



## Original Article

# Poorly Crystalline Fe (III) Oxide excess can to alter the electrochemical paths of hydromorphic soil in the Palm Swampy Vegetation

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## ABSTRACT

Fe oxides are the one of the major constituents of tropical soils, and have very reactive and binding sites. Under flooding conditions used as electron acceptors in respiration of anaerobic microorganisms. The aim of this study was to present the electrochemical and microbiological behavior of a tropical hydromorphic soil under application of Poorly Crystalline Fe(III) oxide. In this way, an iron gel solution was prepared in three different concentrations (0.001, 0.01, 0.03 M) and distributed in four blocks in a microcosm assay. Electrochemical measurements and assessments of soil microbial biomass was made in four different periods (1, 7, 15 and 30 days). Fe (III) oxide changes the pH, Eh and microbial biomass until 15 days of incubation. The 0.03 M concentration prolonged the buffering system, and apparently was change the microbiota more abruptly, on the other hand, at the final incubation, are suggest the development of specific groups capable to degrade crystalline iron.

## 1. Introduction

Tropical soils have a high content of iron oxides in its constitution; especially when very weathered (Camargo et al., 2015). The oxides have a high sorption capacity and energy, which offers the possibility to interact with many soil constituents, whether other minerals or microorganisms (Wang et al., 2009).

Flooding soil system alters the chemical, physical and biological properties. The physical evident change is the occupation of spaces by water, before occupied by air (Fageria, 2011). Chemically, metals initiate a state of reducing caused by anoxic conditions (Richardson & Vepraskas, 2001), and because this selection pressure, the overall soil microbiota changes its aerobic to anaerobic metabolic state (DeAngelis et al., 2010; Fageria, 2011; Picek et al., 2000).

Among these reductions, the iron becomes Fe (III) oxide (Loeppert & Inskeep, 1996; Richardson & Vepraskas, 2001; Fageria, 2011), and has been cited as the most important chemical change that occurs in anaerobic sediment and soil

environments (Lovley, 1991). According to Cornell & Schwertmann (2003) and Nevin & Lovley (2002) Fe (III) oxide is poorly crystallized longer available for microbial degradation. The major factor influencing the bioavailability of iron oxide in the soil is relative to its easy dissolution, which is influenced by particle size (Loeppert & Inskeep, 1996).

The electrochemical phenomena have correlation with the microorganisms in these systems, which allows to understand how works the presence of a chemical species, and how can be harmful to the environment, or otherwise be readily degraded (DeAngelis et al., 2010).

The microbial oxidation of organic compound, associated with Fe (III) reduction form, can to remove of significant amounts of pollutants and contaminants. This ability can be accelerate in areas of flooding conditions with additions of chelating Fe (III) or humic substances (Lovley, 1997; Dia et al., 2015).

The source that gave more response, in cell culture to the development of microorganisms, was Poorly Crystalline Fe

(III) Oxide with a final concentration of the 0.4 M, prescribed in Lovley (1991). Thus, the aim of this study was to test the effect of the presence of different concentration of iron in soil microbial biomass (SMB) and electrochemical indicators in a typical hydromorphic soil in a tropical savannah.

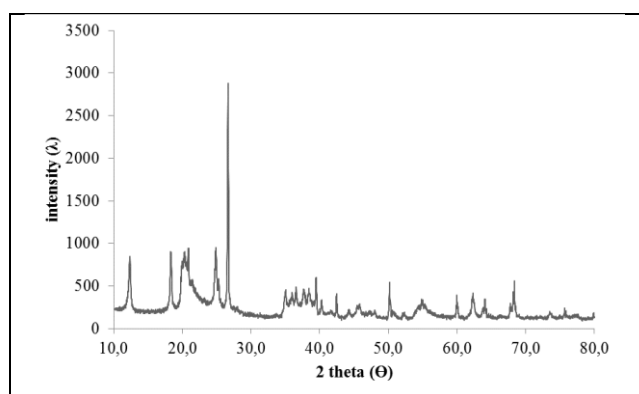
## 2. Materials and methods

Soil samples of the preserved Vereda (Tropical Savannah Grassland) was collect in the Bela Vista de Goiás city, State of Goiás, Midwest Brazil (S17°00'W48°47') to conduct this study. Sampling was made in 2014, during the rainy season (November) and respect the thickness of the A horizon (0-15 cm deep). The relief is level or gently undulating and the soil of these area was clay loam (39.41% clay, 18.14% silt, 42.45% sand) and classified as Bela Vista de Goiás Clay Loam Typic Endoaquolls by Soil Survey Staff (2014). Thereafter, the samples was air-dried and sieved (< 2 mm) and conduced to chemical (Table 1) (Embrapa, 2013) and mineralogical analysis (Figure 1) (Whittig & Allardice, 1986).

**Table 1** – Chemical analyses of soil samples containing organic matter, texture and metals.

							Texture (%)					
							Clay	Silt	Sand			
							39.41	18.14	42.45			
pH	Al	Si	K	Ti	Fe	OM						
							(%)			(dag.dm <sup>-3</sup> )		
4.3	40.70	45.69	0.4	1.8	10	3.02						

Poorly crystalline Fe (III) oxide was produced from an Iron Gel Fe (III) solution (FeCl<sub>3</sub>·6H<sub>2</sub>O) dissolved in water to provide final concentration of 0.4M (Lovley, 2013). The solution was continuously stirred, with pH adjustment to 7.0 from a NaOH solution, in which the product has a brown color. The solution was centrifuge and resuspend to remove dissolved chloride that is harmful to microorganisms (Nevin & Lovley, 2002). From the final concentration of 0.8 M, the solution was dilute to three concentrations: 0.03, 0.01 and 0.001 M.



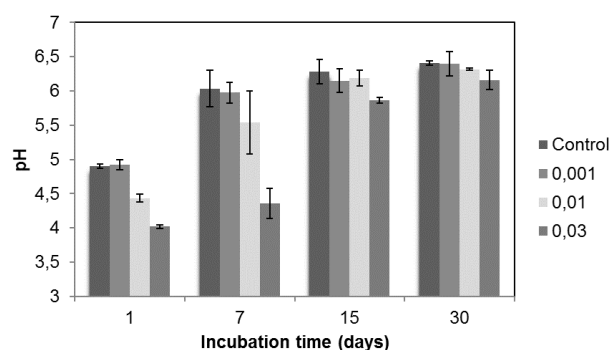
**Figure 1:** X-Ray Diffraction (XRD) evidencing 1:1 clay in hydromorphic soil of the Tropical Savannah, Brazil.

Quadruplicate of sample was incubate in a microcosm assay with ultrapure water. For control conditions and in the presence of different iron solutions was used a ratio 1:1 (100g soil and 100 ml water to control; and 100g soil and 75 ml iron solution + 25 ml water) in plastic vials column (15

X 8 cm) for 4 different periods (1; 7; 15 and 30 days) under flooding. At the end of each period, the samples were evaluate electrochemically. The SMB routine was make by Irradiation-Extraction (Islam and Weil, 1998; Komarova et al., 2008) and the determination of the present carbon in the extracts is according to Tedesco et al. (1995).

## 3. Results and discussion

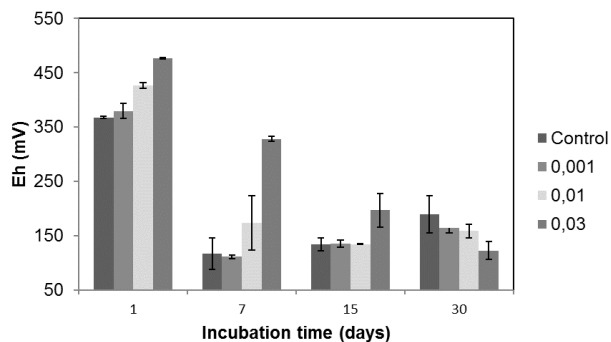
The pH show a tendency to near the neutrality with the incubation time increase (Figure 2), as expected to flooding soils. The concentration of iron added to the soil affected pH values, especially in the first day of incubation. The highest concentration (0.03 M) showed more acid pH until fifteenth day of incubation, and this can demonstrate that the presence of excess iron oxide can keep environments that are more acid. The reducing flooded soils is characterized by an increase in pH and decrease both pH and SMB.



**Figure 2:** pH behavior in Gleysol of Vereda in time to 30 days incubation. Standard error is given by mean of the function bars

The presence of iron oxides in the soil have the capability of charge change at dependent clays, such a kaolinite (Dousova et al., 2014), clay of this study. According Sumner (1963), iron oxides behave amphotericly in soil and contribute significantly to the buffer capacity of tropical soil. The present study demonstrated a direct relationship between the increases in iron oxide concentration solution with a high potential soil to be buffered in the initial stage of flooding process. The present authors suppose of the iron oxides at low pH values is probably due being bound to the kaolinite, confirmed by Sumner (1963) and Pezeshki, DeLaune (2012). Furthermore, at lower pH, kaolinites provide a protective system for some organisms (Silva et al., 2015), that suggest a similar phenomenon in our system.

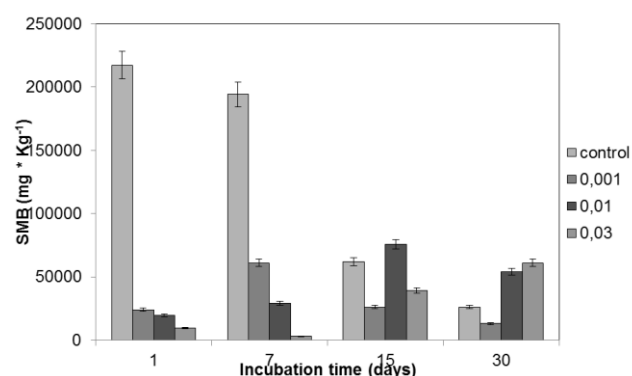
In addition, in these samples have a high level of organic matter (SOM), considering tropical soil (Table 1). The SOM participate of the some interactions with some iron oxides (Nevin & Lovley, 2002), and in soils is highly influenced by the pH and redox potential (Chen et al., 2014), such as stable complexes with Fe<sup>3+</sup> (Loeppert & Inskeep, 1996). The authors believes in this dynamic, because the data show the Fe (III) oxide concentration increase, the redox potential (Figure 3) and pH change the normal behavior expected. All these Fe bio reduction are controlled by general characteristics of iron-oxide occurring in the soil (Lovley, 1991, 2013) and can influence the biogeochemistry dynamic (Thompson et al., 2006).



**Figure 3:** Eh (redox potential) behavior in Gleysol of Vereda in time to 30 days incubation. Standard error is given by mean of the function bars.

Eh changes can direct the type of microorganisms that develops (Husson, 2013), and means imposes the condition for operation of the system (Grybos et al., 2009), since it has the ability to regulate the electrons transferring in the metabolism of microorganisms (DeAngelis et al., 2010; Husson, 2013; Nevin & Lovley, 2002; Sposito 1989), and consequently their development (Dia et al., 2015). The data confirm that all conditions had a similar behavior, with a metabolic inversion to anaerobic microorganisms. However, in a more abrupt form, the samples in the presence of the Fe oxide, the depletion is higher in terms of biomass (Figure 4), suggesting that iron, depending on their specie, may create a selective medium and inhibit the development of groups that are more general and benefiting groups that are more specific.

Dia et al. (2015) comments for every environmental stress there is a multitude of survival strategies for microbial population to acclimate to the new conditions. The same authors say the redox potential in soil indicates changing availability of electron acceptor, requiring fundamental changes in microbial metabolic lifestyles. Our data show a direct relationship between Eh buffering state and SMB suppression in the first stage of incubation and in the final moment (30 days), the microbiota is reestablished, and indicate a specification. Vorenhout et al. (2004) points this redox capacity. Furthermore, the results show at lower concentrations, the suppression affect at final incubation is greater than at higher concentration, which has the potential for selection. It is believe this behavior may be related to the availability of iron oxide to degradation beyond the binding sites of the clays.



**Figure 4:** Eh (redox potential) behavior in Gleysol of Vereda in time to 30 days incubation. Standard error is given by mean of the function bars.

According to Lovley (1997), Fe (III) reductions are most significant when catalysts microorganisms of

sedimentary environments carry out the enzymatic activity, and the most intensively studied are *Geobacter* and *Shewanella* species. Between these two species, Lovley & Nevin (2002) indicate the *Geobacter* species such as the more important, cause have a greater activity and is the more present. Furthermore is the largest user of Fe (III) as electron acceptor in strictly anaerobic environments. This type of microorganism may act as an environmental biotechnology for decontamination of flooded soils, as suggested Lovley (1997).

The higher Poorly Crystalline Fe (III) oxide solution left the soil solution buffered until to half of the assessment incubation (Figure 2), and that can be note by Eh parameter (Figure 3). The explication is the potential of adsorption of the lowest concentration at sites of kaolinite, thus iron oxide excess; the highest concentration had a more prominent suppression when compared to control, or even the other concentrations (Figure 4).

This manuscript present inference about the iron behavior in tropical flooded soils under the bias of the microbial biomass and electrochemical as a change environmental indicator. This is the one of the first steps for the advancement of studies with the same subject, or even molecular studies following the potential of the biotechnological capability of the surviving species.

#### 4. Conclusion

Poorly Crystalline Fe (III) oxide are buffered the system in all assays, but it was more expressive in higher concentration. Fe (III) oxide slowed the soil reduction velocity. Iron, already at very low concentration, is sufficient to reduce quantitatively soil biota in tropical hydromorphic soil, possibly selecting a specific group that acts in the Fe reduction. Finally, to all different concentration show a different succession development of the microbiota in the assay.

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