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ORIGINAL ARTICLE

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Eletrochemical changes in Gleysol of the Amazon estuary

Alterações eletroquímicas em Gleissolo do estuário amazônico

ABSTRACT: Electrochemical reactions are intensified by soil flooding, which changes the dynamics of nutrients and negatively affects plant growth. In this work, we aimed to evaluate the changes in the redox potential (Eh), pH and nutrient availability in a Haplic Gleysol soil from a floodplain of the Guamá River, Belém, Pará State. During the period of floods (61 days), samples soils were collected on alternate days and analyzed in dry and wet conditions. Flooding resulted in higher pH values and decreased Eh, which stabilized after 32 days of flooding and did not affect the values of total nitrogen. An increase in the concentrations of phosphorus, sulfur, iron, manganese, copper and zinc were observed, and they were subsequently reduced with time of submergence. The reduction of sulfur occurred at low Eh and pH values near neutrality. The results show that nitrogen and sulfur do not limit agricultural production in the lowland soils of the Guamá River.

KEYWORDS
Oxidation-reduction
Availability of nutrients
Waterlogged soils

RESUMO: *Reações eletroquímicas são intensificadas com a inundação do solo, o que altera a dinâmica dos nutrientes e afetando negativamente o crescimento das plantas. O objetivo foi de avaliar as alterações no potencial redox (Eh), pH e na disponibilidade de nutrientes de um Gleissolo Háplico em várzea do rio Guamá, Belém, estado do Pará, em função do tempo de inundação. O experimento foi conduzido em delineamento inteiramente casualizado, com quatro repetições, em condição de laboratório. Durante a inundação (61 dias) foram coletadas amostras de solos em dias alternados e analisadas secas e úmidas. A inundação proporcionou elevação dos valores de pH e diminuição no Eh, que estabilizaram-se após 32 dias, e não influenciou o teor de nitrogênio (N) total. Ocorreu aumento nos teores de fósforo (P), enxofre (S), ferro (Fe), manganês (Mn) e zinco (Zn), que foram posteriormente reduzidos com o tempo de inundação. A redução do S ocorreu em valores baixos de Eh e pH próximo da neutralidade. Os altos teores de N e o S demonstram que esses nutrientes não se configuram como limitantes da produção agrícola em solo de várzea do rio Guamá.*

PALAVRAS-CHAVE
Oxi-redução
Disponibilidade de nutrientes
Solos alagados

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1 Introduction

The lowland soils of the Brazilian Amazon constitute one of the most important ecosystems of Brazil because of its biological productivity and biodiversity. The large coverage area (approximately 200,000 km^2) and high fertility of the soil, which is constantly renewed, allows them to have high yield potential (Lima et al., 2001). As a result of the physical, chemical and biological factors and flood regimes affecting the soils, the coastal wetlands, which are also called fluvio-marine wetlands, are classified as Pará River wetlands, Amazon River Estuary wetlands, Amapaense Coastal Plain wetlands and Northeast Paraense and Maranhense Pre-Amazon wetlands (Lima et al., 2001).

The wetland soils of the Guamá River, a tributary of the Pará River, have great economic importance for the state of Pará. Because they have good natural fertility and are located in the vicinity of large urban centers, they benefit agricultural activities and contribute to improving the quality of life of the populations involved. Their natural fertility is associated with the large amount of suspended sediment in the river waters, which maintains the soil fertility level (Lima et al., 2001).

The periodic flooding of wetland soils changes their chemical characteristics, including their nutrient dynamics, which affects the development of crops. In these soils, anaerobic bacteria decompose organic matter using oxidized compounds from the soil as electron acceptors, promoting a series of oxidation-reduction reactions. As a consequence, there is a decrease in the redox potential (Eh) and nitrogen (N), sulfur (S), copper (Cu) and zinc (Zn) contents as well as an increase in pH and phosphorus (P), iron (Fe) and manganese (Mn) availability (Gonçalves & Meurer, 2010; Schmidt et al., 2013).

The increase in pH resulting from waterlogging affects the mobilization dynamics of several elements. Fe^{+3} and Mn^{+4} in the soil surface are reduced to the forms Fe^{+2} and Mn^{+2}, respectively, increasing their solubility in the soil (Schmidt et al., 2013; Pezeshki & Delaune, 2012). P becomes more available mainly because of the reduction of ferric compounds to ferrous forms, and the release of P that was retained by adsorption or by specific chemical bonds (Gonçalves & Meurer, 2010; Ponnamperuma, 1972). The concentrations of Zn and Cu decrease because of their ease in forming low solubility compounds such as hydroxides, carbonates and sulfides, and in flooded acidic soils, these cations may experience increased adsorption onto organic colloids because of the increase in pH (Ponnamperuma, 1972).

In soils under anaerobic conditions, great losses of N occur through denitrification, which is considered the main loss mechanism of this element. In the absence of O_2, anaerobic microorganisms use the oxidized form of N (NO_3^-) as an electron acceptor during the decomposition of organic residues and reduce it to N_2 or N_2O, which leave the system in gas form (Keller et al., 2009).

Under these conditions, sulfate (SO_4^{2-}) is reduced by the precipitation of metal sulfides, especially pyrite (FeS), which decreases the availability of S to crops in the long term (Pezeshki & Delaune, 2012). In soils with high S content, precipitation in the form of FeS prevents the poisoning of plants by H_2S during flooding (Pezeshki & Delaune, 2012). H_2S is toxic to plants, inhibits the absorption of water and nutrients and decreases the availability of S in the soil (Ponnamperuma, 1972).

The magnitude of the changes induced in the physical, chemical and biological characteristics of wetland soils of the Guamá River as a result of flooding regimes must be considered when the sustainable management of these areas is desired. Therefore, the hypothesis that the flooding regime changes the dynamics of available nutrients in these soils and modifies their electrochemical properties is tested.

The objective was to evaluate the changes in pH and Eh values and N, P, S, Fe, Mn, Cu and Zn concentrations of a Haplic Gleysol as a function of the time of submergence.

2 Materials and Methods

The soil samples were classified as Haplic Gleysol (Embrapa, 2013) and collected 400 m from the Guamá River channel in the Amazon estuary in a high floodplain area (1°27’32.92” S and 48°25’55.12” W). A homogeneous 10 ha area was selected for the collection of 10 simple soil samples at a depth of 0-0.2 m for the preparation of composite samples. Three subsamples were extracted for the chemical characterization of the soil, and the remaining material was used to conduct the experiment. Sample preparation consisted of air drying, delumping with wooden tools, passing the soil through a 2.0-mm mesh sieve and subsequently characterizing the soil.

The experiment was conducted using a completely randomized design with four replicates under controlled conditions in the Laboratory of Soil Analysis of the Federal Rural University of Amazonia (Universidade Federal Rural da Amazônia - UFRA). Seven kilograms of soil were placed into four styrofoam boxes, which were flooded with deionized water obtained under quality control for 61 days. The water depth above the soil surface was maintained at 2 cm.

Thirty samplings were conducted from January to March 2006 by extracting a soil sample from each plot using a 10-mL syringe extractor. One group of samples were analyzed after weighing while wet, whereas another group with the same volume were collected and after weighing were oven-dried at 105°C.

The ratio between the wet sample weight and dry sample weight was used to determine the factor that was used to convert the result of the wet soil analysis into oven-dried fine soil (ODFS). The samples were then analyzed according to the method described in Embrapa (1997) with the exception of the available S, which followed the methodology described by Alvarez et al. (2001) (Table 1). The variables evaluated were pH, Eh, available P and S and total N, Fe, Mn, Cu and Zn contents.

pH and Eh were obtained directly from the plots with a potentiometer prepared for the readings with the use of a combined calomel electrode for the pH readings and a platinum electrode for the Eh readings, which were previously calibrated with buffer solutions. The measurements performed with aerobic soil characteristics on the first day shortly after waterlogging were considered time zero. The values of the soil attributes were plotted as a function of time.

3 Results and Discussion

On the first day of waterlogging, the pH value increased by three units, from 4.4 before waterlogging (Table 1) to 8.7 at 61 days after waterlogging (Figure 1a). The increase in pH is attributed to the Fe compounds in the soil that are reduced in the absence of O_2 with the release of OH^- ions in the soil (Ponnamperuma, 1972). In addition, when acidic soils are flooded, anaerobic microorganism activity during the reduction of oxidized Fe compounds consumes H^+ ions, reducing the acidity of the soil (Schmidt et al., 2013; Ponnamperuma, 1972). The H^+ ions are used as electron acceptors for the respiration of anaerobic microorganisms.

Increases in pH from 5.8 to 7.2 after 47 days of waterlogging in the studied Haplic Gleysol were observed by Mattar et al. (2002). These authors found that after the 31st day, the pH values stabilized between 7.1 and 7.2. In Haplic Planosol samples from Capão do Leão, Rio Grande do Sul, Brazil, the pH increased to 6.2 after 15 days of waterlogging (Schmidt et al., 2009).

There was a sharp decrease in Eh values, which varied from +49 mV on the first day of waterlogging to -206 mV on the third day, and they reached -431 mV on the 37th day and stabilized at approximately -390 mV starting on the 39th day (Figure 1b). Eh is a quantitative measure of the tendency of a given system to oxidize or reduce substances or elements susceptible to these phenomena. High and positive values indicate low electron activity and oxidizing conditions, whereas low and negative values indicate reducing conditions (Messias et al., 2013; Pezeshki & Delaune, 2012).

The accumulation of organic load and its mineralization causes further reducing conditions in the sediment (Vinatea et al., 2006). Extremely low Eh values, such as those found in this study, indicate high consumption of organic matter, which most likely stays at intermediate values if it is not naturally replaced.

A sharp decline in Eh in Haplic Planosol samples from Capão do Leão subjected to waterlogging was reported by Schmidt et al. (2009) and explained by the intensification of redox soil processes. Redox processes occur because of the release of substances reduced in the system, with subsequent decreases of the partial oxygen pressure before compounds such as Mn and Fe oxides and hydroxides can exercise their buffering capacity and maintain Eh at intermediate values (Ponnamperuma, 1972).

Eh values of -97.5 mV starting on the fifth day of waterlogging and reaching –240 mV on the 29th day were observed by Ferreira et al. (1998) in lowland soil. These authors attributed this effect to the presence of high contents of total Mn (493 mg kg^{-1}). According to Ponnamperuma (1972), soils with low Mn content can maintain positive Eh for several weeks.

The content of available P (Mehlich 1 extractor) increased significantly during the waterlogging time and ranged from 10.5 mg kg^{-1} on the 1st day to the maximum of 28.9 mg kg^{-1} on the 47th day of flooding, and it then decreased, stabilizing at 26.7 mg kg^{-1} (Figure 2a). The initial increase in the availability of P in the solution of waterlogged soils is possibly because of the reduction of ferric phosphates to more soluble ferrous forms (Gonçalves & Meurer, 2010). The hydrolysis of Fe and

Table 1. Chemical and physical characterization of the 0-0.2 m depth layer of a Haplic Gleysol before flooding.

Tabela 1. Caracterização química e física da camada de 0-0,2 m de profundidade de um Gleissolo Háplico, antes da inundação.

K^+	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	T	V	m
cmol$_c$ dm^{-3}						%	
0.2	2.8	3.9	1.0	6.1	13.0	53.2	13.0
P_{avail}	S_{avail}	C_{org}	N_{total}	pH	Sand	Silt	Clay
mg dm^{-3}		g kg^{-1}		H_2O	g kg^{-1}		
5.6	8.1	18.3	1.7	4.4	23	695	282

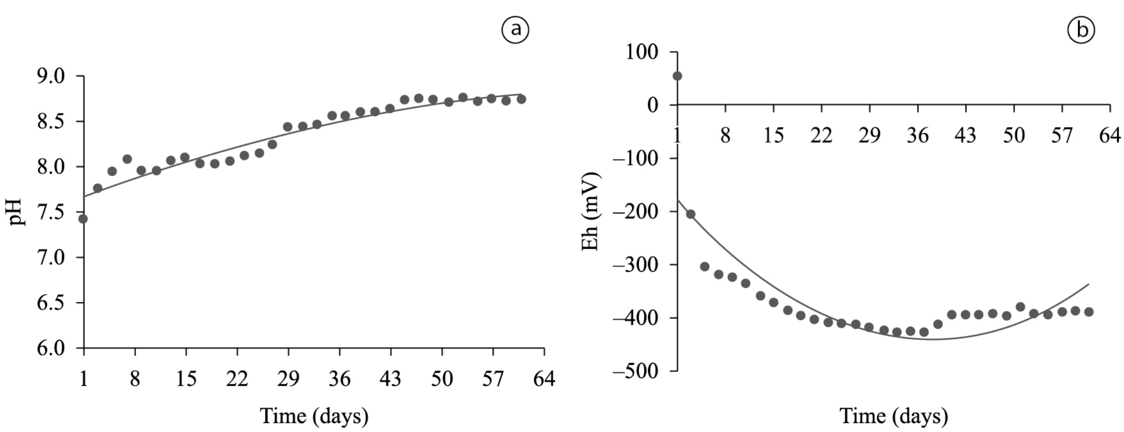

Figure 1. Variation of pH (a) and redox potential (Eh) (b) as a function of the waterlogging time in the studied Haplic Gleysol.

Figura 1. Variação do pH (a) e potencial redox (Eh) (b) em função do tempo de inundação de um Gleissolo Háplico.

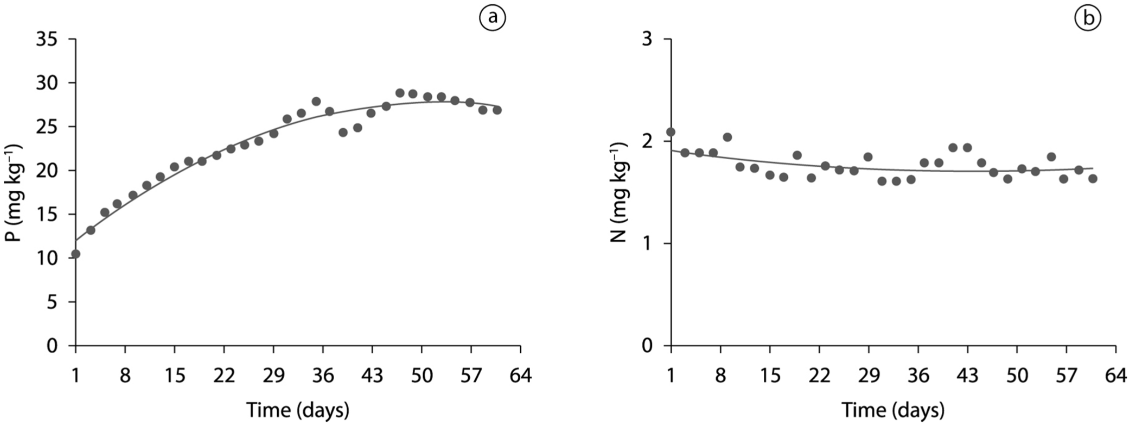

Figure 2. Concentrations of available P (a) and total N (b) as a function of the waterlogging time in the studied Haplic Gleysol.
Figura 2. Concentrações de P disponível (a) e N total (b) em função do tempo de inundação de um Gleissolo Háplico.

Al phosphates caused by the increase in pH in acidic soils and consequent release of the P adsorbed onto clays or onto Fe and Al hydroxides through ionic exchange also contributes to the increased availability of P in the soil. Conversely, the subsequent decrease may be attributed to the readsorption of phosphates by the clays and Al hydroxides in the reduced layer or to the precipitation of ferrous phosphates from the accumulation of Fe^{+2} and increase of pH (Ponnamperuma, 1972).

A similar pattern of P mobility was observed by Mattar et al. (2002) in the floodplain soils of the Guamá River, although the study was conducted for a shorter waterlogging time (47 days). The maintenance of nutrient availability over a longer waterlogging time is important to meet the demand of plants grown in this environment, such as rice (*Oryza sativa*). Knowledge of the availability dynamics of P in flooded soils is essential for sustainable crop management in flood plains.

There was no significant variation in the availability of N with the flood of time (Figure 2b). On the first day of flooding, there was an increase in total N to 2.05 g kg^{-1}, and it subsequently stabilized until the end of the experiment, with mean values of 1.7 g kg^{-1} (Figure 2b). Waterlogged soils have conditions conducive to considerable N losses, especially through denitrification and NH_3 volatilization because of reducing processes where anaerobic microorganisms utilize the oxidized form of N (NO_3^-) as an electron acceptor during decomposition in the absence of O_2 and reduce it to N_2 or N_2O, which leave the system in gas form (Ponnamperuma, 1972).

In contrast, N_2O losses to the atmosphere and decreases in total N from the soil surface, which does not include the presence of plants, are not significant, and the flow of this form of N may underestimate the N losses in flooded ecosystems (Cantarella, 2007). According to this same author, plants grown in flooded soils, such as rice, transport N_2O dissolved in water to the atmosphere through their transpiration system, a mechanism that represents a major drain of total N from the waterlogged soil.

The high initial contents of total N, which were maintained throughout the waterlogged period, are considered elevated. Conversely, Fajardo et al. (2009) found low levels of total N and organic matter in periodically flooded wetland soils in the channel of the Solimões/Amazonas rivers, Central Amazon. According to Alfaia et al. (2007), because N is the main factor limiting production in these wetlands and farmers do not use nitrogen fertilizers, organic matter is the main natural source of the nutrients for plants, which explains the low reported N contents.

The concentration of available S increased from 8.5 mg kg^{-1} on the first day of waterlogging to the maximum of 20.6 mg kg^{-1} on the 32nd day, and it declined thereafter to 11.4 mg kg^{-1} at the end of the experiment (Figure 3). The S-SO_4^{-2} contents between 6.4 and 16.5 mg kg^{-1} in the irrigation water from different rivers supplied the demand required by the rice crops in the Central Depression of Rio Grande do Sul (Carmona et al., 2009). Based on this result, the available S content in the Guamá River wetlands observed during the experimental period may be sufficient for the nutrition of plants grown under waterlogging.

The availability of S after 31 days of waterlogging returned to values near the initial concentration. A decline in the available S-SO_4^{-2} concentration only occurred after a long period of flooding when conditions of intense S-SO_4^{-2} reduction in the soil and precipitation to metal sulfides are established (Ponnamperuma, 1972; Pezeshki & Delaune, 2012).

Certain rice farms in the Rio Grande do Sul Central Depression exhibited low production and symptoms of S being the limiting factor because the reduction of sulfate after a long waterlogging period can cause deficiency of this nutrient because of losses of H_2S through volatilization and flooding may be maintained in this area for over 150 days per year (Carmona et al., 2009).

The Fe dynamics in the soil after waterlogging were characterized by an increase from 1,349 mg kg^{-1} on the first day of flooding to 4,843 mg kg^{-1} on the 31st day, and they decreased thereafter to 3,276 mg kg^{-1} on the 61st day (Figure 4a). Abreu et al. (2007) reported that the waterlogging of a Guamá River Gleysol caused an increase of 1,000% in the levels of Fe in the soil solution.

In a eutrophic Haplic Planosol in Capão do Leão, Schmidt et al. (2013) found that continuous waterlogging caused a decrease in Fe and its release to the soil solution, and

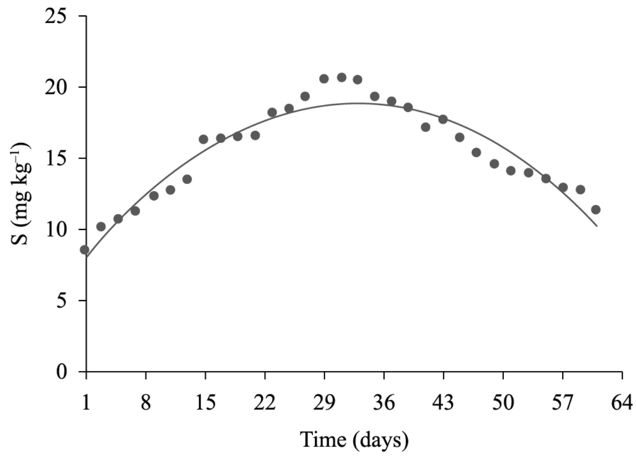

Figure 3. Variation of available sulfur (S) as a function of waterlogging time in the studied Haplic Gleysol.

Figura 3. Variação de enxofre (S) disponível em função do tempo de inundação de um Gleissolo Háplico.

it reached the maximum content in the third week of flooding and decreased thereafter. The authors attributed the decrease in Fe and consequent increase of its content in the soil to the decrease in Eh values.

The available Mn in the soil increased with waterlogging and ranged from 245 to the maximum of 437 mg kg^{-1} on the 39th day of flooding and declined thereafter to values of 294 mg kg^{-1} at the end of the experiment (Figure 4b). The maximum contents of Mn in samples of a Haplic Planosol collected in the city of Capão do Leão were observed at 44 days of waterlogging (Schmidt et al., 2009). Increases in the content of Fe and Mn were also found by Gonçalves et al. (2011) in samples of different soils that were used for irrigated rice cultivation in Rio Grande do Sul and waterlogged for 45 days.

Waterlogging caused an increase in the concentrations of Cu (Figure 5a) and Zn (Figure 5b). Before flooding, the values were 3.75 and 12.6 mg kg^{-1} and increased to the maximum of 50.33 (third week) and 149.6 mg kg^{-1} (fourth week), respectively, and then decreased until the end of the experiment.

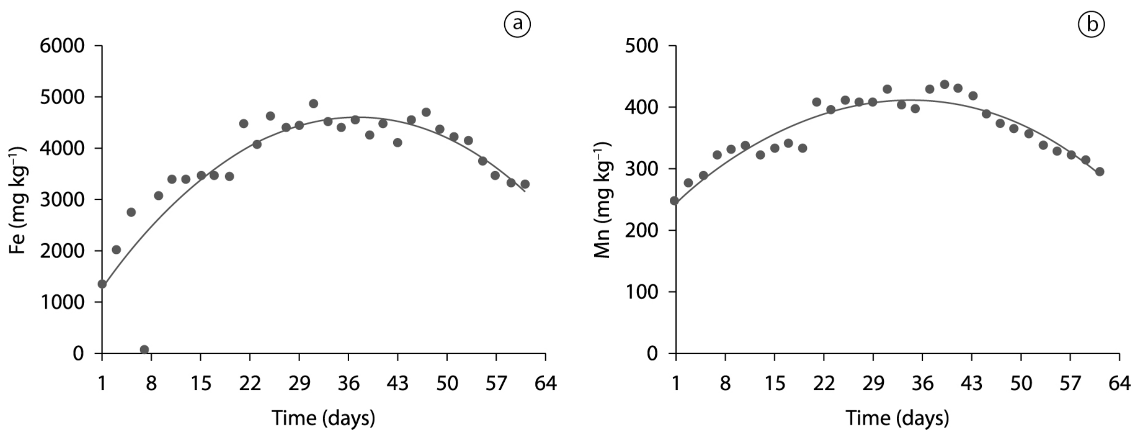

Figure 4. Variation of the concentrations of available Fe (a) and Mn (b) as a function of waterlogging time in the studied Haplic Gleysol.

Figura 4. Variação das concentrações de Fe (a) e Mn (b), disponíveis em função do tempo de inundação de um Gleissolo Háplico.

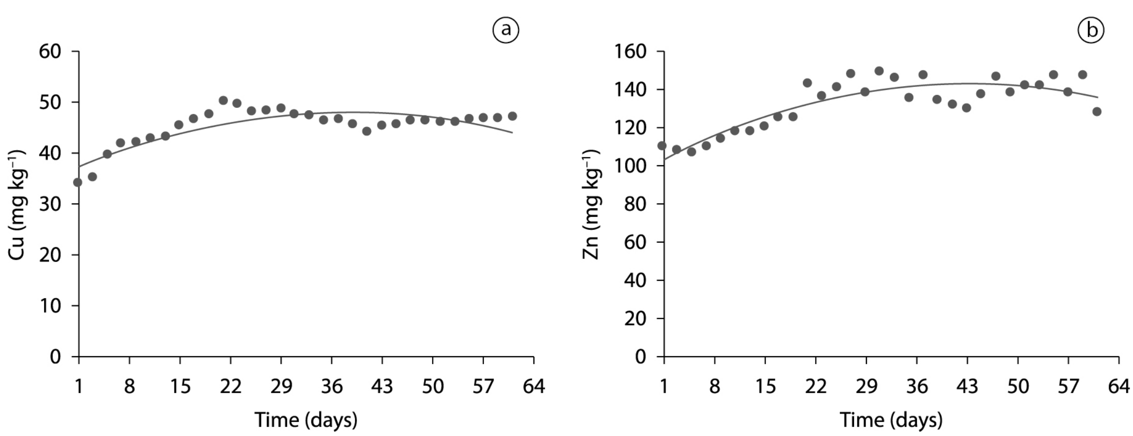

Figure 5. Variation of the concentrations of available Cu (a) and Zn (b) as a function of waterlogging time in the studied Haplic Gleysol.

Figura 5. Variação das concentrações de Cu (a) e Zn (b) disponíveis em função do tempo de inundação de um Gleissolo Háplico.

Ferreira et al. (1998) observed increases in the C and Zn contents in wetland soils of the Guamá River and decreases after 45 days of waterlogging. These authors relate this effect to both the reduction of Fe^{+3} and Mn^{+4} oxides and hydroxides as well as to the production of chelating agents resulting from the increase in pH and the formation of sulfides.

The initial increases in the contents of Fe, Mn, Cu and Zn after soil waterlogging may be related to the reduction of iron and manganese oxides and production of organic complexing agents. In turn, the decreased contents of Fe, Mn, Cu and Zn may have been caused by the increase of pH and the formation of sulfides (Ponnamperuma, 1972; Schmidt et al., 2009).

4 Conclusions

Extended waterlogging periods significantly reduced the redox potential, indicating a high reductive condition influenced by the intensification of oxidation-reduction processes, which causes an increase in pH. The increased availability of P, S, Fe, Mn, Cu and Zn suggests that these elements do not limit the agricultural production in wetland areas of the Guamá River; however, Fe and Mn reached levels that may be toxic to plants when the soil remains waterlogged. The concentration of total N was unchanged but remained high in the waterlogged soil. The waterlogging period corresponding to 61 days showed that the availability dynamics of the evaluated elements varied little compared with those observed in other wetland soils with different characteristics.

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