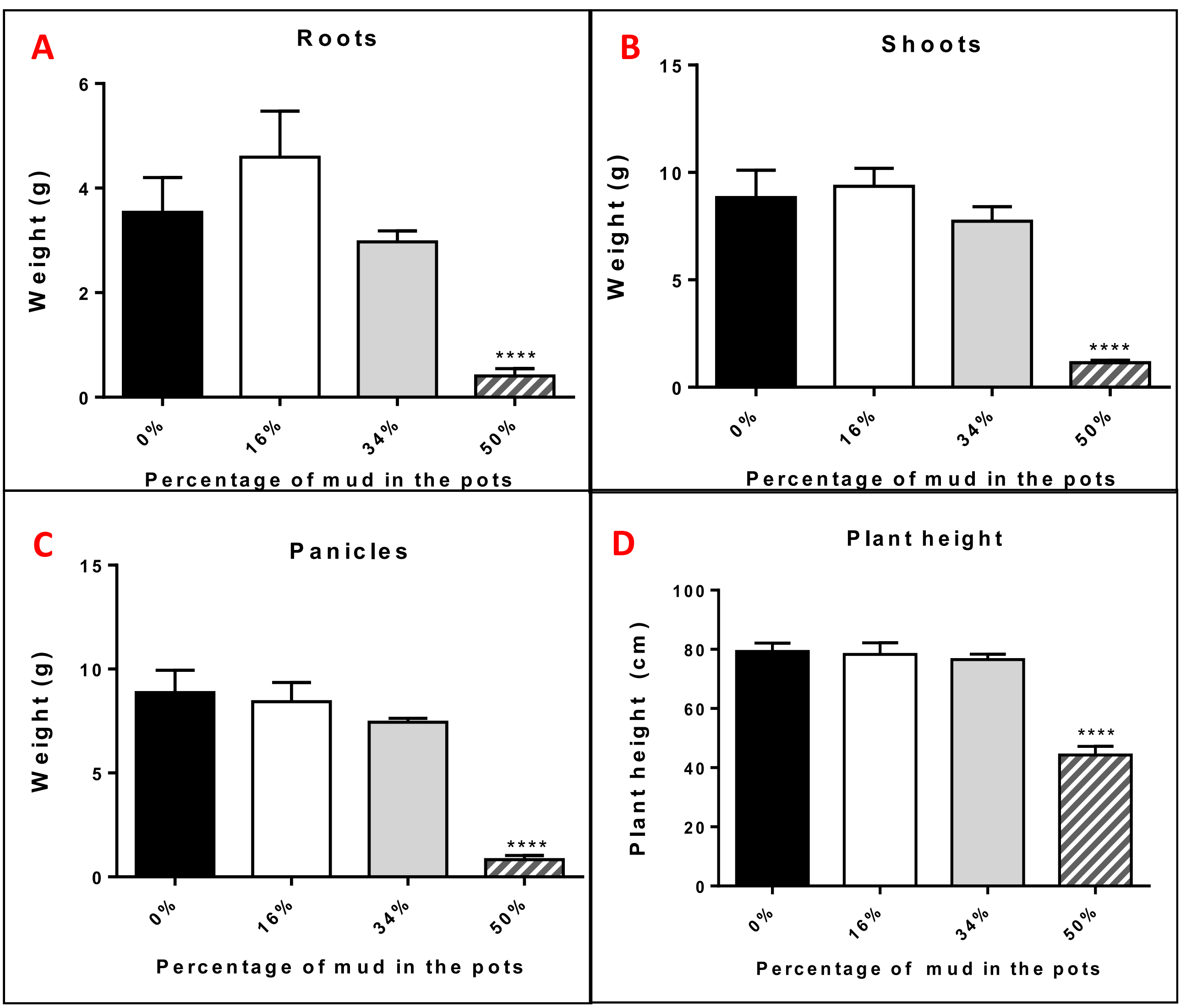

Fig. 5. Determination of agronomic parameters cultivated in pots with different amount of mud spilled from Samarco dam burst. Biomasses of roots (**A**), shoots (**B**) and panicles (**C**). Plant height: **D**. *: Statistically different from control soil ($p < 0.05$).

in line with those observed by Silva et al. (2007), which determined the root translocation index to grains in rice cultivars planted in soil contaminated with potential toxic metals. They have observed an increasing translocation: Zn > Mn > Cd > Cu > Pb > Fe. Concerning other plants, Chary et al. (2008) observed that Zn, Cr, and Cu had a higher soil mobility than Ni, Co and Pb, similarly to the present work.

3.6. Agronomic parameters

Plant height was statistically affected by the addition of mud-50% in the soil ($P < 0.05$) (Fig. 5). Dry weight of roots, shoots and panicles (rice seeds) of control and plants exposed to the mud were measured. Our results showed a significant decrease in biomass of the group mud-50%. The presence of 50% of mud in the soil caused a restriction in the plant growth and a decrease on biomass and, consequently, grain yielding (Fig. 5). Compared to controls, plants grown in mud-50% significantly reduced their height (41.2%), biomasses of roots (88.5%), shoots (87%) and panicles (90.6%).

Plants require water, oxygen, carbon dioxide and mineral elements for adequate nutrition and growth. The elements required at high amounts are nitrogen, P, K, Ca, Mg and S. The micronutrients are Cl, B, Fe, Mn, Cu, Zn, Ni and Mo (Mengel et al., 2001). Deficiency in any of these mineral elements or/and high concentrations of mineral elements in the soil can inhibit plant growth and reduce crop yields. For example, in acid mineral soils high concentrations of Mn and Al can cause toxicity in some plants. Manganese and Fe toxicities can occur on waterlogged or flooded soils (White and Brown, 2010).

In this study the possible toxicity of Mn and Al weren't considered because the concentration of these elements in soils and plants parts are within the typical values found in soils and plants (EMBRAPA, 2006; EMBRAPA, 2010; Vlamis and Williams, 1964; Wang et al., 2015; White and Brown, 2010). However, the concentrations of Fe in roots and soils correspond to values that may be toxic to rice. Further, the cultivar BR IRGA 409 is susceptible to Fe toxicity. Soils in which this kind of Fe-toxicity occurs often have a low CEC and are poor in Ca and K, once the oxidizing capacity of roots is too low (Mengel et al., 2001; Ottow et al., 1983). As previously discussed, Fe toxicity in rice produces Fe-plaques that influence the absorption of nutrients, causing nutritional unbalance in rice plants. In the mud-50% this effect was aggravated by the presence of low concentration of nutrients. The reduced rice growth in the mud can be explained by the soil fertility and texture. Soil composition in the mud-50% is poor in nutrients and organic matter. Mud particles are small, pronouncing soil compaction and, consequently, roots penetration in the soil. This feature affected the plant development once the roots were not deeply enough to uptake the nutrients adequately.

3.7. Determination of photosynthetic pigments

The concentrations of chlorophylls (*a* and *b*) and total carotenoids of rice plants cultivated in pots with different amount of mud are shown in Fig. 6. Although height and plant biomasses did not present significant variations for mud-16% and mud-34%, the concentrations of Chl *a*, Chl *b* and carotenoids are significantly lower in all treatments containing mud. Mud-50% was the group with lower concentrations of all three pigments (Chl *a*, Chl *b*, and carotenoids). Although the concentrations of these pigments were lower in the mud-exposed plants, the relative abundances between Chl *a* and Chl *b* within each treatment were not changed (Fig. 6). Our study showed a ratio of 3:1 of Chl *a*:Chl *b*, which is consistent to previously descriptions (Streit, 2005). Thus, the mud did not cause an unbalance in the synthesis of the photosynthetic pigments, but possibly a reduction in photosynthesis in general.

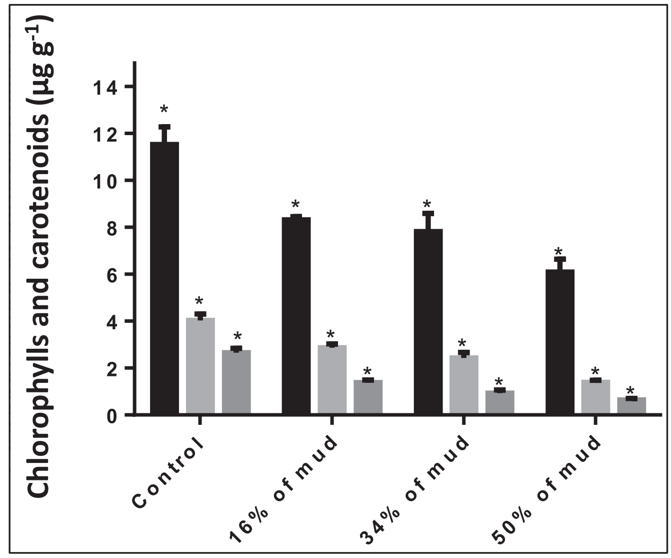

Fig. 6. Concentration of chlorophyll *a* (black), chlorophyll *b* (light gray) and total carotenoids (dark gray) of rice plant cultivated in pots with different amount of mud spilled from Samarco's dam burst.

A plausible explanation for the decreased concentration of photosynthetic pigments is the nitrogen availability. Previous studies showed that improved photosynthetic rate arises from high leaf nitrogen concentration (Hayami, 1982, 1983; Kuroda and Kumura, 1990a, 1990b; Saitoh et al., 1991; Sasaki and Ishii, 1992; Zhang and Kokubun, 2004). The nitrogen available for plants is mostly supplied by the mineralization of organic matter, promoted by microorganisms, with the formation of nitrate. High humidity and lack of oxygen in soils promote denitrification (nitrate is reduced to nitrous oxide, N_2O, or nitrogen, N_2, both gases that are lost to the atmosphere). Microorganisms capable of N_2 fixation may live symbiotically with higher plants, being the way in which plants can absorb the nitrogen (EMBRAPA, 2010; Mengel et al., 2001). Thus, we believe that the amount of microorganisms acting on nitrogen availability for the plant were higher in the groups containing top soil and organic matter.

4. Conclusion

This was the first study to assess whether agricultural activities would be affected in the areas achieved by the spilled mud from the biggest world mining accident. Our findings showed that the spilled mud presented low levels of potentially toxic metals, deficiency of nutrients and physical properties which caused plant alterations. The analysis of the rice grains cultivated in the mud showed that accumulation of toxic elements (As, Cd, Hg and Pb) by the plant were not relevant. The results suggested high difficult for cultivation using mud-50% (mud + sand). However, simple soil amendment provided improvement on rice growth. Plants cultivated with mixture of mud and background fertile soil (organic matter + top soil) presented good development. Therefore, soil correction using the composts such organic matter, fertilizers, eutroferric red latosol among other can be helpful for reforestation and agriculture at the affected areas.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2017.11.099.

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