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**INTERAÇÕES GEOQUÍMICAS NA SUPERFÍCIE
DE GLEISSOLOS NO ESTUÁRIO AMAZÔNICO**

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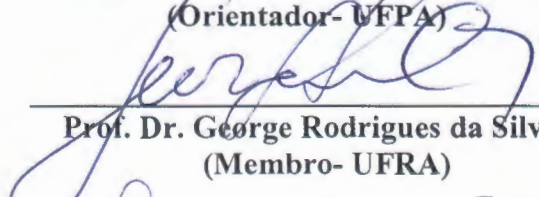
SÉRGIO BRAZÃO E SILVA

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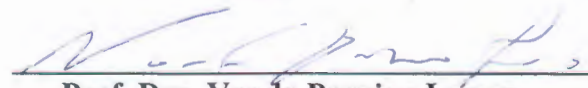
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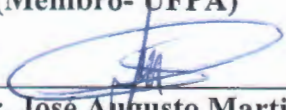
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RESUMO

As várzeas são terrenos baixos e mais ou menos planos que se encontram junto à margem de rios. São abundantes no estuário amazônico e apresentam grande variabilidade ambiental, com ampla diversidade de solos, vegetação, água de inundação e regime de inundação. A grande variabilidade de ambientes encontrados, no entanto, impõe a necessidade de desenvolvimento de estudos visando conhecê-los, para induzir seu aproveitamento e preservação. A fertilidade elevada destes solos se destaca em relação aos demais solos da Amazônia, com fertilidade baixa. Características regionais específicas, entretanto necessitam ser investigadas para compreender o exato mecanismo para a formação da fertilidade do solo, neste ambiente. Pesquisas iniciais apontavam prioritariamente para a contribuição da colmatagem de sedimentos para formação da fertilidade nestes solos. Para auxiliar na compreensão das transformações geoquímicas que afetam e contribuem para a formação da fertilidade nestes solos, se investigou as transformações geoquímicas na superfície de dois Gleissolos, correspondentes a dois ambientes distintos do estuário amazônico: uma várzea de água doce, no rio Guamá e uma várzea salina em ambiente de mangue, no rio Caeté. Paralelamente se avaliou as características do solo e sedimentos em suspensão na água dos rios que circundam as várzeas estudadas, o suspensato. A amostragem do solo, destinada à realização do experimento foi realizada na superfície dos solos estudados, correspondente à profundidade explorada nutricionalmente pelos vegetais. As amostras destinadas à caracterização do solo foram obtidas através de amostragem em seus horizontes, correspondendo seu primeiro horizonte à amostra destinada à realização do experimento. O suspensato foi obtido através de coleta da água dos rios próximos aos locais de amostragem, e deixados em decantação por três meses, após os quais foram separados do sobrenadante, centrifugados, separados novamente do sobrenadante, e secos em dessecador. A seguir foi realizada a caracterização mineralógica, tanto nos solos estudados, como nos suspensatos obtidos. Solo e suspensato também foram avaliados através de determinação química total, granulometria e de sua fertilidade. O estudo realizado, consistiu, na realização de dois experimentos, com 4 repetições cada, que promoveu inundação nos solos, em condição de laboratório, empregando água destilada, para evidenciar as transformações químicas que

ocorrem, sem considerar a água local dos ambientes. Após inundação, amostras eram retiradas periodicamente e analisadas úmidas, obtendo os teores disponíveis de elementos relacionados à nutrição vegetal (P, K, Ca, Fe, Mn, Cu, Zn), valores de carbono orgânico e do pH e Eh. Em terceiro ensaio, a metodologia usualmente empregada para a avaliação da fertilidade de solos, que preconiza a análise no solo previamente seco, foi objeto de investigação, em comparação com metodologia empregada em diversos trabalhos neste tipo de solo, a qual emprega a determinação na amostra ainda úmida para proceder à análise, convertendo os resultados para solo seco empregando fator de correção. Este cuidado é empregado em diversos trabalhos neste tipo de solo, em virtude de após secos, se reverterem as transformações ocorridas, e assim ocorrer a possibilidade de informar resultado não correspondente às condições de campo. Nesta investigação, a variação de resultados na disponibilidade de nutrientes, que ocorre após a inundação foi avaliada pelas duas metodologias, tanto no Gleissolo Háptico, como no Gleissolo Sálico, em dois experimentos. Assim sendo, durante o período inundado, amostragens periódicas nas parcelas experimentais avaliaram as variações nas concentrações disponíveis de P, Ca, K, Fe, Mn, Cu e Zn, através das duas metodologias testadas. Os experimentos demonstraram que a inundação promove alterações profundas na fertilidade dos solos estudados, mas com diferenças relacionadas à sua condição regional. Os resultados obtidos expressam que a ocupação dos poros do solo pela água induzem a grande transformação no comportamento geoquímico do solo, influenciando na disponibilidade dos elementos estudados, no pH e Eh. O Gleissolo Háptico situado no rio Guamá alterou seu pH inicial de 4,69 para estabilizar em torno de 6,6 a partir do 8º dia. Da mesma forma seu Eh também decaiu substancialmente 322 mV para -337 mV durante 4 meses de inundação. Ocorreu grande acréscimo de Fe, P e Mn disponível para o solo. Em relação ao K, Ca, Cu, Zn e Fe, ocorreram pequenos acréscimos de valores disponíveis, entretanto com valores suficientemente adequados à nutrição vegetal, à exceção do ferro que adquiriu valores extremamente elevados. No Gleissolo Sálico, situado no mangue do município de Bragança, o comportamento ocorreu de forma semelhante, embora com escalas de intensidade diferente. A variação no pH não ocorreu de forma tão intensa neste solo, tendo se estabilizado entre 5 e 6, menores que no rio Guamá, mas com valores que impede que os micronutrientes se tornem indisponíveis com o tempo de inundação. Da mesma forma o Eh demonstrou que ocorre redução neste solo, mas não tão acentuada quanto ocorre no solo do rio Guamá, resultando em redução estabilizada em valores situados entre 200 e 300 mV. Este fato ajuda a explicar o acúmulo de matéria orgânica no perfil deste solo, acumulada por falta de aceptores de elétrons e dinâmica acentuada da matéria orgânica que este ambiente possui. Neste solo a

disponibilidade de fósforo diminuiu com o tempo. Ambos os solos e suspensatos estudados apresentaram composição mineralógica semelhante com quartzo, illita, esmectita, caulinita, e o solo do rio Guamá apresentou ainda goethita. Nos suspensatos estudados, a alta fertilidade apresentada, superior que a dos próprios solos, indica a possibilidade de manutenção da fertilidade do solo, após deposições periódicas que ocorrem a cada maré. Associados à presença elevada de matéria orgânica e a presença de argilominerais 2:1 presentes no solo, estes fatores despontam como condição diferencial destes solos, principalmente dentre os solos comumente encontrados na terra firme. No terceiro experimento, referente à comparação entre a análise efetuada no solo seco e a análise efetuada no solo úmido, os resultados indicam que a resposta às transformações que se procedem após a inundação, é percebida em ambos os métodos testados, e que os métodos respondem de forma diferente para cada ambiente testado. Assim, a avaliação estatística aponta os elementos cálcio, no Gleissolo Háptico, e fósforo, potássio, manganês e zinco no Gleissolo Sálico, como indiferentes na escolha do método a ser utilizado em sua determinação. Em seguimento, os elementos fósforo, manganês e cobre no Gleissolo Háptico e o cálcio no Gleissolo Sálico são elementos que apresentaram vantagem estatística para a análise no solo seco. Os elementos potássio, ferro e zinco, no Gleissolo Háptico e Ferro e cobre no Gleissolo Sálico apresentaram resultados favoráveis à determinação no solo úmido. No entanto, embora ambos os métodos possam ser utilizados, a análise no solo úmido é recomendada, pelo acompanhamento das transformações, que são percebidas em detalhes, em especial para os resultados de teores inferiores, comuns no início do período de inundação. Os três estudos realizados nos solos do estuário Amazônico demonstram que as alterações geoquímicas que ocorrem nestes solos após ter seus poros preenchidos com água, não procedem da mesma forma, embora sejam solos da mesma classe pedológica e possuam proximidade geográfica. Fatores regionais influenciam os resultados como características mineralógicas, a água de inundação, biologia do local e outros fatores. Embora a liberação de nutrientes ocorra de forma específica aos solos estudados, as alterações se apresentaram benéficas, proporcionando condições adequadas ao desenvolvimento vegetal. O suspensato, que se apresentou em ambos os locais estudados, com fertilidade elevada, possibilita assim, a manutenção dos altos índices de fertilidade encontrada nestes solos, após ação das marés, quando é depositado no solo. A presença de argilominerais 2:1, representou um diferencial para estes solos, pois estes minerais são ausentes na superfície de solos de terra firme nos solos do entorno, e contribuem para a formação de índices elevados de CTC, que ainda recebe acréscimo devido aos teores elevados de matéria orgânica existente, em especial no Gleissolo Sálico. São condições

distintas em relação aos solos nesta região, que não contam com fatores que proporcionem CTC elevada, assim como fatores que proporcionem a manutenção desta fertilidade, pela adição de material fértil de forma periódica.

Palavras-chave: Várzea - Amazônia. Estuário Amazônico. Nutrientes do solo. Geoquímica de superfície. Solos alagados.

ABSTRACT

The floodplains are the lowlands and about that are near the bank of rivers. Are abundant in the Amazon estuary and have great environmental variability, with wide range of soils, vegetation, water flooding and flooding regime. The great variability of environments found, however, imposes the need to develop studies to know them, to induce their utilization and conservation. The high fertility of these soils stand out compared to other Amazonian soils with low fertility. Specific regional characteristics however need to be investigated to understand the exact mechanism for the formation of soil fertility in this environment. Initial research pointed primarily to the contribution of the clogging of sediment to the formation of fertility in these soils. To assist in understanding the geochemical transformations that affect and contribute to the formation of fertility in these soils was investigated changes in surface geochemical two Gleisols, corresponding to two different environments of the Amazon estuary: a freshwater floodplain, in the Guamá River and a floodplain saline mangrove environment, in Caeté River. In parallel we evaluated the characteristics of the soil and suspended sediment in the rivers that surround the wetlands studied, suspensato. Soil sampling, for the accomplishment of the experiment was performed on the surface of soils, corresponding to the depth explored nutritionally by plants. The samples for soil characterization were obtained by sampling on the horizon, first horizon to its corresponding sample for the experiment. The suspensato was obtained by collecting river water near the sampling sites and left to settling for three months, after which the supernatant were separated, centrifuged, the supernatant separated again, and dried in a desiccator. The following mineralogical characterization was performed in both soils, as in suspensatos obtained. Soil and suspensato were also evaluated by chemical determination, particle size and fertility. The study consisted in carrying out two experiments with four replicates each, with promoted flooding in soils under laboratory conditions, using distilled water, to elucidate the chemical transformations that occur, without regard to local water environments. After flooding, samples were collected periodically and analyzed wet, getting the available contents of elements related to plant nutrition (P, K, Ca, Fe, Mn, Cu, Zn) values of organic carbon, pH and Eh. In the third test, the method usually employed for the assessment of soil fertility, which aims to analyze the soil previously dried, was under investigation, and compared with the determination in the sample still wet, to investigated, converting the results to dry soil using the correction factor. This care is employed in several works in this type of soil, due to

dry after the changes occurred is reversed, and thus place the possibility of informing mismatch results to field conditions. In this investigation, the variation of results in nutrient availability, which occurs after the flood, was assessed by two methods, both in the Haplic Gleysol and Salic Gleysol, in two experiments. Thus, during the flooded, the regular sampling rate plots the changes in the available concentrations of P, K, Ca, Fe, Mn, Cu and Zn, by means of two methods tested. The experiments showed that that flooding promotes profound changes in the fertility of soils, but with different related to their regional status. The results express that the occupation of soil of pores by water induces the great transformation in soil geochemical behavior, influencing the availability of the elements studied, in the pH and Eh. The Haplic Gleysol, Guamá situated on a river, change initial pH of 4,69 to stabilize around 6,6 from the 8th day. Likewise his Eh also declined substantially 322 mV to – 337 mV for 4 months of flooding. There was a large increase of Fe, Mn and P available to the ground. Regarding the K, Ca, Cu, Zn and Fe occurred small additions of available values, but values will be sufficiently adequate plant nutrition, except for iron acquired extremely high values. In the Salic Gleysol, located in municipality of Bragança mangrove, the behavior was similar, although with different intensity scale. The change in pH was not so intensely in the soil stabilized with from 5 to 6, Guamá smaller than the river, but with values that prevent the micronutrient becomes unavailable in the time of flooding. Likewise the Eh demonstrated that there is a reduction in soil, but not pronounced as is the river soil Guamá, resulting in reduced stabilized at values between 200 and 300 mV. This fact helps explain the accumulation of organic matter in the profile of this soil, accumulated due to lack of electron acceptors and sharp dynamics of organic matter that has this environment. In this soil availability of phosphorus decreased with time. Both soil and suspensatos studied showed similar mineralogical composition with quartz, illite, smectite, kaolinite and the soil of the river also presented Guamá goehite. In suspensatos studied presented high fertility, higher than the own soil, indicating the possibility of maintaining soil fertility, periodic deposits that occur after each tide. Associated with the presence of high organic matter and the presence of 2:1 clay minerals in the soil, these factors appear as differential condition of these soils, especially among the soil commonly found on land. In the third experiment on the comparison between the analysis done in dry soil and in moist soil analysis done, the comparison between the analysis done in dry soil and in moist soil analysis done, the results indicate that the response to the changes that com after the flood, is perceived by both methods tested, and that the methods respond differently for each environment tested. Thus, the statistical evaluation shows the elements calcium, in Haplic Gleysol, and phosphorus, potassium, manganese and

zinc in the Salic Gleysol as indifferent choosing the method to be used in its determination. In following, the elements phosphorus, manganese and copper in the Haplic Gleysol, and calcium in Salic Gleysol are elements that showed a statistical advantage for the analysis in dry soil. The elements potassium, iron, and zinc in the Haplic Gleysol, and copper in Salic Gleysol, results were favorable to determine the soil moist. However, although both methods can be used, wet soil analysis is recommended for monitoring the changes the changes that are seen in detail, especially for the results of lower levels, common in early period of flooding. The three studies in soils of the Amazon estuary show that the geochemical changes that occur in these soils after its pores filled with water do not proceed in the same way, although soils of the same class have pedological and geographic proximity. Regional factors influence the results and mineralogical characteristics, the flood water, biology and other site factors. Although the release of nutrients occurs in a specific way to the soils studied, the changes were beneficial, providing suitable conditions for plant development. The suspensato, who performed in both stud sites, with high fertility, thus enable the maintenance of high fertility rates found in these soils after tidal action, when it is deposited in the soil. The presence of 2:1 clay minerals, represented a difference for these soils, and contributes to the formation of high levels of CTC, which still gets increased due to the levels high organic matter, in particular Salic Gleysol. Conditions are distinct from soils in this region that do not rely on factors that provide high CEC, as well as factors that provide the maintenance of fertility by adding fertile material periodically.

Keywords: Amazon - Wetland. Amazon estuary. Soil nutrients. Surface geochemistry. Waterlogged soils.

LISTA DE ILUSTRAÇÕES

2. REVISÃO BIBLIOGRÁFICA

Figura 1- As várzeas no ambiente do estuário amazônico: várzeas flúvio-marinhas da planície litorânea amapaense (verde), várzeas flúvio-marinhas do estuário do rio Amazonas (vermelho), várzeas flúvio-marinhas do rio Pará (azul) e várzeas flúvio-marinhas do nordeste paraense e pré-amazônia maranhense (laranja).5

4. WATER AS A RELEASING AND FERTILIZING FOR THE VÁRZEA SWAMP SOILS OF THE GUAMÁ RIVER IN THE AMAZON ESTUARY COMPLEX

Figure 1- Location of the study area in the *várzea* of the Guamá River, in the rural zone of the municipality of Belém, showing the collection points for the soil sample, EXP-01 (1°27'32.50"S, 48°25'33.89"W) and the sample of suspended material, SUSP-01 (1°27'42.02"S, 48°25'32.35"W).....21

Figure 2- Minerals identified by the XRD powder method for the consolidated sample EXP-01. Quartz (Qtz), kaolinite (Kln), smectite (S), illite (Ill), goethite (Gth), and anatase (An)...24

Figure 3- Minerals identified by the XRD powder method and blades angled for the clay fraction for the suspended material (sample SUSP-01). Quartz (Qtz), kaolinite (Kln), smectite (S), illite (Ill), goethite (Gth), and anatase (An)24

Figure 4- Variation in mean pH (A) and Eh (B) values during the 132 days of inundation26

Figure 5- Variation in mean organic carbon concentrations during the 132 days of inundation28

Figure 6- Variation in the mean concentrations of available iron (A) and manganese (B) during the 132 days of inundation29

Figure 7- Variation in the mean concentrations of available phosphorus during the 132 days of inundation.....29

Figure 8- Diagrams of linear dispersion for the correlations between P and Ca, P and Mn, and P and Fe31

Figure 9- Variation in the mean concentrations of available calcium (A) and potassium (B) during the 132-day flood period33

Figure 10- Variations in the mean concentrations of available zinc and copper during the 132 days of inundation.33

5. GEOCHEMICAL INTERACTIONS BETWEEN THE WATER AND SOIL OF THE MANGROVE FOREST AS A PROCESS OF FERTILIZATION IN BRAGANÇA, NORTHERN BRAZIL

FIGURE 1- Location of the study area in the rural zone of the municipality of Bragança on the northeastern coast of the Brazilian state of Pará, and the locations at which soil (0°50'38.38" S, 46°38'51.67" W) and water samples (0°50'43.33" S, 46°38'53.12" W) were collected. ...45

FIGURE 2- Patterns of X-ray diffraction obtained for the soil samples and the respective oriented fractions of the clay minerals, with the principal mineral phases being identified as: smectite (S), illite (Ill), kaolinite (Kln), quartz (Qtz), and anatase (A).	48
FIGURE 3- Patterns of X-ray diffraction obtained for the sample of suspended material and the respective oriented fractions of clay minerals, with the principal mineral phases being identified as: smectite (S), illite (Ill), kaolinite (Kln), quartz (Qtz), and anatase (A).	49
FIGURE 4- Variation in the mean pH (A) and Eh (B) values recorded during the 132 days of immersion	52
FIGURE 5- Variation in the mean concentrations of dissolved organic carbon over the 132 days of immersion	53
FIGURE 6- Variation in the mean concentrations of iron and available phosphorus over the 132 days of immersion	53
FIGURE 7- Variation in the mean concentrations of exchangeable manganese and zinc made available during the 132 days of immersion.....	56
FIGURE 8- Variation in the mean concentrations of calcium (A) and exchangeable potassium (B) released during the 132 days of immersion.....	58

6. COMPARISON OF METHODS FOR THE EVALUATION OF THE FERTILITY OF GLEYSOLS IN NORTHERN BRAZIL

FIGURE 1- Location of the study sites in the várzea of the Guamá River (1°27'32.50" S, 48°25'33.89" W), where the samples of haplic gleysol were obtained, and the mangrove of the Caeté Estuary (0°50'38.38" S, 46°38'51.67" W), where the samples of salic gleysol were collected.....	73
FIGURE 2- Variations in the concentration of phosphorus over time, according to the results of the two analytical procedures (humid and pre-dried soil).....	76
FIGURE 3- Variations in the concentration of iron over time, according to the results of the two analytical procedures (humid and pre-dried soil).....	77
FIGURE 4- Variations in the concentration of manganese over time, according to the results of the two analytical procedures (humid and pre-dried soil).....	79
FIGURE 5- Variations in the concentration of calcium over time, according to the results of the two analytical procedures (humid and pre-dried soil)	79
FIGURE 6- Variations in the concentration of potassium over time, according to the results of the two analytical procedures (humid and pre-dried soil)	80
FIGURE 7- Variations in the concentration of zinc over time, according to the results of the two analytical procedures (humid and pre-dried soil).....	81
FIGURE 8- Variations in the concentration of copper over time, according to the results of the two analytical procedures (humid and pre-dried soil).....	82

LISTA DE TABELAS

4. WATER AS A RELEASING AND FERTILIZING FOR THE VÁRZEA SWAMP SOILS OF THE GUAMÁ RIVER IN THE AMAZON ESTUARY COMPLEX

TABLE 1- The pH values and concentrations of the elements and compounds relevant to soil fertility found in the soil samples and suspended material from the Guamá River.....	25
TABLE 2- Analysis of Variance of the effect of inundation of the soil on time (days), during laboratory experiment with distilled water	26
TABLE 3- Mean values recorded per day during the inundation experiment (inundation of gleysol from soil horizon A ₁ with distilled water) for pH, Eh and the concentrations of available P, Ca, K, Zn, Cu, and Fe (132 days) and organic carbon (276 days).....	27
TABLE 4- Pearson correlation coefficient (n = 40) for P, Ca, Mn, and Fe in the inundated ..	32

5. GEOCHEMICAL INTERACTIONS BETWEEN THE WATER AND SOIL OF THE MANGROVE FOREST AS A PROCESS OF FERTILIZATION IN BRAGANÇA, NORTHERN BRAZIL

TABLE 1- Parameters of fertility recorded during the present study, including the concentrations of available and exchangeable elements in the samples of soil and suspended material from the Caeté River	50
TABLE 2- Analysis of variance for the effects of immersion of the soil in the laboratory with distilled water over time (days)	51
TABLE 3- Mean values obtained from the four experimental mangrove soil samples for pH and Eh, and the chemical concentrations of available P, Ca, K, Zn, Cu, and Fe, during immersion with distilled water over a 132-day period, and for organic carbon over 276 days of immersion.....	51
TABLE 4- Pearson's linear correlation coefficients for the concentrations of P, Ca, Mn, and Fe recorded in the gleisol immersed during the present experiment (n = 40).....	55

6. COMPARISON OF METHODS FOR THE EVALUATION OF THE FERTILITY OF GLEYSOLS IN NORTHERN BRAZIL

TABLE 1- The pH, concentrations of elements and available compounds, and granulometry of the samples EXP-GH and EXP-GS, for the analysis of the fertility of the respective soils (adapted from Silva & Costa, 2011, and Silva & Costa, 2012).....	71
TABLE 2- Variation in the mean concentrations of available P, Ca, K, Zn, Cu, and Fe in the samples of haplic gleysol (horizon A ₁) over the 52 days of immersion under distilled water .	74
TABLE 3- Variation in the mean concentrations of available P, Ca, K, Zn, Cu, and Fe in the samples of salic gleysol (horizon A ₁) over the 52 days of immersion under distilled water ...	74
TABLE 4- Results of the ANOVA for the effects of immersion with distilled water on the haplic gleysol samples over time (days) and the two treatments	75
TABLE 5- Results of the ANOVA for the effects of immersion with distilled water on the salic gleysol samples over time (days) and the two treatments.....	75

SUMÁRIO

DEDICATÓRIA.....	iv
AGRADECIMENTOS	v
RESUMO	vii
ABSTRACT	xi
LISTA DE ILUSTRAÇÕES	xiv
LISTA DE TABELAS	xvi
1 INTRODUÇÃO.....	1
1.1 O AMBIENTE DA VÁRZEA	1
1.2. APRESENTAÇÃO DO PROBLEMA	3
1.3 OBJETIVOS.....	4
2 REVISÃO BIBLIOGRÁFICA	5
2.1 AS VÁRZEAS NO ESTUÁRIO AMAZÔNICO.....	5
2.2. CLASSIFICAÇÃO DOS SOLOS DE VÁRZEA.....	6
2.4. A TRANSPARÊNCIA DA ÁGUA DO RIO E A VÁRZEA.....	7
2.5. RELAÇÃO ENTRE A O RIO E A FERTILIDADE DO SOLO	8
2.6. MODIFICAÇÕES DAS CARACTERÍSTICAS QUÍMICAS DOS SOLOS INUNDADOS	9
3 MATERIAIS E MÉTODOS	14
3.1. PESQUISA BIBLIOGRÁFICA	14
3.2. AMOSTRAGEM E CARACTERIZAÇÃO DA AMOSTRA.....	14
3.3. EXPERIMENTAÇÃO	15

4 WATER AS A RELEASING AND FERTILIZING FOR THE VÁRZEA SWAMP SOILS OF THE GUAMÁ RIVER IN THE AMAZON ESTUARY COMPLEX	17
ABSTRACT	17
1. INTRODUCTION	18
2. MATERIALS AND METHODS	20
3. RESULTS AND DISCUSSION.....	23
3.1. Mineralogical and granulometric characteristics and fertility	23
3.2. Availability of chemicals during prolonged inundation	26
4. CONCLUSIONS	34
5. ACKNOWLEDGMENTS	35
6. REFERENCES	35
5 GEOCHEMICAL INTERACTIONS BETWEEN THE WATER AND SOIL OF THE MANGROVE FOREST AS A PROCESS OF FERTILIZATION IN BRAGANÇA, NORTHERN BRAZIL	41
ABSTRACT	41
1. INTRODUCTION	42
2. MATERIALS AND METHODS.....	44
3. RESULTS AND DISCUSSION.....	47
3.1. Mineralogy, fertility, and granulometry	47
4. CONCLUSIONS	59
ACKNOWLEDGMENTS	60
REFERENCES	60
6 COMPARISON OF METHODS FOR THE EVALUATION OF THE FERTILITY OF GLEYSOLS IN NORTHERN BRAZIL	67
ABSTRACT	67
1. INTRODUCTION	68

2. MATERIALS AND METHODS	71
4. CONCLUSIONS	83
5. ACKNOWLEDGMENTS	84
6. REFERENCES	85
7. CONCLUSÕES E CONSIDERAÇÕES FINAIS	89
REFERÊNCIAS	92
ANEXOS	97
ANEXO A - CONFIRMAÇÃO DA SUBMISSÃO DO ARTIGO DO CAPÍTULO IV PARA APPLIED GEOCHEMISTRY	98
ANEXO B - CONFIRMAÇÃO DA SUBMISSÃO DO ARTIGO DO CAPÍTULO V PARA GEODERMA	99
ANEXO C - CONFIRMAÇÃO DA SUBMISSÃO DO ARTIGO DO CAPÍTULO VI PARA GEODERMA	100

1 INTRODUÇÃO

1.1 O AMBIENTE DA VÁRZEA

Ambientes de várzeas são ambientes hidromórficos, representados por sedimentos silticos, depositados às margens de rios e estuários durante o período sazonal de cheias ou intermarés, e, por conseguinte em íntima relação com a água fluvial, lacustre e das marés, aos quais se adapta ou participa a vegetação. Neste espaço amazônico, de grande extensão, a várzea surge com grande variabilidade, existindo de diversas formas de apresentação, podendo adquirir características próprias de acordo com a especificidade local. O dicionário geológico - geomorfológico (Guerra & Guerra, 1997) define várzea como terrenos baixos, mais ou menos planos, que se encontram junto à margem de rios. As várzeas constituem na linguagem geomorfológica o leito maior dos rios.

Em menção clássica, Sioli (1951) descreve que “nas margens do Amazonas e de seus tributários estendem-se planícies ou várzeas periodicamente recobertas pelas águas lodosas das enchentes anuais, as quais deixam sobre elas os depósitos das vazantes”. Esta expressão é naturalmente relacionada ao rio Amazonas, região em que a ação sazonal das enchentes se sobrepõe ao efeito das marés. Neste aspecto, o solo depende dos depósitos das enchentes anuais, ocorrendo, entretanto da mesma forma nos imensos estuários do estado do Pará, onde predomina o sistema de maré. A partir deste período, novos estudos foram realizados e importantes informações somaram-se para caracterizar este importante ambiente.

A Amazônia é uma das regiões da terra mais abundante em várzea. São 8.000.000 ha no estado do Amazonas, 6.000.000 ha no Pará, 380.000 ha em Roraima, 680.000 ha no Amapá e 374.000 ha no estado do Maranhão (Fageria, 1884). Os ambientes de várzea aparecem em imensa área de ocorrência, desde o estado do Acre até a foz do rio Amazonas, incluindo alguns afluentes e rios que não fazem parte da bacia do rio Amazonas, como a bacia do rio Guamá, Tocantins e outros formadores do rio Pará, assim como outras regiões com várzeas na Amazônia legal. Em razão deste fato, esta ocorrência se dá em ambientes com características regionais, que naturalmente influenciarão a fertilidade e o comportamento dos elementos nutritivos neste ambiente de superfície. Dentre as diversas características ambientais encontradas pode-se destacar a inundação de aproximadamente seis meses que submerge parte das planícies inundáveis no baixo Amazonas, o sistema de maré apresentado no ambiente dos diversos estuários existentes na costa do estado do Pará e a influência organo-salina que ocorre nos ambientes de mangue. É interessante destacar as várzeas com

argilominerais de maior capacidade de troca de cátions, como as existentes no Acre (Guyot *et al.*, 2007; Costa *et al.*, 2009).

Relatos históricos mostram que os solos de várzeas já eram utilizados em quase toda a região amazônica para a agricultura, do plantio de culturas de ciclo curto como milho e feijão (Oliveira, 1983). Inicialmente extraíam cacau, a virola (*Virola surinamensis*, Warb.), andiroba (*Carapa guianensis* Aubl.) e látex da seringueira (*Hevea brasiliensis*, Muell. Arg.), além de espécies madeireiras diversas, como macacaúba (*Platymiscium trinitatis*, Benth.) e pau-mulato (*Calycophyllum spruceanum*, Benth.) (Gama, *et al.*, 2009).

Os solos de várzea apresentam excelente produção quando comparados com aqueles sistemas de produção que empregam técnicas e insumos em solos de terra firme. Nas várzeas a produção não decai com o passar dos anos mantendo-a constante, e como consequência fixando o homem neste ambiente (Lima & Tourinho 1994). Em trabalho clássico, comparando dados de produção de arroz (EMBRAPA, 1991) em áreas de terra firme (sequeiro), com áreas de produção irrigadas e com a produção na várzea, se percebe que na várzea, apesar de ocupar área até seis vezes menor que a área ocupada para a produção na terra firme e ocupar área de produção semelhante a do arroz irrigado, proporciona colheita mais de duas vezes maior que a dos sistemas irrigados, e cerca de seis vezes maior que o sistema de produção na terra firme.

No estado de Roraima, com o direcionamento da produção do arroz para as áreas de várzea, se realizou comparação entre os sistemas de produção naturais, também chamados de várzea úmida, em relação com a produção em sistemas inundados com lâmina d'água (Cordeiro *et al.* 2010). Neste caso, as pesquisas indicaram resultados favoráveis aos cultivos realizados em áreas com água ocupando todos os poros do solo durante a etapa de produção, sem necessidade da presença de lâmina d'água, ressaltando, entretanto resultados favoráveis em ambientes reduzidos (Cordeiro *et al.*, 2010; Suhre *et al.*, 2008).

No entanto, apesar de dispor os rios como “estradas” para escoamento da produção, e a despeito de sua enorme ocorrência na Amazônia, as várzeas são pouco empregadas para a produção de alimentos em larga escala. Diversos fatores apontam para isto, como a distância da Amazônia de grandes centros consumidores, a falta de infraestrutura em portos, a falta de industrialização e beneficiamento para os alimentos e a ausência da inserção dos alimentos Amazônicos no mercado nacional e mundial. Outro aspecto importante para permitir o desenvolvimento racional desta atividade está relacionado com o desenvolvimento de pesquisa que permita entender os mecanismos geoquímicos existentes nestes solos a fim de permitir o manejo dos mesmos.

1.2. APRESENTAÇÃO DO PROBLEMA

Parte da pesquisa acerca da geoquímica de superfície destes solos nesta região foi realizada no rio Guamá, estuário do rio Pará, em trabalhos exploratórios e pioneiros, em parte devido à proximidade de centros de pesquisa e universidades (Silva, 1995; Silva *et al.*, 1996; Ferreira *et al.*, 1998; Ferreira *et al.*, 1999; Mattar *et al.*, 2002; Silva, 2010). Embora sejam contribuições relevantes, estas pesquisas não corresponderam aos seguintes questionamentos:

- 1) Não havia resposta sobre as alterações e disponibilidade dos elementos nutritivos avaliadas em período prolongado, no qual as transformações processadas apresentassem estabilidade em suas disponibilidades. O período de quatro meses, correspondente ao desenvolvimento de culturas de ciclo curto e ao início do desenvolvimento de plântulas de alguns vegetais de ciclo longo, seria período em que estes fatos poderiam ser avaliados. No entanto os trabalhos realizados corresponderam há trinta dias ou no máximo 60 dias de observações. Dessa forma não se construía uma avaliação clara da condição de fertilidade que o ambiente adquire após tornar-se anaeróbico;
- 2) Alguns estudos apontavam comportamento anômalo de certos elementos nutritivos, como no caso do zinco e do enxofre, que em virtude de tempo curto de observação, não se podia afirmar que permaneceriam na tendência apresentada. Dessa forma, existia a necessidade de confirmar estes resultados através da observação prolongada que comprovaria o real comportamento destes elementos;
- 3) Como existe a possibilidade de locais com características distintas das encontradas na várzea do rio Guamá produzir resultados diferentes, seria de bom alvitre conhecer a dinâmica geoquímica em solo com estas condições diferenciadas. De fato, a realização de pesquisas, concentradas em sua maioria, em um só ambiente, não permitiu transportar estes resultados, para outros ambientes existentes no estuário amazônico, dentre eles o ambiente de manguezal.
- 4) Todos os estudos acerca da das transformações geoquímicas relacionadas à fertilidade do solo do rio Guamá, não consideraram o avaliação da mineralogia dos solos estudados, excluindo assim parâmetro importante para a explicação de alguns fenômenos que ocorrem nestes solos;
- 5) A obtenção de informações acerca do conteúdo total dos elementos do solo também não era realizada. Pelo mesmo aspecto, a investigação no suspensato da água dos rios acerca de sua fertilidade e mineralogia também não foi considerada anteriormente;

6) A metodologia de avaliar a fertilidade do solo inclui a análise química do solo, que de acordo com a metodologia empregada nacional e internacionalmente emprega a análise do solo previamente seco durante o preparo da amostra. Dessa forma as transformações que o solo sofre quando reduzido, são revertidas à condição oxidada, as quais passarão a constar nas informações do resultado das análises. Alguns pesquisadores empregam análise da solução do solo, resultado que não pode ser empregado rotineiramente, de interpretação diferenciada e sujeito a variações em virtude de diluições com a reposição de água no solo. Em busca de metodologia para utilizá-la de forma rotineira e em atividades de pesquisa, as investigações no rio Guamá empregaram com sucesso a análise do solo úmido. No entanto, não foi realizada comparações dos resultados para comprovar sua utilidade prática.

1.3 OBJETIVOS

O objetivo central desta tese foi de investigar experimentalmente as transformações geoquímicas que ocorrem na superfície de solos de várzea em condição redutora, e como elas podem afetar a fertilidade desses solos.

Por conseguinte os objetivos específicos foram os seguintes:

- Monitorar as transformações geoquímicas em função do tempo no período de quatro meses. Obter demonstrativos das variações apresentadas para cada parâmetro estudado;
- Acompanhar as transformações em dois ambientes de várzea com características distintas relativas ao ambiente. Dessa forma se pode associar contribuição que o ambiente ofereceu para produzir alterações específicas que ocorreram durante os processos de redução do solo;
- Caracterizar os ambientes (solo e suspensato) quanto aos aspectos químicos, físicos e mineralógicos estudados, para subsidiar a interpretação dos fenômenos que ocorreram nos ambientes testados.
- Confrontar a metodologia de análise do solo úmido à análise química realizada de modo tradicional na amostra seca.

2 REVISÃO BIBLIOGRÁFICA

2.1 AS VÁRZEAS NO ESTUÁRIO AMAZÔNICO

O estuário amazônico apresenta expressivas variações microclimáticas, topográficas, de coberturas vegetais e hídricas, e outras que refletem na formação de diferentes ambientes de várzea. Tendo em vista estes aspectos, Lima *et al.* (2001) realizaram subdivisão das várzeas nesta região, partindo do estado do Amapá, como: **a)** várzeas flúvio-marinhas da planície litorânea Amapaense, **b)** várzeas flúvio-marinhas do estuário do rio Amazonas, **c)** Várzeas flúvio-marinhas do estuário do rio Pará, e, **d)** várzeas flúvio-marinhas do nordeste paraense e pré-amazônia maranhense (Figura 1).

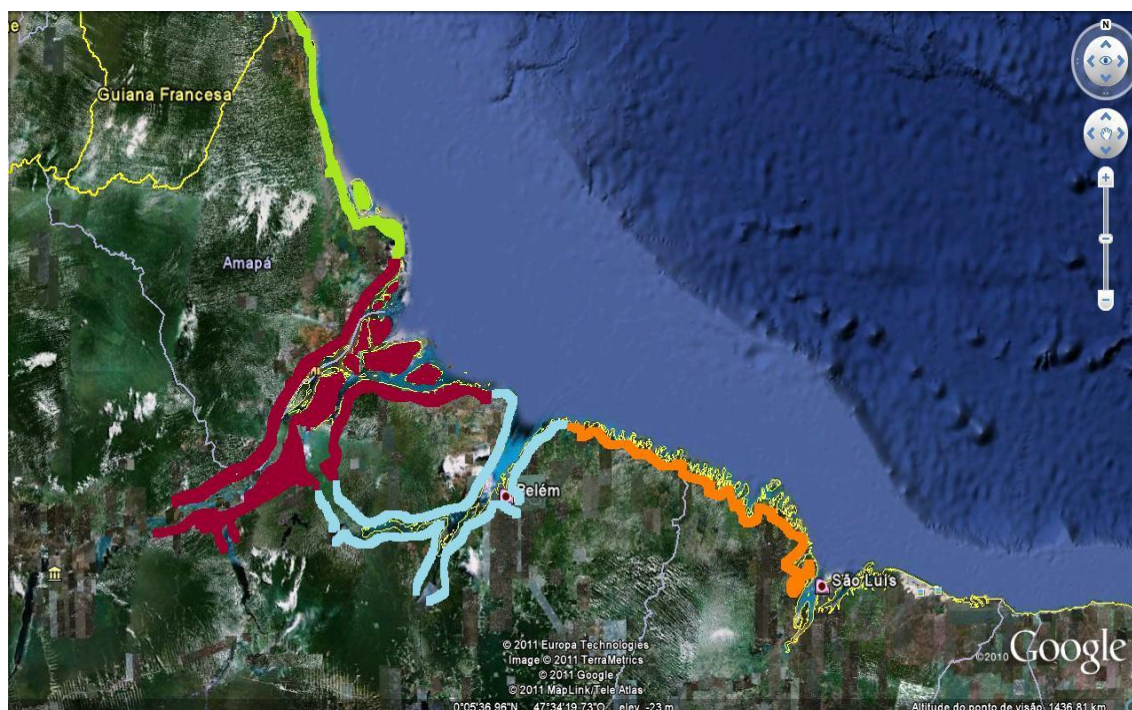


Figura 1. As várzeas no ambiente do estuário amazônico: várzeas flúvio-marinhas da planície litorânea amapaense (verde), várzeas flúvio-marinhas do estuário do rio Amazonas (vermelho), várzeas flúvio-marinhas do rio Pará (azul) e várzeas flúvio-marinhas do nordeste paraense e pré-amazônia maranhense (laranja).

Fonte: A figura foi estabelecida sobre imagem disponibilizada pelo Google 2010.

As várzeas flúvio-marinhas da planície litorânea Amapaense ocorrem desde a foz do rio Araguari até foz do rio Oiapoque. A imensa planície inundada, que ocorre desde a orla marítima até o início da terra firme apresenta dezenas de quilômetros no sentido leste oeste. Possui como característica a ausência de contato com a água do mar, que permanece afastada

por faixa de água barrenta proveniente do rio Amazonas, que é desviada para o norte, ao longo da costa amapaense por ação da corrente marítima Equatorial Norte. Nesta planície costeira desembocam nesta costa os rios Uaçá, Cassiporé, Aporema, Macarri e Flexal. (Lima *et al.*, 2001).

As várzeas flúvio-marinhas do estuário do rio Amazonas estão situadas a jusante da confluência do rio Amazonas com o rio Xingu (Tourinho *et al.*, 2009), de onde se percebe ação das marés. De acordo com Golding *et al.* (2003), efeitos da maré podem existir da foz do rio até Santarém com oscilação de 20 cm de maré, porém tornando-se significativa para a formação das várzeas de marés, a partir da foz do rio Xingu com a oscilação de 1 metro, até alcançar 4 metros no lado oeste da ilha do Marajó.

As várzeas flúvio-marinhas do estuário do rio Pará ocorrem na região correspondente ao rio Pará. Esta denominação é empregada para o estuário formado pelo deságüe de diversos rios, que fluem para a parte oriental da ilha do Marajó (Lima, 1979). Esta região extensa e rica em várzeas possui área extensa, que compreende além da área de seus rios formadores, a costa sul da ilha do Marajó, as baías das Bocas, de Curralinho, de Goiabal, do Guajará e a extensa baía do Marajó, até desaguar no oceano Atlântico. Os rios Guamá, Tocantins, Capim, Acará, Mojú, Anapu, Jacundá, Pacajás e Araticu são exemplos de rios entre mais de 40 outros, que contribuem na formação do estuário do rio Pará.

As várzeas flúvio-marinhas do nordeste paraense e pré-amazônia Maranhense são aquelas formadas pelos rios que deságuam diretamente no oceano Atlântico, na região compreendida entre a foz do rio Pará até a baía de São Marcos, abrangendo cerca de 450 km ao longo da costa. Os rios Piriá, Urumajó, Caeté, Maracanã, Marapanim, Gurupi, Maracaçumé, Uru e Mearim são exemplos de rios que formam estuários e as várzeas flúvio-marinhas no nordeste paraense e pré-amazônia maranhense. Grande parte destes rios apresenta regiões com mangue na proximidade de sua foz e várzeas de água doce a montante dos rios (Lima & Tourinho, 1995).

2.2 CLASSIFICAÇÃO DOS SOLOS DE VÁRZEA

Os solos de várzeas do Estuário Amazônico se enquadram em Gleissolos, mais abundantes, e em Neossolos Flúvicos (Vieira, 1988). Os Gleissolos segundo a última aproximação do Sistema Brasileiro de Classificação de Solos (EMBRAPA, 1999) são subdivididos em Gleissolo Háplico, com a maior ocorrência no estuário amazônico, o

Gleissolo Sáfico (Vieira 1988), com menor expressão, e o Gleissolo Melânico e o Gleissolo Tiomórfico muito restritos.

Os Neossolos Flúvicos representam na classificação atual (EMBRAPA, 1999) a antiga categoria dos solos aluviais. São solos derivados de sedimentos aluviais, recente, com horizonte A em contato direto com o horizonte C, preservando camadas estratificadas dos sedimentos. São raros na região do estuário amazônico.

2.3 VÁRZEAS QUANTO SUA POSIÇÃO TOPOGRÁFICA

As várzeas recebem denominações regionais de acordo com sua posição na topografia do terreno. Os termos várzea alta e várzea baixa são empregados nos ambientes do estuário do rio Amazonas, enquanto os termos restinga e teso são empregados no médio e baixo Amazonas (Lima & Tourinho, 1994). As várzeas altas e restingas representam as denominações para os terrenos em cota elevada com cerca de quatro metros. Sofrem inundação nos estuários apenas por ocasião dos equinócios. Correspondem ao dique marginal da planície de inundação.

As várzeas baixas também denominadas de tesos em algumas regiões, representam os terrenos de várzea com cota baixa cerca de 30 ou mais baixo da cota da várzea alta. Na região do estuário amazônico, sob o efeito da maré, a várzea baixa apresenta-se sempre umedecida e é freqüentemente invadida pela água durante a lua cheia e nova. A largura das várzeas baixas pode atingir alguns quilômetros e apresentam maior área de ocorrência que a das várzeas altas.

2.4 A TRANSPARÊNCIA DA ÁGUA DO RIO E A VÁRZEA

Sioli (1951) com base na cor e transparência das águas dos rios da Amazônia os classificou em três tipos em três tipos:

a) Rios de água branca ou barrenta: como próprio nome diz são rios de águas turvas com transparência entre 10 a 60 cm. Os rios Amazonas, Madeira e Branco, na bacia do rio Amazonas e os rios Guamá e Caeté no nordeste paraense se enquadram nesta categoria. Estes rios movimentam lateral e rapidamente os seus cursos, são sinuosos, na planície erodindo suas margens, carreando muito material siltico em suspensão e simultaneamente os depositando ao longo de suas margens construtivas modificando constantemente seu leito. As várzeas assim formadas nestes rios apresentam média e alta fertilidade.

b) Rios de água clara: são aqueles em que a água varia de cor amarelada para o verde escuro, com transparência entre 60 cm e 4 metros. Os rios Tapajós e Xingu são apontados como exemplo deste tipo de rio. Normalmente seu leito fluvial é estável, pouco sinuoso, e com pouco material em suspensão. Suas várzeas são de fertilidade média a baixa.

c) Rios de água preta: A cor de suas águas varia de cores escuras, muito próxima do preto, até o verde escuro com transparência entre 1 a 2 metros em consequência de sua mínima carga em suspensão. Os rios, Negro e Cururu, no estado do Amazonas, assim como o rio Capim na bacia do rio Guamá, são exemplos desta categoria. Os vales desses rios interceptam áreas florestadas, em geral desenvolvidas sobre solo de baixa fertilidade; elas temporariamente são inundadas, dessa forma suas águas são enriquecidas com material orgânico morto, proveniente da própria dinâmica de vida da floresta. Esse material humificado se dissolve na água dotando-as de alta acidez.

Golding *et al.* (2003) no entanto ressalvam o emprego do termo água branca, ou “água blanca” como comumente é empregado na Bolívia e Peru. Na língua inglesa a expressão “whitewater” é empregada em águas mais claras que o termo sugere. Para evitar confusão de termos os autores sugerem o emprego de “muddy water” para indicar águas barrentas como as encontradas no rio Amazonas e seus afluentes, como os rios Madeira, Purus e Juruá.

2.5 RELAÇÃO ENTRE A O RIO E A FERTILIDADE DO SOLO

Para Konhauser *et al.* (1993) os rios da Amazônia são física e quimicamente heterogêneos com reflexos na composição dos solos das várzeas. Por exemplo, as águas do rio Solimões, com expressiva carga inorgânica em suspensão (suspensato), oriunda da erosão dos sedimentos e rochas sedimentares em suas margens, cuja procedência pode ter sido em parte as rochas da cadeia Andina, redepositam parcialmente este material ao longo de suas margens, que se apresentam naturalmente férteis. Em contraste, as águas do rio Negro, deficientes em suspensato inorgânico, refletem os materiais geológicos de sua bacia de drenagem, representados por rochas cristalinas, lateritos e podzólicos, que formam várzeas restritas e de baixa fertilidade. Estes autores concluem que é possível classificar a composição química dos rios da Amazônia com base nos solos de suas bacias de drenagens e vice-versa (Konhauser *et al.*, 1993).

Neste sentido, Guyot *et al.* (2007) citam a avaliação dos argilominerais dos solos, como mecanismo mais importante para avaliar a maturidade dos sedimentos em suspensão, a intensidade do intemperismo e sua procedência geográfica. Ao investigar o rio Amazonas os

autores destacam a abundância de illita+clorita em nos rios Madeira e Solimões, enquanto a esmectita é acrescida na várzea à medida que se avança no rio, na direção do oceano. Concluem os autores que os argilominerais no rio Amazonas provém de três diferentes fontes: as montanhas andinas; os escudos amazônicos e da base de vales. Os autores ressaltaram, entretanto a importância da erosão da base de bancos laterais de rios, para a introdução de argilominerais no rio enriquecidos de esmectita. A presença de esmectita contribui positivamente com a fertilidade do solo.

Martinelli *et al.* (1993) investigou a presença de elementos químicos, dentre esse, os micronutrientes ao longo das várzeas do rio Amazonas. Nestas a concentração química dos elementos mais abundantes decresce na seguinte ordem: Si>Al>Fe>Na>Ca>K>Mg>Ti. A concentração de Al, Na e Mg decrescem a jusante e enquanto as Si aumentam as concentrações de Fe, K e Ti permanecem constante. Este quadro químico reflete a composição mineralógica representada pelo o decréscimo da concentração dos plagioclásios à jusante, e aumento de quartzo, esmectita-caulinita e caulinita, enquanto a concentração de illita permanecia constante. O balanço de massa indica que a esmectita-vermiculita e o plagioclásio são decompostos nas várzeas enquanto forma a caulinita (Martinelli *et al.* 1993). Estes elementos encontrados, presentes na várzea, favorecem a nutrição vegetal, assim como sua retenção pelos minerais presentes.

A composição mineralógica apresenta importância relacionada à fertilidade do solo quando ocorrem minerais que possibilitem retenção de elementos nutritivos que podem ser disponibilizados aos vegetais. Dentre esses, Vilhena *et al.* (2010) relatam no ambiente de mangue no rio Caeté, a presença de minerais autigênicos com importante reflexo na fertilidade do solo, tendo como exemplo as esmectitas. Na mesma região, Berredo *et al.* (2008), citam esmectita, feldspato, pirita, halita e jarosita como minerais autigênicos existentes nos sedimentos de manguezais de Marapanim.

2.6 MODIFICAÇÕES DAS CARACTERÍSTICAS QUÍMICAS DOS SOLOS INUNDADOS

Quando um solo sofre inundação, seja por processo natural, ou induzido pelo homem, uma série de transformações se desenvolve no seu interior. A água ocupa gradualmente os poros expulsando o ar que preenchia os mesmos e deflagra uma série de reações químicas, que são auxiliadas por microorganismos que passam a dominar este ambiente (Boyd, 2002).

Poucas horas depois da inundação, os microorganismos aeróbios através da respiração, consomem o ar dissolvido na água, de forma que após este consumo o ambiente passa a ser

ocupado por microorganismos aeróbios facultativos e pelos estritamente anaeróbicos, que se multiplicam muito rapidamente, e decompõe a matéria orgânica utilizando compostos oxidados do solo como captadores de elétrons, reduzindo-os quimicamente, originando um ambiente de condições redutoras (Assis *et al.*, 2000). Mas nem toda a matéria orgânica se oxida, e desta forma pode se acumular no próprio solo-sedimento. Sahrauat (2003) afirma que um solo que contenha matéria orgânica em excesso, e contenha poucos aceptores de elétrons, acumula matéria orgânica, explicando assim o mecanismo de acúmulo que pode acontecer em região de mangue, extensível às várzeas.

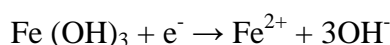
É também possível a formação de uma zona com domínio de ambiência oxidante na superfície devido a difusão do oxigênio ser maior que seu consumo pelos microorganismos. No entanto a concentração do oxigênio não é constante, podendo variar da saturação na superfície, à zero no limite entre zona oxidante e a redutora. Naturalmente a espessura desta zona será resultante do balanço entre a difusão do oxigênio e de seu consumo. A concentração média de oxigênio desta zona, a 25°C, é de oito ppm (Ponnamperuma, 1972).

As plantas, visando se desenvolver em ambiente de solo inundado ou saturado com água, desenvolvem mecanismos capazes de permitir respiração de suas raízes, eliminando produtos tóxicos, acumular nutrientes e promover o crescimento do vegetal. O arroz, por exemplo, possui canais especiais denominados aerênquimas, através dos quais transporta oxigênio de suas folhas para as raízes (Silva *et al.*, 2003).

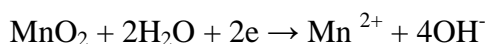
Na zona redutora, substâncias formadas por componentes químicos oxidados, como os nitratos, sulfatos, oxi-hidróxidos de manganês, (3+, 4+) e de ferro (Fe^{3+}) e vários produtos orgânicos são reduzidos durante a oxidação da matéria orgânica (Pires *et al.*, 2002). Os nitratos são reduzidos a nitritos, os sulfatos são reduzidos a sulfetos, o dióxido de carbono é reduzido a CH_4 e o H^+ para H_2 , o ferro e o manganês dos oxi-hidróxidos a Fe^{2+} e Mn^{2+} , que em solução, mais tarde podem dar origem a sulfetos de ferro e manganês. O consumo de nitrato e sulfato por redução favorece a solubilização de ferro e manganês reduzidos (Fageria, 1984).

Os cálculos termodinâmicos permitem determinar a ordem de redução de destes componentes. O primeiro a reduzir-se é o oxigênio, precisando de apenas um dia apenas um dia de inundação. Em seguida se dá a redução do nitrato, do manganês dos oxi-hidróxidos e finalmente do Fe^{3+} para Fe^{2+} . Durante o período de estiagem o oxigênio volta a ocupar os poros do solo revertendo as reações de oxi-redução, oxidando os íons, ânions e as substâncias anteriormente reduzidas (Ponnamperuma, 1972).

Nestas condições de reações de oxi-redução, os valores de pH se modificam, que interferem também na estabilidade dos compostos minerais e da matéria orgânica mencionados, atingindo principalmente os carbonatos, sulfetos, fosfatos e silicatos. Ele regula a precipitação, adsorção e dessorção de íons, como Al^{3+} , Fe^{2+} , H_2S , H_2CO_3 , e ácidos orgânicos não dissociados (Boyd & Tucker, 1998). Os solos ácidos experimentam aumento do pH para próximo de 7,0 em decorrência da liberação de hidroxilas proveniente da quebra da estrutura de minerais como $\text{Fe}(\text{OH})_3$ a $\text{Fe}(\text{OOH})$ durante a redução do ferro, conforme representado a seguir:



A redução do manganês também contribui de forma significativa da forma a seguir:



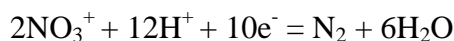
Em termos de valores, os processos de oxi-redução, assim descritos como Eh, estão na ordem de 200 mV a -400 mV com condição reduzida (submersos ou inundados) e de 300 mV a 800 mV em condições oxidadas.

O efeito do pH é benéfico desde que se situe nos valores próximos da neutralidade. Sanches (1976) denomina este fenômeno de auto-calagem, pois os valores alcançados pelo pH permitem disponibilização da maioria dos nutrientes, além da completa insolubilização do Al^{3+} que se precipita ao pH 5,5.

O nitrogênio orgânico, nos solos inundados produz amônia durante sua mineralização. Esta ocorre em sua quase totalidade em apenas duas semanas de inundação, se a temperatura for favorável, de forma a permitir o desenvolvimento da atividade microbiana e o solo se apresentar ligeiramente ácido ou desprovido em fósforo disponível (Ponnamperuma, 1972).

De acordo com Fageria (1984) a nitrificação e a desnitrificação são os mais importantes processos que ocorrem com o nitrogênio no solo inundado. Durante a nitrificação as bactérias oxidam o íon nitrogênio da amônia para N^{2-} , formando o ácido nitroso, que por sua vez é oxidado a N^{5+} , que dá origem ao nitrato. A desnitrificação, que dá nos solos alagados, é exatamente a reação inversa, de nitrato, passando por nitroso até a formação de N_2 , uma típica reação de oxi-redução. Quando o nitrato substitui o oxigênio como captor de elétrons durante o processo da respiração anaeróbica dos microorganismos, o nitrogênio N^{5+} é reduzido a N^{4+} , mais conhecido como nitrito (NO_2^-), em seguida a N^{2-} , nitroso (N_2O) e então a

Nº finalizando um processo que resulta em perda do nitrogênio para o solo (Fageria & Stone 2003). A reação completa de oxi-redução pode ser assim representada:



Durante a desnitrificação os microorganismos decompõem a matéria orgânica consumindo prótons e empregam os elétrons para a redução do nitrato, além de utilizar também o carbono e a amônia para o desenvolvimento de suas células. Portanto, a desnitrificação será restrita ou não ocorrerá quando os solos forem pobres em matéria orgânica.

Naturalmente, em razão das transformações que ocorrem com o nitrogênio, alguns solos inundados respondem ao emprego de adubação nitrogenada. Ponte *et al.* (1981) ao compararem efeito da adubação nitrogenada na várzea do rio Guamá, testando o emprego de diversos adubos nitrogenados, obtiveram excelente resposta para o emprego do Sulfato de Amônio como o adubo mais eficiente. Por outro lado, Aulakh *et al.* (2002) ressaltam que este tipo de resposta deve-se além do fenômeno da desnitrificação, mas, sobretudo ao efeito do enxofre contido naquele adubo, em virtude da possibilidade deste elemento poder se tornar fator limitante para determinadas culturas em solos alagados.

Em solos inundados também se observa a redução do S^{6+} , do SO_4^{2-} para S^{4-} , o sulfito (SO_3^{2-}) e então para sulfeto (S^{2-}) com formação de H_2S , com paralela diferenciação dos aminoácidos cisteína, cistina e metionina em thiols, amônia e ácidos graxos. Nestas condições esses solos se tornam cada vez mais ácidos, e a medida que a redução progride, os teores de SO_4^{2-} obviamente diminuem e aumentam os de H_2S , que dissociado leva a formação de FeS_2 , a pirita, pois essas reações de oxi-redução atingem sucessivamente, como já demonstrado anteriormente os oxi-hidróxidos de ferro, formando, formando Fe^{2+} . Se por outro lado, os solos são pobres em ferro, ocorre a formação de H_2S . Se a concentração de H_2S ultrapassar 10^{-6} M estabelece-se condição tóxica e limitante para o desenvolvimento da maioria dos vegetais (Wang *et al.*, 1976).

O fósforo é sabidamente elemento fundamental desenvolvimento vegetal, e ao lado do nitrogênio e o potássio são macronutrientes primários aos vegetais. Nos solos o fósforo ocorre sob duas formas: uma orgânica de liberação lenta e outra inorgânica, na forma de fosfatos de cálcio, ferro e/ou alumínio, de diferentes solubilidades. Durante a inundação do solo esses fosfatos em geral liberam o fósforo, aumentando a concentração de fósforo solúvel. Isto se dá pela hidrólise dos fosfatos de Fe e Al quando sob condições ácidas; contribui com o aumento

de fósforo, ao aumento da mineralização do fósforo orgânico ocasionada pela elevação do pH a valores entre 6 e 7; a solubilização da apatita, se presente, seja orgânica ou inorgânica e a difusão de H_2PO_4^- , proveniente destas reações. Durante a redução do ferro e consequente solubilização dos óxidos de ferro nos solos inundados, como demonstrado anteriormente, ocorre também a liberação do fósforo, que desta forma se torna disponível ao solo (Silva *et al.*, 2005; Vahl, 1999).

Pelo exposto anteriormente, a inundação de solos, com a liberação de íons como Fe, a condutibilidade elétrica, naturalmente aumenta, devido à produção de Fe^{2+} , Mn^{2+} , NH_4^+ e outros íons, que, no entanto sofre queda pela precipitação do ferro como FeS.

Durante a inundação de solos, elementos como Ca, Mg, K e Na e seus respectivos que constituem a composição de sua CTC, as bases trocáveis, não são afetadas diretamente por esta. Seu incremento na solução do solo é devido simplesmente ao deslocamento nas partículas do solo devido ao efeito de massa ocasionado pela quantidade de Fe^{2+} , NH_4^+ e Mn^{2+} produzidos.

Por outro lado as concentrações disponíveis dos micronutrientes como cobalto, cobre, molibdênio e podem ser alteradas após a inundação do solo, em decorrência das alterações sofridas no pH do meio, da redução do ferro e do manganês, que constituem os seus oxihidróxidos, que decompostos, os liberam e se fixam nos sítios de troca e produção de compostos orgânicos quelatantes (Fageria 1984). Em certos casos, por exemplo, o zinco se torna indisponível após a inundação, em virtude de ocorrer a cada aumento de unidade no pH, diminuição na solubilidade do zinco em 100 vezes (Ponnamperuma, 1966; Sanches, 1976). Discordando do exposto Silva *et al.* (1996) verificaram que os teores de zinco na várzea do rio Guamá, aumentaram de $10,27 \text{ mg/dm}^3$ no primeiro dia a $15,02 \text{ mg/dm}^3$ no 19º dia, tendo, ao mesmo tempo, ocorrido aumento no pH de 4,5 no primeiro dia, à 6,4 no 7º dia de inundação, dessa forma, contrariando a informação acerca da insolubilidade do zinco neste caso.

O cobre também diminui sua disponibilidade em solos inundados, devido ao aumento do pH, causando sua indisponibilidade. Silva *et al.* (1996), em curto período de amostragens, encontraram valores de cobre que decresceram no rio Guamá de $4,93 \text{ mg/dm}^3$ ao primeiro dia de inundação para estabilizarem entre $1,96$ e $2,87 \text{ mg/dm}^3$ ao 27º dia de inundação.

3 MATERIAIS E MÉTODOS

Para alcançar os objetivos propostos foram empregados vários métodos e técnicas de investigação entre as quais se destacam:

3.1 PESQUISA BIBLIOGRÁFICA

As pesquisas enfocando as transformações geoquímicas que ocorrem em solos sob regime anaeróbico da região dos rios Guamá e Caeté, da Amazônia foram objeto de consulta, e outros correlacionáveis pelo mundo.

3.2 AMOSTRAGEM E CARACTERIZAÇÃO DA AMOSTRA

As amostragens de solo foram realizadas na superfície de Gleissolos encontrados no município de Belém e Bragança, próximo a margens dos rios Guamá e Caeté respectivamente, e realizadas em duas etapas: uma etapa relacionada à coleta em horizontes do perfil do solo, empregada em sua caracterização, e a etapa seguinte relacionada à amostra destinada à experimentação em vasos. As amostras para os experimentos foram obtidas a partir da coleta de amostras simples superficiais, em sítios de 10.000 m² em cada local estudado, e a seguir foi concentrada em uma amostra composta para cada experimento. Realizada em quantidade suficiente para preencher os vasos e caracterizar o solo, as amostras foram secas ao ar, em tabuleiros plásticos e destorroados com instrumentos de madeira.

Parte da amostra coletada no perfil foi enviada para o Acme Analytical Laboratories (Vancouver) Ltda. para obtenção dos resultados dos teores totais dos elementos nas amostras. A outra parte das amostras coletadas nos perfis de solo foi submetida à análise química, relacionadas à de fertilidade e granulometria do solo de acordo com o descrito por EMBRAPA (1997). Paralelamente foram realizadas análises granulométricas e mineralógicas por difração de Raios-X, empregando o método do pó na caracterização total das amostras, e lâminas orientadas para identificação dos argilominerais.

Para conhecer o material em suspensão, o suspensato, que é fundamental para o entendimento dos solos de várzea, a água dos rios Caeté e Guamá foram coletadas e acondicionadas em recipiente plástico com 3.000 litros e 600 litros de capacidade, e decantada naturalmente pelo período de dois meses, retirando-se o sobrenadante e centrifugando o restante para obter o suspensato. A caracterização química, relacionada ao suspensato foi

realizada da mesma forma que é realizada no solo. A determinação mineralógica também empregou o método do pó para a determinação total dos minerais e o emprego de lâminas orientadas para a identificação dos argilominerais.

3.3 EXPERIMENTAÇÃO

- 1) Experimento 1: Neste experimento o solo coletado na várzea do rio Guamá, após preparado, foi acondicionado em vasos de isopor, com sete litros de capacidade, em condições de laboratório, com quatro repetições, aos quais foi adicionado água destilada, de forma a preencher os poros existentes no solo e manter uma lâmina d'água de 2 cm acima do solo. Periodicamente, a partir do 1º dia de inundação foi retirada amostra com 10 ml de volume, e após sua pesagem, encaminhada para análise úmida. Outra amostra com 10 ml era retirada, encaminhada para estufa à 105° C, e pesada após resfriamento em dessecador. A relação entre os pesos úmidos e secos fornecia um fator, que convertia os resultados de TFSA (Terra Fina Seca ao Ar) para TFSE (Terra Fina Seca em Estufa). Às amostras retiradas das parcelas experimentais foram submetidas à determinação do fósforo disponível e os teores de Ca, K, Fe, Mn, Cu, Zn trocáveis, além do carbono orgânico e dos valores de pH e Eh, que foram medidos diretamente nas parcelas. Para acompanhar as transformações geoquímicas até estabilização dos resultados, se manteve as parcelas inundadas pelo período de 132 dias. Os resultados foram submetidos à análise de variância e construção de gráfico demonstrando a evolução de suas concentrações com o tempo de inundação
- 2) Experimento 2: O experimento 2 foi realizado empregando o solo coletado no manguezal do estuário do rio Caeté. Neste experimento foi empregada a mesma metodologia empregada no experimento 1, visando atender o objetivo de monitorar as transformações geoquímicas em ambiente com condições diferenciadas das que frequentemente são investigadas na região, e assim, avaliar se diferentes condições presentes neste solo podem influenciar nos resultados comumente apresentados pelo nos solos até estudados, concentrados no Gleissolo Háptico.
- 3) Experimento 3: A metodologia de determinação química no solo úmido foi confrontada com a determinação realizada no solo seco, neste experimento. O solo foi acondicionado em caixas de isopor, com sete litros de capacidade e quatro repetições, que foi preenchido

com água destilada onde foram realizadas amostragens periódicas em duplicidade. Em cada parcela experimental era retirado duas amostras, sendo que uma das amostras era encaminhada para a análise úmida e outra encaminhada para secagem antes da realização da determinação química. Foram determinados os teores de Ca, K, Mn, Fe e Zn trocáveis e fósforo disponível em 52 dias de inundação. Foi realizada comparação estatística e teste de significância entre os resultados das amostras que eram analisadas úmidas com os resultados das amostras que eram realizadas secas. Os resultados foram representados graficamente apresentando comparação da evolução geoquímica no solo por ambas as metodologias.

4 WATER AS A RELEASING AND FERTILIZING FOR THE VÁRZEA SWAMP SOILS OF THE GUAMÁ RIVER IN THE AMAZON ESTUARY COMPLEX (Submetido a Applied Geochemistry)

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ABSTRACT

The estuary of the Guamá River, part of the estuarine complex of the Amazon River in northern Brazil encompasses ample areas of highly fertile *várzea* swamps, which have considerable potential for agriculture. Despite this, there are few plantations, and the area is used primarily for the extraction of native forest products. The most common soils in these swamps are haplic and saline gleysols. These soils suffer the influence of the tides and invariably present a reduced zone throughout most of their profile. The reductive environment found in these soils induces transformations that modify their fertility. The reduction process leads to an increase in pH, a buildup of NH_4^+ , increase in the concentration of Mn^{2+} , reduction of Fe^{3+} , reduction of sulfates to SO_3^{2-} and S^{2-} , increase in the availability of PO_4^{3-} , increase in the concentration of cations through substitution with Fe^{2+} , NH_4^+ , and Mn^{2+} in the exchange complex and the formation of organic products such as CO_2 , CH_4 , aldehydes, organic acids and other compounds. These geochemical phenomena occur in response to changes in Eh. For the evaluation of the effects of inundation on the soil and its fertility, a prolonged inundation experiment was conducted on a sample of haplic gleysol collected from the margin of the Guamá River in Belém, northern Brazil, while the fertility and mineralogical characteristics of samples of the soil and suspended material from the river water were also analyzed. In the experiment, the soil was inundated with distilled water and samples were taken at regular intervals. During the experiment, accentuated reduction was recorded, from an initial +322 mV on the first day to -337 mV by the 132nd day of inundation. The pH increased rapidly from 4.69 to stabilize at 6.6 from the 8th day onwards. The elements iron, phosphorus, and manganese increased considerably in the exchange complex, with iron reaching levels considered too high for plant nutrition. Inundation did not provoke any increase in available potassium, which, together with calcium, varied little during the course of the experiment. The concentrations of the micronutrients copper and zinc increased only slightly during inundation, but remained within adequate levels. The mineralogical characteristics of this soil included the presence of goethite, quartz, smectite, illite, kaolinite, and anatase. The suspended material was analyzed for the determination of adsorbed and available cations, as for soil, and revealed high levels of exchangeable cations adsorbed in the sediment, with high CEC, low saturation of aluminum, and high alkaline saturation. Mineralogically, the suspension contains quartz, kaolinite, smectite, and illite. The study indicated that inundation produces an environment with fertility adequate for most crops, except for the relatively high levels of iron, which may be toxic for some cultivars. The high levels of exchangeable cations adsorbed in the suspended material, the abundance of humidified organic material, and the presence of clay minerals of the 2:1 type all contribute to the maintenance of the fertility of this environment.

Key-Words: Floodplain, surface geochemistry, flooded soil, soil fertility, Amazon lowland

1. INTRODUCTION

The coastal zone of northern Brazil, in the states of Amapá and Pará, includes some three million hectares of tidal *várzea* swamps with soils of medium to high fertility, with high concentrations of calcium and magnesium (Falesi, 1972). Within this region, the estuaries of the Amazon and Pará rivers encompass vast areas of *várzea* soils with reduced seawater input. The Pará River is the local denomination for the estuarine complex located to the east of Marajó Island, which is formed by more than 40 different rivers, such as the Guamá, Tocantins, Capim, Acará, Moju, Anapu, Jacundá, Pacajás, and Araticu.

The *várzeas* of the Guamá River, located upstream from Belém, which is one of the major cities of Brazilian Amazonia, were selected for the present study. This area was occupied during the first centuries of European colonization, when plantations of sugar cane were established for the production of sugar, ethanol, and liquors to supply Europe (Tourinho et al., 2009). To this day, this area is used for the extraction of natural resources such as cocoa (*Theobroma cacao*, L.), andiroba (*Carapa guianensis*, Aubl.), latex (*Hevea brasiliensis*, Muell. Arg), and açai (*Euterpe oleracea*, Mart.), as well as the lumber of a number of tree species, such as the macacaúba (*Platymiscium trinitatis* Benth.), virola (*Virola surinamensis*, Warb.), and pau-mulato (*Calycophyllum spruceanum*, Benth). (Hiraoka, 1995; Tourinho et al., 2009). Recent agricultural experiments have confirmed the possibility of productive plantations of cultivars such as sugar-cane, banana, and rice (Hiraoka, 1995; Lima et al., 2001). Given the historical importance and future potential of this environment, a strategic area of *várzea* located on the Belém campus of the Brazilian Enterprise for Agricultural Research (EMBRAPA-Eastern Amazonia) was selected for the present study.

The *várzeas* of the Guamá are formed by haplic gleysols that suffer the influence of the tide and seasonal variations in fluvial discharge which may result in periodic inundations and modifications of the soils' fertility (Lima et al., 1996). These soils are extremely fertile, and are well-suited to the production of food crops (Lima et al., 2001), and as productivity does not decline over time, they are appropriate for the establishment of permanent agricultural settlements (Mascarenhas & Modesto Júnior, 1998). These soils contrast considerably with those of the region's *terra firme* environments, which are of low fertility. Lopes et al. (2006) nevertheless found that, while the soils of the *várzea* of the Guamá

provide excellent conditions for the production of a variety of crops, agriculture leads to a reduction in the concentrations of available elements, such as phosphorus and potassium, indicating the need for adequate management and the replacement of the nutrients removed by the plantations.

These low-lying soils are permanently waterlogged, and as a consequence, present a horizon in which the products of redox reactions predominate over those of reduction. The characteristics of these soils are altered considerably when they contain water or when they are completely inundated (Ponnamperuma, 1972). The principal physical-chemical and chemical transformations of these soils are (a) an increase in pH due to redox reactions, when the iron and manganese of their oxy-hydroxides are reduced, leading to an increase in the concentrations of Mn^{2+} and Fe^{2+} ; (b) reduction of the S of the sulfates to S^{4+} , such as SO_3^{2-} and S^{2-} , (c) chemical reduction of the nitrates, and the formation and buildup of NH_4^+ , and (d) oxidation of the organic material. This results in an increase in the availability of PO_4^{3-} and H_4SiO_4 , and an increase in the concentration of cations. The oxidation of organic material produces CO_2 and HCO_3^- , and the decomposition of this material produces CH_4 , aldehydes, organic acids, and other compounds (Ponnamperuma, 1972; Camargo *et al.*, 1999; Assis *et al.*, 2000; Lima *et al.*, 2005).

Otero *et al.* (2009) concluded that the decomposition of the minerals $OHFe$ and $OHMn$, with a consequent reduction in Fe and Mn, is one of the most important reactions in the gleysols. When these minerals are present in these soils in large quantities, they are released into its solution, and also produce hydroxils, which contribute to the elevation of the pH to values close to seven. An increase in the levels of available phosphorus is commonly observed during these redox reactions, which may be related to the structure of these oxy-hydroxides. This may also be a result of the hydrolysis of the iron and aluminum phosphates (Camargo *et al.*, 1999). The release of adsorbed phosphorus through anionic exchange in the clays or unstable iron and aluminum hydroxides under these physical-chemical conditions may also represent another source of available phosphorus.

The dynamics of the nutritional chemical elements of the gleysols of the Guamá várzeas under intense redox conditions have been investigated by Silva *et al.* (1996), Ferreira *et al.* (1998), Ferreira & Botelho (1999), Mattar *et al.* (2002), and Silva (2008). These studies, collected over a short period of time, recorded anomalous patterns, such as the levels of zinc and sulfur, which were expected to decline, but were available in the soil throughout the study period. However, these studies did not consider the mineralogical content of the soils and

suspended material present in the water of the rivers that flood this habitat and play a crucial role in the mobility, fixation, and desorption of chemical elements, whether nutrients or not.

The principal objective of the present study is to investigate the geochemical processes that occur in the superficial horizon of the gleysols with the input of flood waters and the resulting redox reactions, in this case, those of the Guamá River, part of the Amazon estuarine complex. The study focuses on a period of four months, which corresponds to the growth period of short-cycle crops.

2. MATERIALS AND METHODS

The present study was based on the analysis of soil samples collected from the *várzea* and samples of the suspended material in the waters of the Guamá River, with the primary objective of evaluating the degree of correlation in the composition of the two substrates. The soil samples were obtained for the characterization of the soil profile, with samples being obtained from horizons A₁, AB, and B_g, and for inundation experiments in which samples were soaked in distilled water in order to test their capacity for the absorption and desorption of chemical elements. The samples for soil profiling were designated according to their soil horizon, A₁ (depth of 0-18 cm), AB (18-70 cm), and B_g (70-120 cm). The experimental sample was compiled from a number of separate subsamples, collected with a Dutch auger at depths of up to 20 cm, which correspond to horizon A₁, the stratum from which plants normally extract their nutrients. A total of 63 samples were collected randomly from within an area of approximately 10,000 m², and were mixed and homogenized to form the single experimental sample, denominated EXP-01, which represents horizon A₁.

All the samples were collected in the rural zone of the municipality of Belém, within the campus of the Brazilian Enterprise for Agricultural Research (EMBRAPA). The soil profile was collected from a point 500 m from the right bank of the Guamá River (1°27'32.50" S, 48°25'33.89" W), 10 km upstream from the mouth of the river, where it enters Guajará Bay (Figure 1).

This area was chosen because it has yet to be used for either agriculture or agricultural experiments. The vegetation is characteristic of the *várzea* forest, with trees such as acapurana (*Campsiandra laurifolia*, Benth.), ubim (*Geonoma baculífera*, K.), mamorana (*Pachira aquatic*, Aubl.), ananim (*Symphonia globulífera*, L.), palheteira (*Clitoria arbores*, Benth.), and ucuúba (*Virola sebífera*, Aubl.).

The sample of suspended material from the Guamá, a river of white (muddy) waters, was collected in front of the area in which the soil samples were obtained. A single sample of 3000 liters of water was obtained in a polyethylene vessel, which was stored for natural decantation, that is, with no addition of chemicals for precipitation. Following decantation, the supernatant was removed and the remainder was decanted into a smaller recipient (5 l), and then centrifuged, with the supernatant being retrieved once again. The solid residue was stored in a dessicator for 24 h. This sample was denominated SUS-01. The three thousand liters of water rendered 45.2 g of solid material.

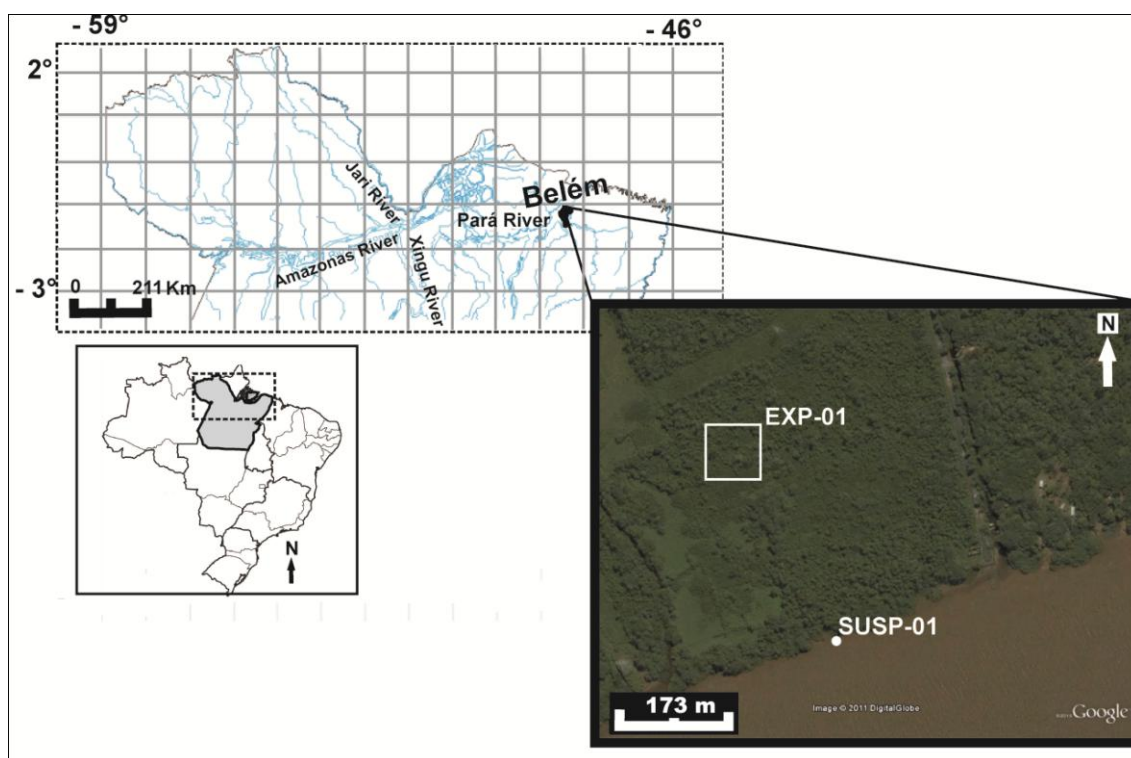


Figure 1. Location of the study area in the *várzea* of the Guamá River, in the rural zone of the municipality of Belém, showing the collection points for the soil sample, EXP-01 ($1^{\circ}27'32.50''\text{S}$, $48^{\circ}25'33.89''\text{W}$) and the sample of suspended material, SUSP-01 ($1^{\circ}27'42.02''\text{S}$, $48^{\circ}25'32.35''\text{W}$)

Following collection, the soil samples were air dried and then crushed using a wooden roller to prepare them for analysis. The analyses were as follows:

- 1) Granulometric analyses of sample EXP-01 by sieving and the EMBRAPA (1997) pipette method in the UFRA laboratories;
- 2) Analyses of fertility, following EMBRAPA (1997), of the three soil profile samples and the suspended material, in the UFRA laboratories;

- 3) Mineralogical analysis of samples EXP-01 and SUS-01 by X-Ray Diffraction (XRD) in the X-Ray laboratories of the UFPA Geosciences Institute. The analyses were applied to the whole sample, using the powder method, as well as the clay fraction method, using blades angled for the best diagnosis of clay minerals. The samples analyzed using angled blades were also glycolated and heated for additional XRD, following the classic procedure for the determination of clay minerals. Measurements were obtained using an X'Pert Data Collector (version 2.1a) diffractometer, and processed using the X'Pert HighScore (version 2.1b) software;
- 4) Total chemical analyses (major, minor, and trace elements) were conducted on the superficial and lower horizons of the profile by Acme Analytical Laboratories Ltd. in Vancouver, Canada, using ICP-OES and ICP-MS;
- 5) The experimental procedure was carried out in the Chemical Analyses Laboratory of the UFPA Geosciences Institute. Sample EXP-01, weighing 28 kg, was divided into four equal parts, which were stored in seven-liter polystyrene containers. These containers were filled with distilled water until the samples were covered to a depth of 2 cm, with the water being topped up whenever necessary. Samples of the inundated soil of all four replicates were taken at irregular intervals, ranging from 1 to 15 days, but concentrating on the first few days, and beginning on the first day of inundation, given that the most accentuated chemical transformations tend to occur during the first few days (Ponnamperuma, 1972). A total of 100 samples were collected. Samples were collected daily during the first five days, then every two days during the rest of the first month, and then over increasingly longer intervals, up to 15 days, during the rest of the experiment. A separate sampling protocol was followed for the determination of organic carbon, with a sample being taken every 15 days during a period of 276 days. All other elements and parameters were monitored over a 132-day period. The pH and Eh values were recorded using a potentiometer, while the concentrations of available P were determined by spectrophotometry. Exchangeable Ca, K, Zn, Mn, Cu, and Fe concentrations were determined by atomic absorption, while organic carbon was measured using the Walkley-Black method (EMBRAPA, 1997). The analyses were carried out in the UFPA Geosciences Institute.

As the transformations are reversible, the samples were not dried, but the results were converted into dry fine earth in a stove. For the conversion of the results, two samples of equal volume were taken from each replicate sample. One was kept humid, weighed, and analyzed, whereas the other was dried in a stove at 105°C, weighed and then stored in a

dessicator for 24 h. The ratio between the dried and humid sample was used to convert the results obtained for the humid sample, following the recommendations of Silva *et al.* (1996), Ferreira *et al.* (1998), Ferreira & Botelho (1999), Mattar *et al.* (2002), and Silva (2008).

The results were treated statistically considering the variance, for comparisons using the SNK test, and presented in dispersion diagrams. Overall, 200 measurements were obtained for each parameter, except for organic carbon, for which the total was only 56 (Ferreira, 2007). The results for phosphorus were correlated with those for Ca, Fe, and Mn.

3. RESULTS AND DISCUSSION

3.1. Mineralogical and granulometric characteristics and fertility

According to the XRD analyses, the gleysol of sample EXP-01 is composed of quartz, kaolinite, illite, smectite, goethite and anatase (Figure 2), in decreasing order of relative abundance. The composition of the suspended material is similar to that of the soil, except for the absence of goethite and anatase (Figure 3). Minerals such as quartz, kaolinite, and goethite are also the principal components of the *terra firme* soils of the area adjacent to the study area. The *terra firme* soils may thus have been the origin of these minerals in the *várzea*, although the illite and smectite, which are not found in the *terra firme* soils, must have been derived from the water of the Guamá. The presence of smectite, in particular, but also illite is of major importance, given the capacity of these minerals to retain cations in the soil. These minerals are relatively rare in most tropical Amazonian *terra firme* soils. The presence of smectite indicates environments with poorly-drained soils, whereas that of kaolinite is characteristic of well-developed and leached soils, that is, *terra firme*, which are associated with tropical environments (Guyot *et al.*, 2007).

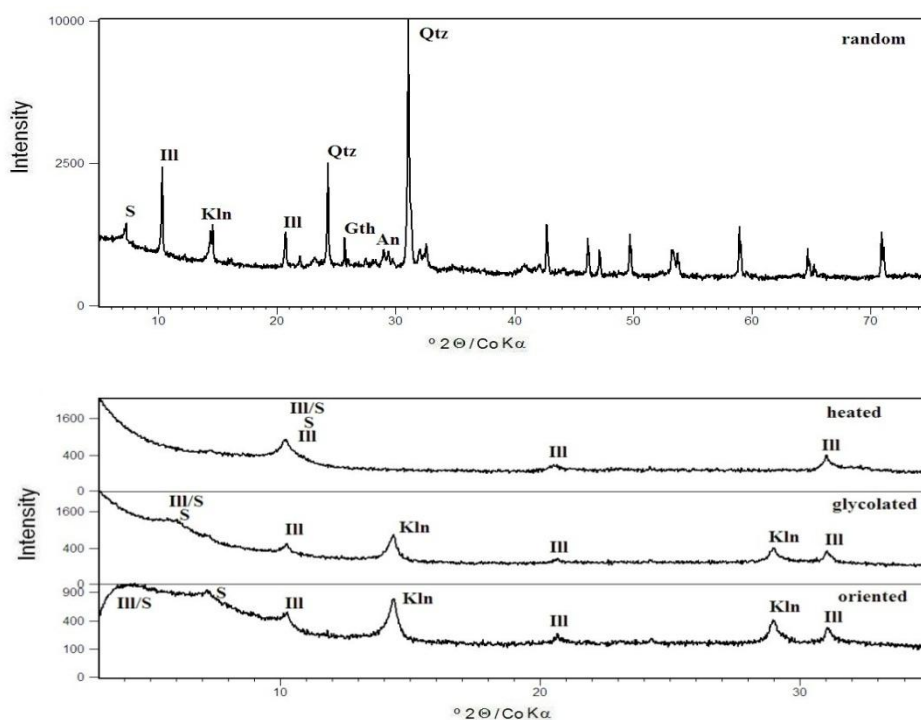


Figure 2. Minerals identified by the XRD powder method for the consolidated sample EXP-01. Quartz (Qtz), kaolinite (Kln), smectite (S), illite (Ill), goethite (Gth), and anatase (An)

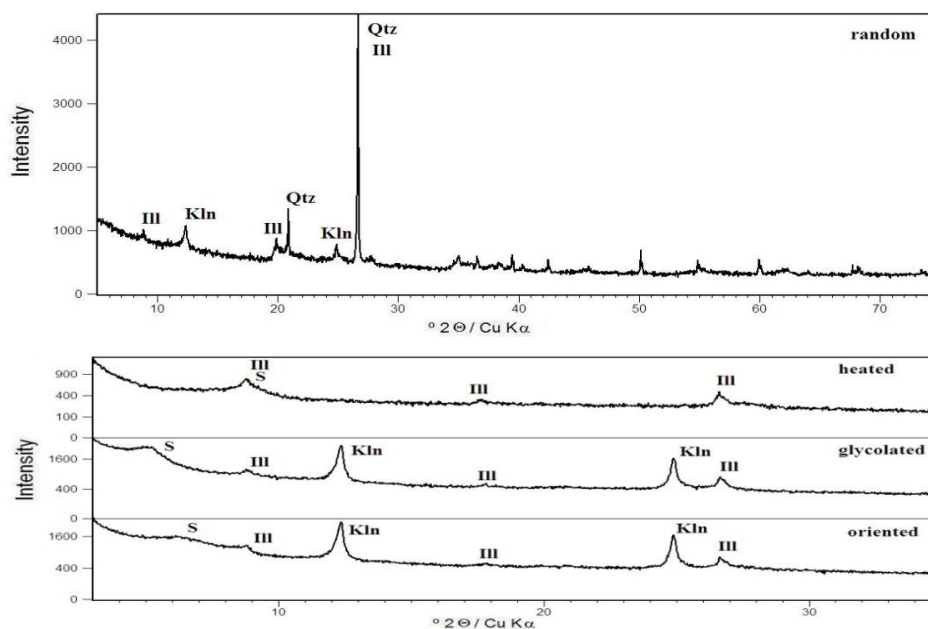


Figure 3. Minerals identified by the XRD powder method and blades angled for the clay fraction for the suspended material (sample SUSP-01). Quartz (Qtz), kaolinite (Kln), smectite (S), illite (Ill), goethite (Gth), and anatase (An)

The soil profile is typical of that of a gleysol (Table 1), with mean fertility increasing from horizon A₁ to B_g. The pH is acid, and the ΔpH indicates the predominance of negative

charges throughout the horizon, which is characteristic of haplic gleysol. The CEC is relatively high for a soil with only a slightly sandy texture (Lopes & Guilherme; 2004). Organic carbon and other organic material are relatively abundant, especially in the B_g horizon, which further emphasizes the gleysol configuration. The $\leq 50\%$ base saturation indicates the presence of other ions occupying space in the exchange complex, such as aluminum, at 28.67%, which would be considered a high value by Lopes & Guilherme (2004). During the dry season, there was no water in the superficial horizons, which made the environment aerobic, with an acid pH in water, which enhances the solubilization of the aluminum (Table 1). The gleysol analyzed in this study is characterized by low levels of calcium and potassium, but high concentrations of magnesium and aluminum, forming an effective CEC of 5.68 cmol_c/dm³, which can be considered average, but close to the potential CEC of this soil (Table 1).

Table 1. The pH values and concentrations of the elements and compounds relevant to soil fertility found in the soil samples and suspended material from the Guamá River

Sample	pH		C	M.O	P	Ca	Mg	K	SB	H	Al	T	V	M
	H ₂ O	KCl	g kg ⁻¹	mg.dm ³	cmol _c .dm ³					%				
A ₁	4.69	3.59	3.9	6.72	2.52	1.52	2.48	0.08	4.08	3.94	1.60	9.62	42.41	28.67
AB	5.26	3.58	1.17	2.02	0.20	1.52	4.38	0.05	5.95	2.45	2.35	10.75	53.34	28.31
B _g	4.74	3.51	7.79	13.43	0.30	1.62	7.24	0.09	8.95	2.40	1.88	13.23	67.64	17.35
Suspended material					20.84	3.30	0.72	0.155	7.37	2.59	0.26	10.57	69.77	7.64

OBS: Sample A₁ (equivalent to EXP-01) returned the following granulometric composition: coarse sand = 2.90 g/kg; fine sand = 28.00 g/kg; silt = 743.00 g/kg; clay = 226.30 g/kg.

Phosphorus concentrations were relatively low in comparison with the typical saline gleysols of the Amazon estuary (Vieira, 1966). Iron was distributed regularly throughout the profile, but once again, with concentrations lower than those of the saline gleysols. While aluminum is present in the soil analyzed, it is not available as an exchangeable ion, and thus does not affect alkaline saturation. Similarly, potassium concentrations are low on the surface, and in the lower horizons, indicating a reduced participation in the CEC of this soil.

3.2. Availability of chemicals during prolonged inundation

The experiment showed that the inundation of the gleysol (represented by horizon A₁) with distilled water provoked highly significant modifications of all the parameters analyzed (Table 2). The pH, which was initially 4.6, increased gradually until the 15th day of inundation, when it stabilized at around 6.5 to 6.7 (Table 3 and Figure 4-A). These values contribute to the fertility of the soil, providing conditions favorable to the maintenance of the availability of the chemical elements which are essential to plant growth, and at the same time precipitating the aluminum (Lopes, 1989).

Table 2. Analysis of Variance of the effect of inundation of the soil on time (days), during laboratory experiment with distilled water

FV	pH	Eh	P	Ca	K	Cu	Zn	Fe	Mn
Days	**	**	**	**	**	**	**	**	**
d.f.	24	24	24	24	24	24	24	24	24
Rep	3	3	3	3	3	3	3	3	3
CV%	0.71	7.86	49.20	12.63	71.77	35.56	15.96	14.08	8.34

** $p < 0.01$.; CV. Coefficient of Variation; Rep. Repetition.

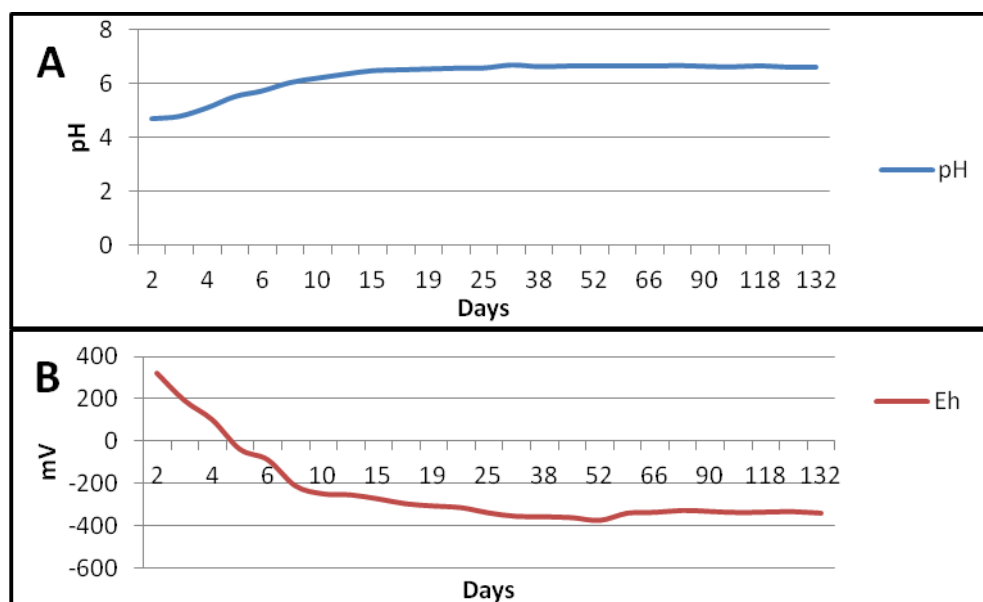


Figure 4. Variation in mean pH (A) and Eh (B) values during the 132 days of inundation

In contrast with pH, Eh decreases immediately during the first 25 days, when it fell from +322 to -336 mV to stabilize at around -350 mV from the 31st day onwards (Table 3 and

Figure 4-B). This indicates a major reduction in the redox potential, which subsequently remains constant during inundation.

Table 3. Mean values recorded per day during the inundation experiment (inundation of gleysol from soil horizon A₁ with distilled water) for pH, Eh and the concentrations of available P, Ca, K, Zn, Cu, and Fe (132 days) and organic carbon (276 days).

Day	pH	Eh mV	P mg/dm ³	Ca mg/dm ³	K mg/dm ³	Zn mg/dm ³	Mn mg/dm ³	Cu mg/dm ³	Fe mg/dm ³	Day	C mg/dm ³
1	4.69	322	7.77	225.25	1.28	6.75	151.5	1.25	1048	1	3.89
2	4.78	193	8.91	395.25	1.11	11.25	227	3.75	1179.25	14	3.01
3	5.1	103	10.58	346	0.71	12	226.75	1	1479.75	30	2.56
4	5.52	-36	13.15	249.25	0.13	11.25	309.25	1	1787.25	38	2.75
5	5.74	-85	11.102	243.75	0.37	13.75	340.75	2	2799.5	60	1.99
8	6.05	-208	20.63	270.25	1.39	13.25	373.75	2	2628	81	2.33
10	6.22	-246	15.42	285	1.06	16	367	2	2886.25	97	2.18
12	6.37	-251	16.46	496.75	0.17	14.5	324.75	2	5330	115	2.04
15	6.5	-270	23.12	456.5	0.18	14.5	360	1.25	5806.25	133	2.19
17	6.53	-293	20.96	404	0.48	15.25	316.25	1.75	6203.25	170	1.97
19	6.56	-303	18.6	446.25	1.01	18	355.75	2.25	6952	187	2.37
23	6.59	-311	38.62	434.75	1.24	14.75	334.5	2.25	7165	202	0.03
25	6.6	-336	48.06	426	1.04	14	346	0.75	6690.25	221	0.65
31	6.71	-352	119.15	390	0.15	10	365	3.75	2539	276	0.68
38	6.65	-354	72.32	338.5	0.15	15.25	343.75	1.75	3887.75		
45	6.67	-358	75.3	352.5	0.16	24.25	331.75	1.25	8136.25		
52	6.68	-371	111.47	353.5	0.16	20	526	5	7919.5		
59	6.68	-337	48.92	355.75	0.41	16.5	321.25	2.25	7703.75		
66	6.67	-333	57.94	385.75	0.58	17	335	1.5	8615.25		
73	6.69	-324	61.97	389.75	0.15	13	366.25	1	10245.5		
90	6.66	-329	67.62	456.25	0.14	18.75	392.75	1.5	9655		
97	6.64	-334	48.66	419.5	0.21	18.75	376.25	1	6941.5		
118	6.68	-332	63.08	408.25	0.14	21.75	350.75	1.25	5950.25		
125	6.63	-330	68.14	414.5	0.14	17.25	332.25	1.75	6145.75		
132	6.63	-337	75.78	472.5	0.14	22.5	338.5	1	6663.75		

During the first 132 days, organic carbon levels followed a pattern of variation similar to that of Eh (Table 3 and Figure 5). During the first 38 days, organic carbon decreased from 3.89 g/dm³ to 2.56-2.75 g/dm³, and from the 60th day onwards, it remained at around 2.00 g/dm³, decreasing abruptly again after the 202nd day. These decreasing values indicate the intense oxidation of the organic material, as suggested by the Eh values, related to the

presence of oxygen in the samples and that dissolved in the water. The consistency of the values recorded during the course of the experiment indicate that the redox reactions ceased, as demonstrated by the Eh values and, indirectly, the pH levels, in other words, the environment was reducing throughout the experimental inundation period. On the 202nd day, however, an additional major consumption of organic carbon began, followed by considerable bacterial activity, represented by the slight increase in organic material. Obviously, it was not possible to monitor possible changes in the other parameters during this period.

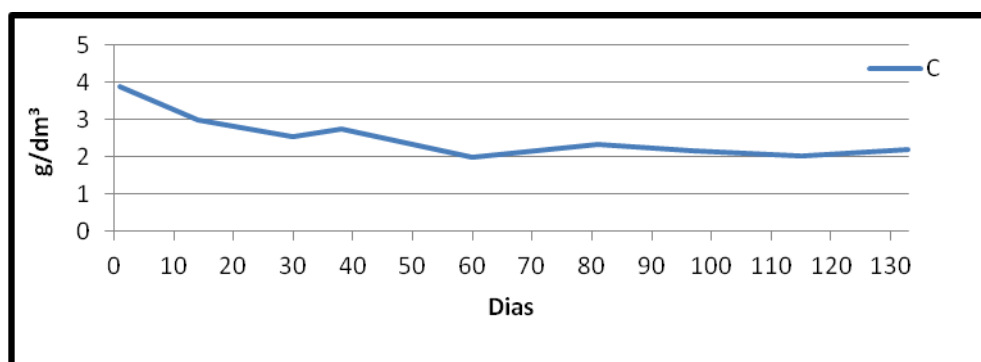


Figure 5. Variation in mean organic carbon concentrations during the 132 days of inundation

Iron was among the elements most available in the samples, increasing irregularly to reach 10,245.5 mg/dm³ by the 73rd day (Table 3 e Figure 6-A). In general, these changes appear to be related to shifts in the redox potential, although the distribution curve suggests that part of the dissolved iron is being immobilized in some of the time intervals as the experiment proceeds, probably by being precipitated as ferrous minerals, such as siderite or pyrite, which are expected to occur in these environments, through diagenesis (Ferreira *et al.*, 2007; Kristensen *et al.*, 2008; Otero *et al.*, 2009). The values obtained for iron may represent toxic levels for some crops, such as rice, although native cultivars, such as açai (*Euterpe oleracea*, Mart.), bacaba (*Oenocarpus bacaba*, Mart.), and buriti (*Mauritia flexuosa*, L.) easily tolerate the levels recorded, as confirmed by the exuberance of the várzea forest of the study area. Silva & Ranno (2005) tested the availability of nutrients in a variety of soils, and recorded a greater release of iron in gleysols. However, Lima *et al.* (2005) concluded that this was directly related to the higher levels of total iron in these horizons, possibly as destabilized and dissolved ferrous oxides and hydroxides, associated with an increase in the availability of phosphorus. Zou *et al.* (2009) nevertheless warned that iron is released more intensively on the surface of the soil, and that this effect is insignificant in the lower horizons.

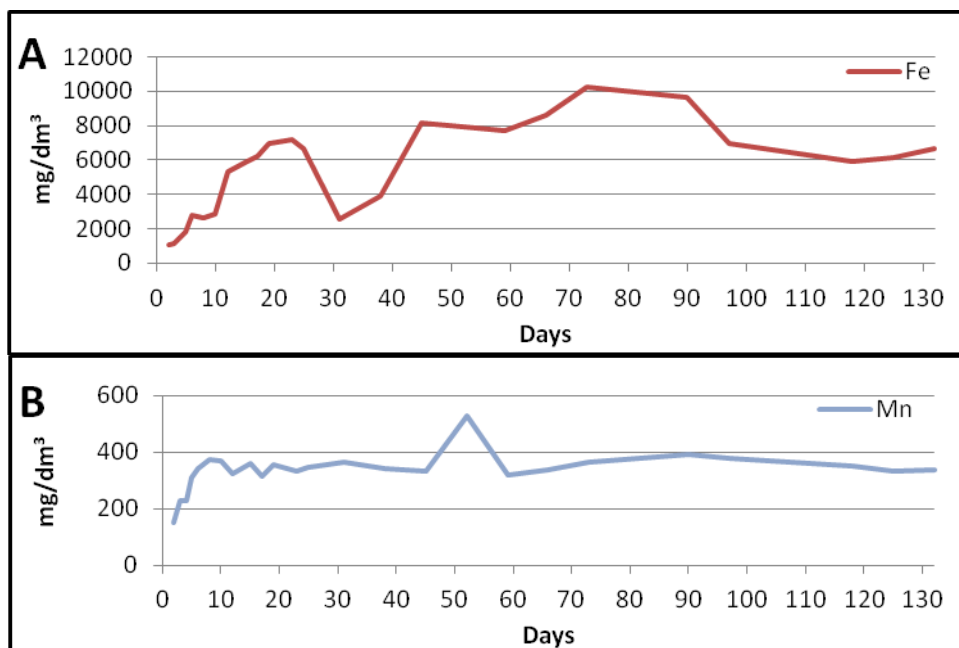


Figure 6. Variation in the mean concentrations of available iron (A) and manganese (B) during the 132 days of inundation.

The concentrations of available manganese behaved in a similar manner to those of iron, that is, they increased progressively over time. Silva (2008) concluded that this solubility of the manganese is a result of the decomposition of Mn minerals, which are generally represented by oxy-hydroxides such as romanèchite, cryptomelane, lithioforite, or even as a minor component of the OHFe , and when Mn^{4+} is reduced to Mn^{2+} . On the other hand, Sanches (1981) explained that, in some cases, the eventual reduction in Mn levels may be due to the precipitation of Mn^{2+} as MnCO_3 , i.e. rhodochrosite, or in the structure of siderite (FeCO_3). In the present experiment, manganese reached a maximum solubility of 526 mg/dm^3 on the 52nd day of inundation, and subsequently remained at $300\text{--}400 \text{ mg/dm}^3$ (Table 4 and Figure 6-B), suggesting the occurrence of precipitation.

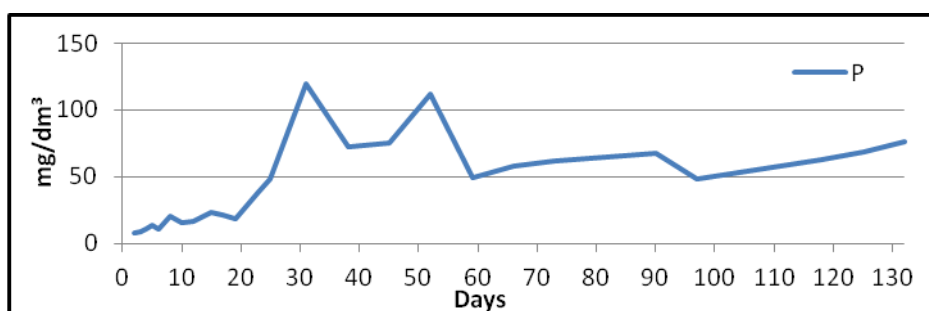


Figure 7. Variation in the mean concentrations of available phosphorus during the 132 days of inundation

Available phosphorus also increased over time (Table 3 and Figure 7), although the highest values (119.15 and 111.47 mg/dm³) were recorded between the 31st and 52nd days, with a slight increase from the 118th day onwards. This pattern is directly related to the available Fe levels (Table 3 and Figure 7-A), as would normally be expected, when the phosphorus linked to the OHFe minerals are released through their decomposition and the subsequent reduction in Fe, as well as available Mn and Ca, among other elements (Mello *et al.*, 1992; Ferrando *et al.*, 2002). A slight correlation with Mn can be observed. Goethite, lepidocrocite and ferrihydrite (the most common forms of OHFe in the soils), in particular goethite, which was identified in the gleysol, have a significant specific surface, as well as chemical reactivity for the adsorption of phosphorus and are thus important for the release of this element under reductive conditions (Schwertmann & Taylor, 1989). The levels of phosphorus available in the soil, which were initially very low, reached relatively high values by the end of the experiment. This increase occurs soon after the oxidation of the organic carbon, as indicated by the abrupt decline in the levels of this carbon, from 389 mg/dm³ to around 200 mg/dm³ during the first few days (Table 3 and Figure 5), which results in the formation of carbon dioxide or bicarbonate ions, which contribute to the formation of carbonates, such as siderite-rhodochrosite or siderite alone.

In a study of periodically flooded soils, Chancon *et al.* (2005) found that seasonal differences in humidity may influence the release of phosphorus, and that a prolonged period of inundation, together with high levels of carbon in the soil, may provide the conditions necessary for the microbial reduction of the stable forms of the minerals in the soil. Over short periods, by contrast, the release of phosphorus was associated with the mineralization of organic phosphorus, while total phosphorus was also present in significantly larger quantities after the soil had dried. Willet (1989) confirmed both organic and mineral contributions to the release of phosphorus into the soil and in particular, the existence of conditions in some soils that permit the re-absorption of part of this phosphorus, which may have occurred in the gleysol studied here. Given this, the factors linked to the presence of organic material and the inundation cycles are important for the release of this element, as well as the mineral constituents formed, which can re-absorb the released phosphorus. This has been confirmed by Nguyen & Marschner (2005), who observed a relatively rapid increase in the availability of organic phosphorus, but a gradual increase in inorganic phosphorus in seasonally flooded systems, in comparison with constantly waterlogged or dry soils.

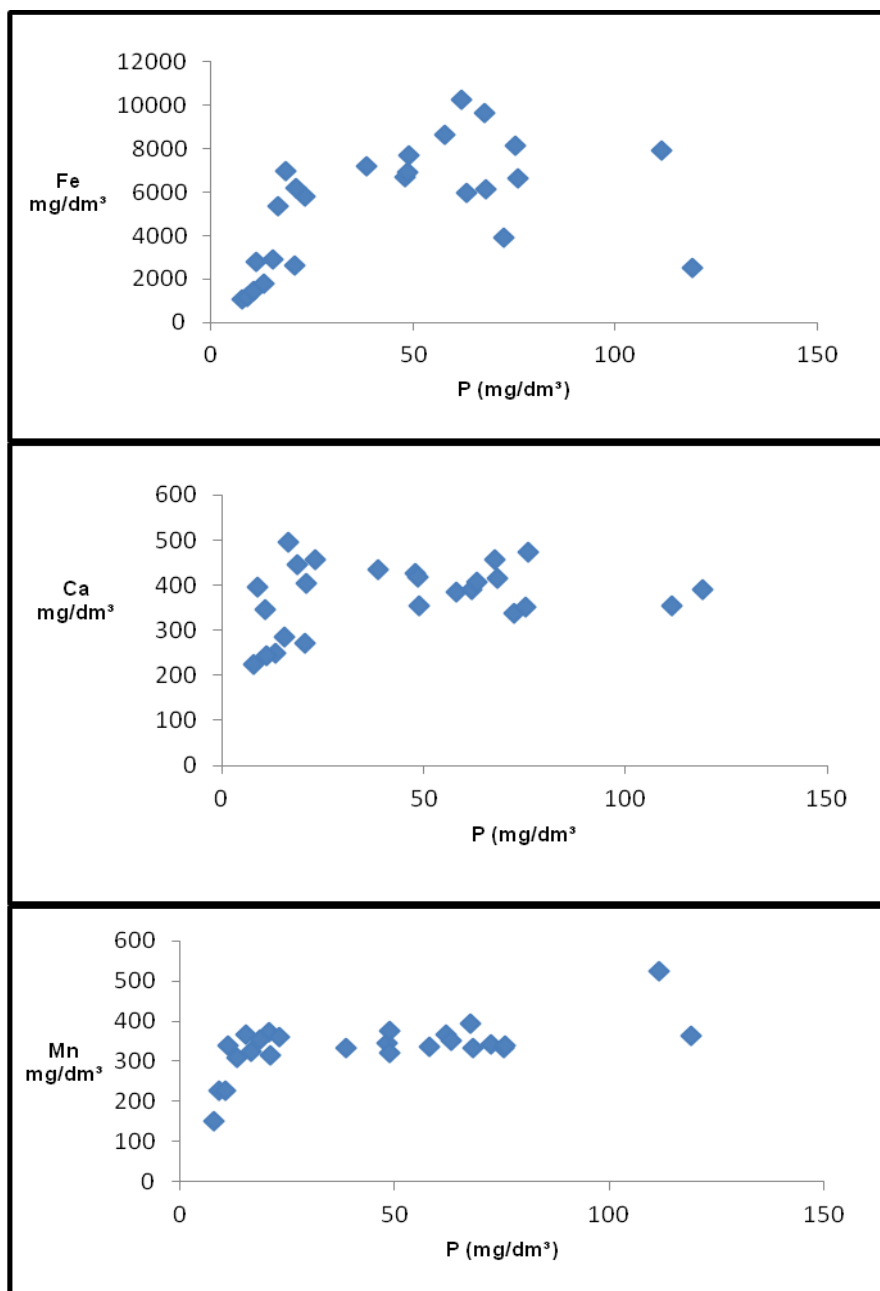


Figure 8. Diagrams of linear dispersion for the correlations between P and Ca, P and Mn, and P and Fe

Calcium and potassium were characterized by reduced availability throughout the soil profile, and low values predominated in the experiment. Calcium increases considerably and irregularly during the first 12 days before reaching a plateau of between 350 and 470 mg/dm³ (Table 3 and Figure 9-A), which are average values, even though they tend to increase over time. Potassium presents a similar pattern, although with much lower values, reflecting its much lower levels in the soil, with considerable oscillation during the first 25 days, between 0.2 and 1.2 g/dm³, and then between 0.14 and 0.20 g/dm³ from the 31st day onwards, except

for the interval between the 59th and 66th days, when it increased to 0.50 g/dm³ (Table 3 and Figure 9-B), suggesting stability with a slight tendency to decrease. These oscillations, in particular during the first 12 days, probably reflect intense cationic exchange over a short period of time, which occurs between the illite and smectite present in the soil. Oscillations in these values were typical for most of the parameters analyzed, given the relatively unstable environmental conditions of the gleysol.

Table 4. Pearson correlation coefficient (n = 40) for P, Ca, Mn, and Fe in the inundated gleysol

	Ca	Mn	Fe	P
Ca	1	0.2735**	0.6213**	0.3129**
Mn	0.2735**	1	0.5512**	0.6650**
Fe	0.6213**	0.5512**	1	0.7811**
P	0.3129**	0.6650**	0.7811**	1

** p < 0.01.

The solubilization of zinc also increased during the inundation of the gleysol, from 6.75 to 24.5 mg/dm³ by the 45th day, with average values being observed by the 19th day, and major oscillations of between 13.0 and 22.5 mg/dm³ (Table 3 and Figure 10), as seen in the other elements, with a tendency to increase during the course of the experiment, from the 70th day onwards. This pattern is the opposite of that recorded by Ferreira et al. (1998), Sanches (1981), Ferreira & Botelho (1999), who found that the availability of zinc tended to decrease during long periods of inundation. However, the results of the short-term studies of Mattar et al. (2002) and Silva (2008) were consistent with those of the present research.

Copper was relatively similar to zinc (Table 3 and Figure 10), but with very much lower values, varying between 1.25 and 5.00 mg/dm³, although the highest value was recorded on the 52nd day, whereas levels oscillated between 1.00 and 2.25 mg/dm³ during the rest of the experiment. The release of Zn and Cu was equivalent, at a ratio of four to one. These micronutrients are normally linked to both OHFe as well as organic material, such as organic chelating compounds (Sanches, 1991).

As shown by the results of the present study, then, the inundation of the gleysol provoked considerable modifications in pH and Eh values, which underpinned the rapid dissolution of the OHFe compounds and possibly also the OHMn, with a consequent reduction in the ions of Fe and Mn, among others, and consumption of electron-donating

organic material and oxygen. These conditions resulted in the release of elements such as Zn and Cu, the availability of which tends to decrease in any soil with high pH (Tisdale *et al.*, 1985; Lopes, 1988). However, the pH values recorded in this experiment were not high enough to render these elements unavailable. Given this, the quantities of exchangeable zinc and copper in the exchange complex were adequate for plant growth until the end of the experiment.

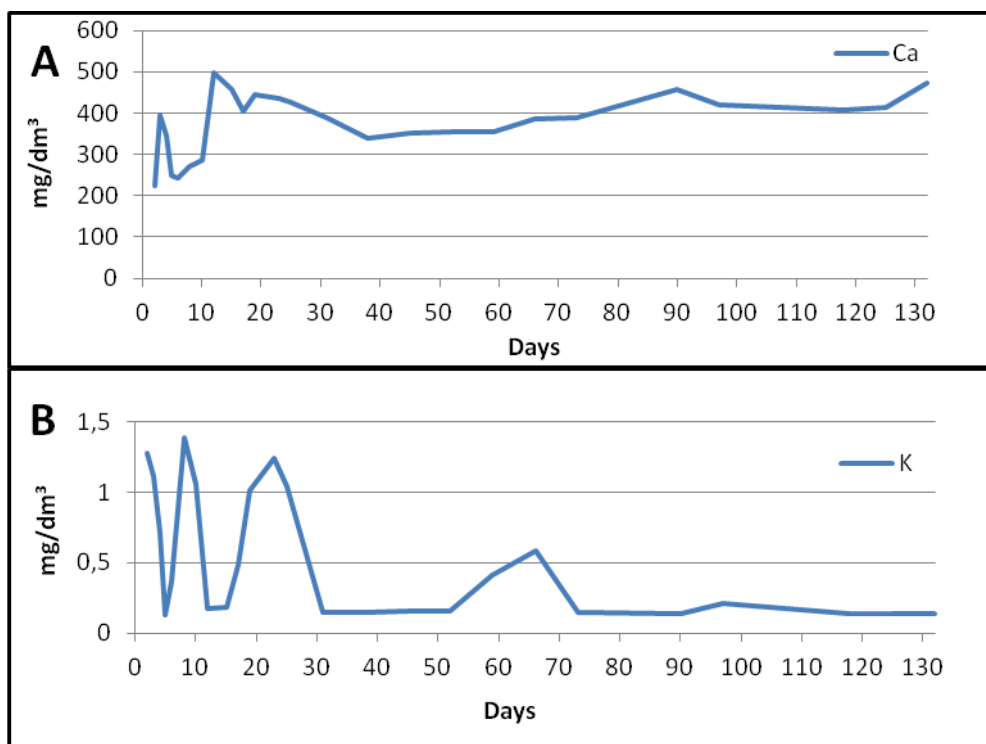


Figure 9. Variation in the mean concentrations of available calcium (A) and potassium (B) during the 132-day flood period

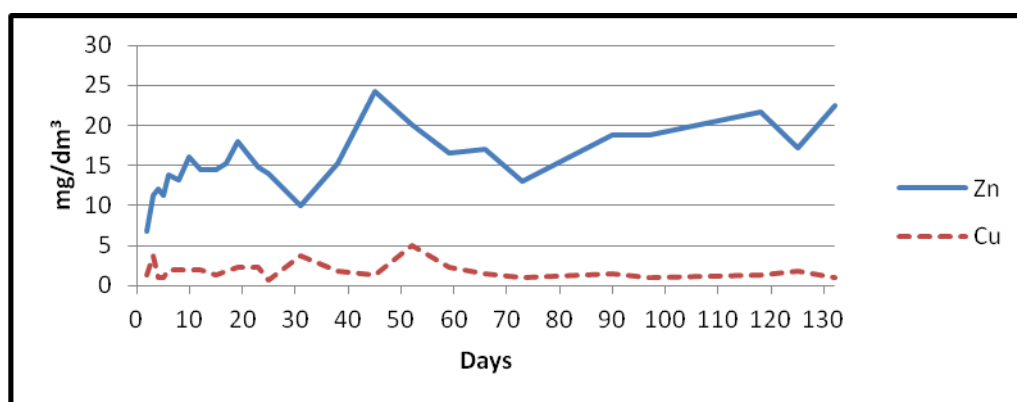


Figure 10. Variations in the mean concentrations of available zinc and copper during the 132 days of inundation.

4. CONCLUSIONS

The soils of the *várzea* swamps of the Guamá River are of average fertility, with a predominance of negative charges, high CEC, a high concentration of organic carbon in the B_g horizon, and alkaline saturation of less than 50%, which indicates aluminum at the exchange site, equivalent to a haplic gleysol. In addition to kaolinite and quartz, the mineralogy of the soil includes smectite and illite, which contribute to the above characteristics, as well as granulometry dominated by silt. This mineralogy, with clay at 2:1 and smectite and illite, is the exclusive contribution of the suspension of the Guamá River, the principal source of the *várzea* soils.

Inundation provoked profound geochemical modifications in the soil in relation to the availability of elements essential to plant growth. On the whole, the modifications were favorable, contributing to the availability of the chemical elements analyzed, with most macro- and micronutrients being found at satisfactory levels, exception for potassium, which remained at low levels throughout the experiment. Illite, the potassium mineral, is relatively stable, with a smaller CEC than smectite. While the levels of zinc and copper varied slightly during the experiment, they persisted in the soil's exchange complex, maintaining satisfactory conditions for plant nutrition. On the other hand, the availability of iron and manganese increased considerably, with iron reaching levels that would be toxic to some cultivars, but do not have visible effects on the local native vegetation. The modifications resulted in a shift in pH, which approached neutrality in the environment, which could be verified by the concomitant reduction in the Eh, observed during the period of inundation.

While the experiment demonstrated the consumption of the carbon in the soil through redox reactions, in the natural environment, there is a constant renovation of this material through deposits of leaf litter, which promotes a buildup of humidified organic material throughout the soil profile. The organic material and relative fertility of this gleysol distinguishes it from the adjacent *terra firme* soils, which are typically used for the production of food crops in the region. As they are mostly of low fertility, food production on these soils demands a considerable input of fertilizers. In comparison with saline gleysols, the soils analyzed here are appropriate for the cultivation of a wide variety of plant species, rather than only saline-tolerant native species.

The present study identified a number of different components that contributed to the fertility of the soil in this environment. The study of the effects of inundation revealed that the permanent presence of water in the soil provokes a modification of fertility through the

release of ions into the soil solution, resulting in short-term benefits. The presence of clay minerals of the 2:1 type permits an increase in CEC levels, which contributes to the maintenance of fertility in conjunction with the organic material in the soil. Clogging, that is, the natural deposit of the inorganic fraction in suspension, which occurs during each tide, has been identified as the primary factor determining the fertility of these *várzea* soils. The constant addition of the suspended material from the river water during tidal incursions contributes to the maintenance of fertility levels. As shown in the experiment conducted here, however, inundation of gleysols of the same mineral content and granulometry with water lacking the suspended material may also contribute to a temporary increase in fertility, confirming the possibility of conducting irrigated agriculture on these *várzea* soils.

5. ACKNOWLEDGMENTS

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5 GEOCHEMICAL INTERACTIONS BETWEEN THE WATER AND SOIL OF THE MANGROVE FOREST AS A PROCESS OF FERTILIZATION IN BRAGANÇA, NORTHERN BRAZIL (Submetido à Geoderma)

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ABSTRACT

Mangrove soils, which are salic gleisols in pedological terms, are abundant on the northeastern coast of the Brazilian state of Pará. These soils are of considerable importance to the local human populations, which depend on the natural resources provided by the mangrove, in particular crustaceans, for their subsistence. The present study evaluated the availability of nutrients in this soil following immersion in distilled water. The study area is located on the estuary of the Caeté River in the municipality of Bragança, a region dominated by extensive tracts of mangrove forest. Soil samples were collected from each of the principal horizons and a sample of the suspended material (suspensate) was also obtained for analysis from the water adjacent to the soil profile. A separate sample of 97 kg of soil was collected for the experimental procedure. The soil and suspensate samples were investigated by granulometry, XRD mineralogy, total chemical analysis by ICP-OES/MS, and fertility analyses. For the experimental procedure, four subsamples of the soil were placed in Styrofoam containers and immersed in distilled water. Subsequently, the pH and Eh of these samples were measured, and the available concentrations of Ca, K, Cu, Fe, C, and P were determined over a 132-day period. The results indicated that both the soils and the suspended material were relatively fertile, with high levels of organic material only in the soil profile. The soils and suspensate had a similar composition – quartz, kaolinite, illite, and smectite, as well as anatase as an accessory mineral. The presence of halite reflects the high salinity of the water, and is precipitated when the water evaporates. Immersion provoked profound alterations in the fertility of the soil, with the pH increasing during the first few days, but never exceeding 6, and stabilizing at between 5 and 6 after the 15th day of immersion. The Eh readings fell abruptly during the first days of immersion, reaching negative values after the 15th day, but never exceeding -281.25 mV. Carbon decreased erratically as it was consumed, principally during the first 115 days of the experiment. Some of the nutritional elements analyzed varied considerably. Iron accumulated to reach relatively high, but fluctuating values, as did manganese, although with relatively low soluble values in comparison with other gleisols in the same region. Phosphorus accumulated during the first 12 days, but then decreased erratically until the end of the experiment, although in this case, the values were invariably relatively high. Zinc behaved in a manner similar to manganese, but with even lower values, as expected, but accumulating following immersion. Calcium and potassium also behaved in a similar fashion, increasing erratically until the 20th day, and then decreasing until the 45th day. From this moment onwards, Ca continued to accumulate erratically, while potassium fluctuated between 0.96 and 1.43 mg/dm³. The values for Ca were around 200 times the levels recorded for K. The study confirmed that the local gleisols are highly fertile, and are more fertile than the other gleisols that have been studied in the region. The presence of 2:1 clay minerals and high levels of organic carbon contributed to the considerable fertility of this soil. The high levels of phosphorus in the soil were probably related to the ferrous oxy-

hydroxides it contained, as well as the organic material. The experimental procedure confirmed the alterations that occurred in the environmental conditions and fertility of the soil, resulting in the presence of the key elements at levels adequate for plant nutrition, including those of potassium, despite its reduced concentrations. The study also indicates the importance of the suspensate for the maintenance of the fertility of the soil, given its high levels of exchangeable cations and available phosphorus.

Key-Words: Floodplain, surface geochemistry, flooded soil, soil fertility, Amazon lowland

1. INTRODUCTION

The characteristics acquired by soils following inundation have been described by a number of authors (Ponamperumma, 1972; Fageria, 1984; Camargo *et al.*, 1999; Assis *et al.*, 2000; Otero *et al.*; 2009). In general, this process appears to have potential benefits for the fertility of the soil, such as an increase in pH and reduction in Eh. In Japan, where rice is grown in artificial paddies, research has shown that the alterations that affect the soil are mainly due to the flooding of these fields, which increases the fertility of the soil (Otowa, 1967; Matsuzaka, 1969; Matzuzaka *et al.*, 1971). Water is present naturally in the profile of the soils of the estuary of the Amazon River, which has unique properties, including high fertility, with two types of soil being especially abundant – haplic gleisol in the freshwater floodplains, and salic gleisol in the mangrove sediments.

The effects of inundation on the local haplic gleisol, which is abundant on the lower stretches of the rivers of the Amazon estuary, have been analyzed experimentally in both short- (Silva *et al.*, 1996; Ferreira *et al.*, 1998; Mattar *et al.*, 2002; Silva, 2008) and long-term studies (Silva & Costa, 2011). The latter study focused on the sediments of the floodplain of the Guamá River adjacent to the city of Belém, and investigated the effects of flooding on the haplic gleisol, and the contribution of the mineralogical components of the suspended sediments of the water of this river (the suspensate) to the formation of these plains and, subsequently, their soils. The results indicated that flooding contributed to an increase in the fertility of the soil, for which organic matter and 2:1 clay minerals, which are present in this soil and the suspended material, were the principal agents.

In an overview of the formation of mangrove soils, Ferreira (2007) concluded that the pedogenetic processes involved are subsequent to the colonization of the habitat by plant species adapted to the local conditions. These soils are typically gleisols, quartzarenic or alluvial typics or podzols (Prada-Gamero *et al.*, 2004).

In the coastal region of Pará, however, salic gleisols predominate, as shown in Ferreira & Botelho's (1999) study of the estuary of the Morcegos River adjacent to the city of Marapanim. In this study, the effects of flooding were tested using distilled water over a 45-day period, so the role of the mineralogical composition of the soil or the suspended material in the water that floods the mangrove was not taken into account. Despite the short period of this study, it demonstrated an increase in fertility (availability of nutrients) and increased pH.

Mangroves are important not only in terms of the extension of the area they occupy, but also because of their environmental and social relevance. In Brazil, they cover a total area of 13,000 km², extending from Laguna, in the state of Santa Catarina, to northern Amapá. This area corresponds to approximately half of the mangroves found in the Americas (Burke *et al.*, 2001; Souza Filho, 2005). In the state of Pará, the soils of the mangrove, which is also known as a fluvial-marine swamp, extend between the mouths of the Pará and Gurupi rivers, that is, along the whole of the length of the state's northeastern coastline. This region is known locally as the Salgado zone (Lima & Tourinho; 1995; Lima *et al.*; 2001), and is classified as a macrotidal mangrove coast (Souza Filho, 2005). These mangroves represent 56.6% (7591 km²) of the total area of this type of ecosystem in Brazil, and constitute the largest continuous tract of mangrove forest anywhere in the World.

Mangrove forests represent an important ecosystem in tropical coastal regions, and are characterized by a specific flora, adapted to these swampy environments immersed in brackish waters of moderate to high salinity (Shaeffer-Novelli; 1999). These habitats are an economically important source of animals such as mussels (*Mytilus edulis*), oysters (*Ostrea edulis*), shipworms (*Neoteredo reynei*), shrimp (*Macrobrachium carcinus*), marine crabs (*Scylla serrata*), and mangrove crabs (*Ucides cordatus*), as well as numerous fishery resources (Furtado *et al.*, 2006), that are essential to the subsistence of the local human population, which exports the excess production to other regions around the country. The Management and Dynamics of Mangroves (MADAM) Project, based in the region of Bragança, in the northeast of the Brazilian state of Pará, has shown that approximately 80% of the rural families in this region depend on mangrove resources – either directly or indirectly – for their subsistence (Lieberei *et al.*; 2002). Mangrove forests also play an important role in the capture of atmospheric carbon, with an index of 210 g of CO₂ m⁻² yr⁻¹ (Chimura *et al.*, 2003; Otero *et al.*, 2009; Kristensen, *et al.*, 2008).

The exuberant mangrove vegetation of the region of Bragança includes trees that may reach 30 m in height and a meter in diameter, although the biological diversity of this ecosystem is naturally much lower than that found in typical Amazonian *terra firme* forest, or

even its freshwater swamps. This hydromorphic environment, which is dominated by a subsaline, muddy substrate, with a tendency for the predominance of reducing conditions, is highly unfavorable for most plant species. The tree species adapted to this environment are the red mangrove (*Rhizophora mangle*, L.), the white mangrove (*Laguncularia racemosa*, L.), the black mangrove (*Avicennia* sp. L.), and the button mangrove, *Conocarpus erectus*, L. (Vilhena *et al.*, 2010). In these species, the seeds germinate while still attached to the mother-plant, which guarantees their pre-development before they are immersed in the saline hydromorphic substrate below the tree. The leaf litter accumulating beneath these trees determined the black and grayish coloration of the soil profile (Cintrón & Schaeffer-Novelli; 1983). The present study evaluates the geochemical dynamics of the availability of the nutrients in the mangrove soils of Bragança, in northern Brazil, when immersed under distilled water.

2. MATERIALS AND METHODS

The present study was based on the methods used by Silva & Costa (2011) to evaluate the geochemical transformations of a haplic gleisol on the estuarine floodplain of the sediment-laden Guamá River, which is part of the estuarine complex of the Amazon River. Here, samples of the soil and suspended material (suspensate) were collected from the estuary of the Caeté River, which feeds into part of the mangrove system of Bragança, in order to examine the possible relationship between them. Soil samples were collected with two objectives, to (i) characterize the soil profile, based on samples representing the A₁, AC, and C_g horizons, and (ii) conduct an experimental analysis of the effects of the immersion of the soil with distilled water, in order to evaluate the adsorption and desorption capacity of the soil in relation to the chemical elements that determine its fertility.

Each sample was designated according to its horizon: A₁ for depths of zero to 36 cm, AC for those between 36 cm and 75 cm, and C_g for depths of 75 to 180 cm. The lower limit of the latter category is only an estimate, given the rapid flooding of the hole excavated for the collection of samples, which impeded the reliable visualization of its bottom. The sample denominated EXP-01 was composed of 65 separate samples collected with a Dutch auger from the upper 20 cm of horizon A₁, the stratum from which plants normally extract their nutrients. The samples, which each weighed around 1.5 kg, were distributed randomly within an area of approximately 10,000 m². The 65 samples were mixed and homogenized, and then air-dried, crushed with a wooden roller and allocated to experimental lots.

Samples were collected in the rural zone of the municipality of Bragança, on the estuary of the Caeté River, approximately 5.2 km from its mouth (location of the profile: $0^{\circ}50'38.38''$ S, $46^{\circ}38'51.67''$ W), close to the highway that links Bragança to the coastal village of Ajuruteua (Figure 1). The vegetation at the site is exuberant, and includes the principal tree species – *Rhizophora mangle*, L. (red mangrove), *Laguncularia racemosa*, L. (white mangrove), and *Avicennia sp.*, L. (black mangrove) – found in this region.

The sample of suspended material, SUSP-01, was subtracted from water collected from the left margin of the Caeté River (location of the sampling station: $0^{\circ}50'43.33''$ S, $46^{\circ}38'53.12''$ W), 140 meters from the location of the soil profile. A total of approximately 600 liters of water was collected in three 200-l polyethylene containers, which were left to decant naturally (without the addition of flocculant) for three months. The supernatant was then removed and the remaining material was transferred to a smaller container and decanted and centrifuged a second time. The solid residue, or suspensate, was transferred to a desiccator for 24 hours. A total of 12.677 g of suspensate was obtained. The fertility of this sample was analyzed, including the identification of available chemical elements, mineralogical analysis by X-ray diffraction (Table 1, Figure 3), and the determination of the total chemical composition.

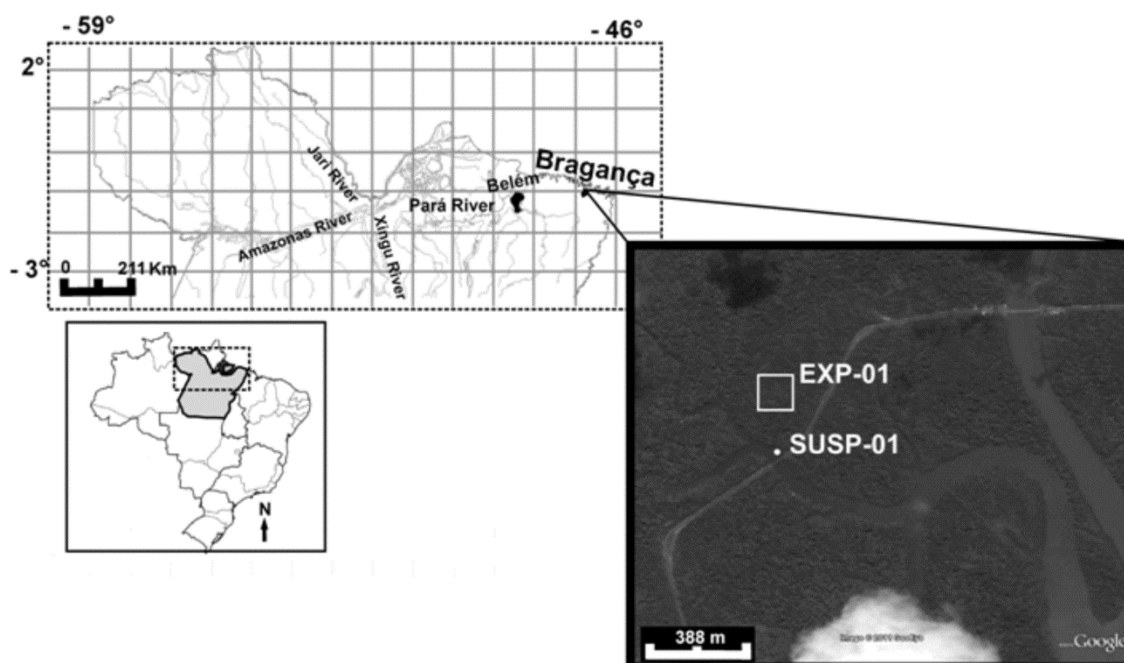


Figure. 1. Location of the study area in the rural zone of the municipality of Bragança on the northeastern coast of the Brazilian state of Pará, and the locations at which soil ($0^{\circ}50'38.38''$ S, $46^{\circ}38'51.67''$ W) and water samples ($0^{\circ}50'43.33''$ S, $46^{\circ}38'53.12''$ W) were collected.

The soil samples were subjected to the following analyses:

- 6) Granulometric analyses of sample EXP-01 by the sieving and pipette method, as described by EMBRAPA (1997) in the UFRA laboratories;
- 7) Analysis of fertility, based on EMBRAPA (1997), for the three samples of the soil profile (A_1 , AC, C_g) and the EXP-01 and SUSP-01 samples, in the UFRA laboratories;
- 8) Mineralogical analysis of the EXP-01 and SUSP-01 samples by X-Ray Diffraction (XRD) at the UFPA Geosciences Institute, including the total sample, powder method, clay fraction with oriented blades for the precise characterization of the minerals in the clay. The samples in oriented blades were glycolated and then warmed, following the classic procedures for the determination of clay minerals, and each step was submitted to XRD. An X'Pert Data Collector diffractometer (version 2.1a) was used for the collection of the data, which were processed in the X'Pert HighScore software (version 2.1b) for the confirmation of the minerals;
- 9) The samples of the upper (A_1) and lower horizons (C_g) and the suspended material were used for total chemical analyses (major, minor, and trace elements) in order to verify genetic affinities between the samples, as well as to evaluate their contribution as a source of nutrients. The ICP-MS and ICP-OES analyses were conducted at the Acme Analytical Laboratories Ltd., in Vancouver, Canada. The samples to be converted into liquid analyte were compressed and assimilated with lithium metaborate, and then dissolved in nitric acid. Another part of the sample was dissolved in aqua regia for analysis by ICP (Acme Labs, 2008).
- 10) The experimental procedure was carried out in the Chemical Analyses Laboratory of the UFPA Geosciences Institute. A subsample of 28 kg of sample EXP-01 was divided into four lots, which were placed in four 7-l Styrofoam boxes. Each box was filled with distilled water up to a depth of 2 cm above the upper limit of the sample, which was topped up to maintain the level as the water evaporated. Samples were taken from the immersed soil in the four boxes every day over the first five days of immersion, and then at irregular intervals, varying from one to 15 days over the subsequent days. The shorter interval during the initial sampling was important because the greatest variation tends to occur during the first few days of immersion (Ponnamperuma, 1972). The samples were collected on alternating days during the first month of the experiment, and then at gradually increasing intervals until a maximum of 15 days, with a total of 100 samples being collected. The experiment lasted 132 days, except for the analysis of carbon, which was continued until the 276th day. For each sample, the physical-chemical parameters pH and Eh were measured using a potentiometer, and the concentrations of available P and exchangeable Ca, K, Zn, Mn, Cu, and Fe were determined. The levels of the latter (Ca, K,

Zn, Mn, Cu, and Fe) were determined by atomic absorption, P by spectrophotometry, and organic carbon by the Walkley-Black method (EMBRAPA, 1997). All these analyses were conducted in the laboratories of the UFPA Geosciences Institute.

The available levels of the nutrients in the samples (step 5 above) were determined based on the development of a specific analytical procedure for their collection and analysis. The preparation of the samples for these analyses normally began with the drying of the soil, followed by crushing and, in some cases, grinding, followed by sieving through a 2 mm mesh. As mentioned above, the transformations occurring in the soil while immersed revert to the conditions presented by the aerobic soil when it is dried. Given this, the alterations that may have occurred in the pH, Eh, and nutrient availability are modified to aerobic conditions, which may be considerably different from the conditions presented by the environment at the moment of sampling. In order to obtain results consistent with these humid conditions, the analyses were conducted on the humid soil, as recommended by Silva *et al.* (1996); Ferreira *et al.* (1998); Ferreira & Botelho (1999); Mattar *et al.* (2002), and Silva (2008).

For this, the samples removed from the experimental lots included 10 ml of humid soil, which were weighed and analyzed. To convert the results obtained from this humid analysis to those of dry soil, a humidity factor was obtained. For this, a new humid sample was taken, which was dried at 105°C in a stove followed by a period in a desiccator, before weighing. The correction factor was based on the difference between the humid and dry weights. This factor was used to adjust the results obtained from the analysis of the humid soil, for the dry weight in grams.

3. RESULTS AND DISCUSSION

3.1. Mineralogy, fertility, and granulometry

The gleisol analyzed in the present study is composed of quartz, kaolinite, illite, smectite, and anatase, in decreasing order of abundance. The suspended material consisted of these same minerals, although in a slightly different order of abundance – quartz, kaolinite, smectite, illite, and anatase. The halite identified in the sample must represent the precipitation of the salts dissolved in the water, following the drying of the sample.

As retainers of cations, smectite and illite are of particular importance for the fertility of this soil, and are present in both the soil itself and the suspended material, indicating that the

former was supplied by the latter. The suspended material of the Caeté River is derived from the erosion of the river bed and the re-suspension of the finer particles during the ebb and flow of the tidal currents.

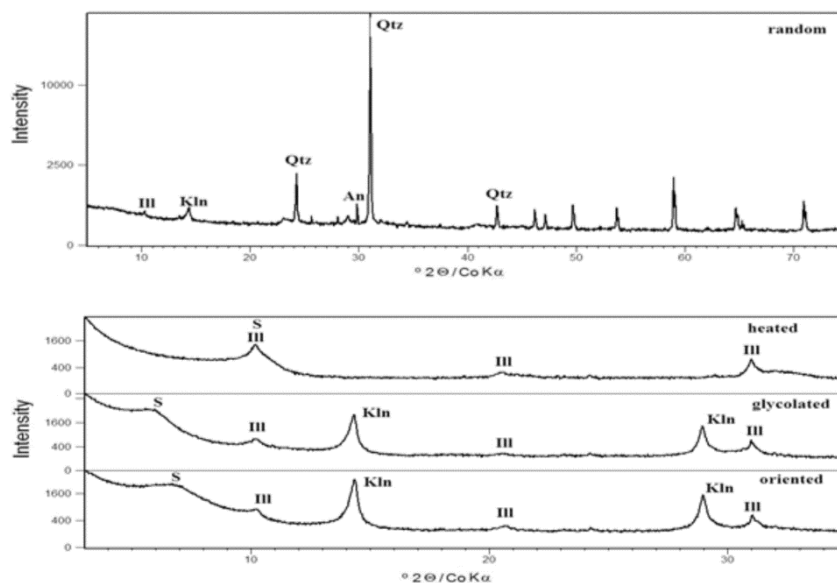


Figure. 2. Patterns of X-ray diffraction obtained for the soil samples and the respective oriented fractions of the clay minerals, with the principal mineral phases being identified as: smectite (S), illite (Ill), kaolinite (Kln), quartz (Qtz), and anatase (A).

In addition to these minerals, Costa *et al.* (2004), Silva *et al.* (2005), Berredo *et al.*, (2008), and Vilhena *et al.* (2010) have identified K-feldspar, pyrite, halite, and jarosite in mangrove sediments from the same region, and concluded that they were of autologous origin. However, the smectite found in the suspended material must be derived from the sediments of the regional substrates that contribute to the discharge of the rivers that form the Amazon estuary. Smectite represents 48% and kaolinite, 24% of the clay minerals of the upper 10 cm of the mangrove soils of Bragança (Costa *et al.*, 2004).

In addition to these minerals, the soils analyzed here are rich in organic material, varying from 18.14 g/dm³ in the A₁ horizon to 45.67 g/dm³ in the C_g horizon, values much higher than those recorded for the haplic gleisol of the Guamá River, where a concentration of 6.72 g/dm³ was recorded in the A₁ horizon, and 13.43 mg/dm³ in the C_g horizon (Silva & Costa, 2011). The organic material, together with the 2:1 clay minerals, which are abundant in these sediments, is important for the soil's cation exchange capacity (CEC).

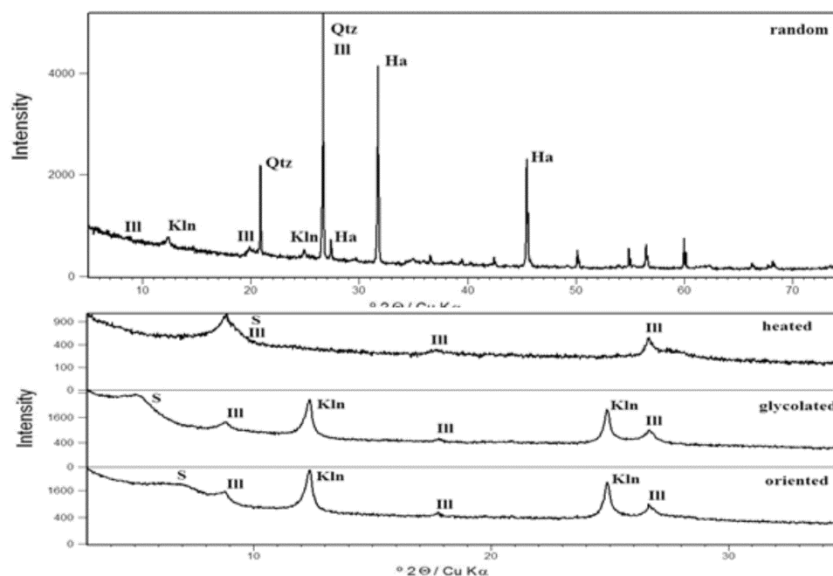


Figure. 3. Patterns of X-ray diffraction obtained for the sample of suspended material and the respective oriented fractions of clay minerals, with the principal mineral phases being identified as: smectite (S), illite (Ill), kaolinite (Kln), quartz (Qtz), and anatase (A).

The results of the analysis of the fertility of the soils and the suspended material indicate that both are fertile, although more so in the case of the suspensate, in which there was considerable base saturation and extremely high concentrations of phosphorus. The greater abundance of 2:1 clay minerals in the suspended material undoubtedly contributed to the fixation of cations, but more importantly, the fact that, as these minerals have yet to be consumed by the plants, they remain adsorbed in the suspended material, allowing their transportation and deposition. This indicates the fundamental importance of this suspended material for the maintenance of the fertility of the soil, through the incorporation of both the solid component (the sediment) and the water, which contains dissolved nutrients, during the tidal cycle.

The total chemical analysis of the salic gleisol recorded a concentration of 0.10% of CaO in the superficial layer, and 0.31% in the C_g horizon, with 0.47% and 1.69% of total MgO in the A₁ and C_g horizons, respectively. Similarly, potassium was present in the form of K₂O, with a concentration of 0.72% in the A₁ horizon, and 1.70% in the C_g horizon. Typically, in Amazonian soils, the total levels of these elements, even when relatively high, do not reflect the available levels. In the present case, however, the available levels of calcium and magnesium, and even those of potassium, are relatively high (Table 1), both in the soil and the suspended material.

Phosphorus is an interesting example of this phenomenon. The total values for this element were 0.05% of P₂O₅ in the A₁ horizon, and 0.09% in the C_g horizon. The levels of

available phosphorus were relatively high, however, in both the soil (20.67 mg/dm³) and suspended material (86.58 mg/dm³), indicating the occurrence of a continuous renovation of this element in the soil. This would occur daily through the influx of the tides, bringing suspended material rich in chemical nutrients.

Table 1. Parameters of fertility recorded during the present study, including the concentrations of available and exchangeable elements in the samples of soil and suspended material from the Caeté River

Horizon	pH		C	Organic material	P	Ca	Mg	K	SB	H	Al	T	V	M
	H ₂ O	KCl		g kg ⁻¹	mg.dm ³				cmol _c .dm ³				%	
A ₁	6.08	5.55	10.52	18.14	20.67	3.81	12.85	2.10	18.74	2.35	0.05	21.14	88.64	0.26
AB	5.44	5.10	16.75	28.88	25.40	4.57	12.00	2.18	18.75	2.14	0.05	20.94	89.54	0.26
C _g	4.26	4.01	26.49	45.67	19.46	4.76	12.38	2.34	19.48	4.25	0.14	23.87	81.60	3.21
SUSP	-	-	-	-	86.58	2.60	0.53	1.79	4.92	1.22	0.26	6.4	76.87	5.01

OBS: The A₁ sample (equivalent to EXP-01) had the following granulometric composition: coarse sand = 105.80 g/kg; fine sand = 528.30 g/kg, silt = 76.60 g/kg, and clay = 298.3 g/kg.

The ΔpH indicates the predominance of negative charges in all the horizons, emphasizing the importance of the 2:1 clay minerals observed during the study for the retention of cations. This explains the relatively high values for CCE. Aluminum, which presented total values of 5.35% of Al₂O₃ in the A₁ horizon, and 16.52% in the C_g horizon, did not participate actively in the saturation complex, with only 0.26% of saturation in the A₁ horizon and 3.21% in the C_g horizon (Table 1), which were fully occupied by nutrients, presenting 88.64% base saturation in the A₁ horizon and 81.60% in the C_g horizon.

3.2. Availability of chemicals under prolonged immersion

The immersion of the soil samples in distilled water for a period of approximately four months provoked alterations in the fertility of the soil and the availability of the elements that function as plant nutrients. The analysis of variance indicated that the alterations were highly significant for all of the parameters studied (Table 2).

Table 2. Analysis of variance for the effects of immersion of the soil in the laboratory with distilled water over time (days).

FV ¹	pH	Eh	P	Ca	K	Zn	Mn	Fe
Days	*	*	*	*	*	*	*	*
D.F. ²	22	22	22	22	22	22	22	22
Repetitions	3	3	3	3	3	3	3	3
CV ³ (%)	5.06	29.23	23.37	11.49	45.61	15.92	33.64	15.40

*Significant ($p < 0.01$).

¹Variation Factor; ²D.F. = degrees of freedom; ³ CV = coefficient of variation.

Table 3. Mean values obtained from the four experimental mangrove soil samples for pH and Eh, and the chemical concentrations of available P, Ca, K, Zn, Cu, and Fe, during immersion with distilled water over a 132-day period, and for organic carbon over 276 days of immersion.

Day	pH	Eh mV	P mg/dm ³	Mn mg/dm ³	Fe mg/dm ³	K mg/dm ³	Ca mg/dm ³	Zn mg/dm ³	Day	C g/dm ³
1	3.73	266	103.18	14	1168.25	0.15	353	3	1	2.84
2	4.13	240.25	105.28	6	1284	0.15	369.25	4.25	14	3.52
3	4.25	214.5	111.49	7.75	1387.75	0.67	342.25	3.5	30	2.38
4	4.29	182.5	110.62	7	1311.5	1.31	348.5	3	38	2.29
5	4.31	172	142.4	8	1720.25	1.31	279	2.5	60	1.52
8	4.48	131	136.31	6.75	1408.75	0.67	291.25	3	81	1.98
10	4.65	100.25	148.36	8	1850	0.15	289.75	4.25	97	2.10
12	4.67	24	173.43	9.25	2084.5	0.39	456.75	3.25	115	1.18
15	5.13	-39.75	33.04	6.75	1606.25	1.29	476.25	3.25	133	2.64
17	5.41	-170	35.89	5.25	2429.75	1.92	442	3.75	170	2.00
19	5.49	-147.75	45.63	8.5	2386	2.62	461.5	5.25	187	2.10
23	5.59	-200	50.77	7.5	2410	1.51	389	2.25	202	0.89
31	5.48	-221.75	144.05	9	1549	1.29	400	4.25	221	0.38
38	5.37	-228.5	87.2	10.75	2133.75	1.43	373	4	276	1.43
45	5.39	-262.5	66.12	4.75	4450.5	1.28	278	6.75		
59	5.37	-273.5	48.92	5.75	5074.75	0.96	496	4.75		
66	5.44	-271.25	67.63	12.5	5136.5	1.32	348.25	2.25		
73	5.25	-272.25	69.74	10.25	4252	1.09	439.25	4		
90	5.35	-264.5	50.12	11.75	4701.75	1.22	493	5.25		
97	5.36	-275	38.03	11.25	3929	1.39	407.25	4.75		
118	5.43	-247	53.7	12.75	2184	1.27	552.25	6.75		
125	5.6	-279	56.78	-	2799	1.43	543	6.25		
132	5.34	-281.25	52.46	-	2451	1.24	546	6.5		

The pH readings (Table 3 and Figure 4-A) increase rapidly during the first week, from initial values of less than 4 to moderately acidic values of between 4.1 and 5.6, remaining

practically stable – between 5.3 and 5.6 – between the 17th day and the end of the study period. This pattern differs from that of other haplic floodplain gleisols, which were close to neutrality (Silva *et al.* 1996; Mattar *et al.*, 2002; Lima *et al.*, 2005). It seems likely that the acidic conditions recorded in the present study were the result of the accumulation and decomposition of organic material. The availability of nutrient elements also depends on the pH (Lopes, 1986), given that most macronutrients are found in unavailable forms at low pH. By contrast, the availability of some micronutrients (Cu, Co, Fe, Mo, and Zn) declines substantially at high pH levels. However, the pH levels recorded in the present study support the availability of most elements considered essential for plant growth.

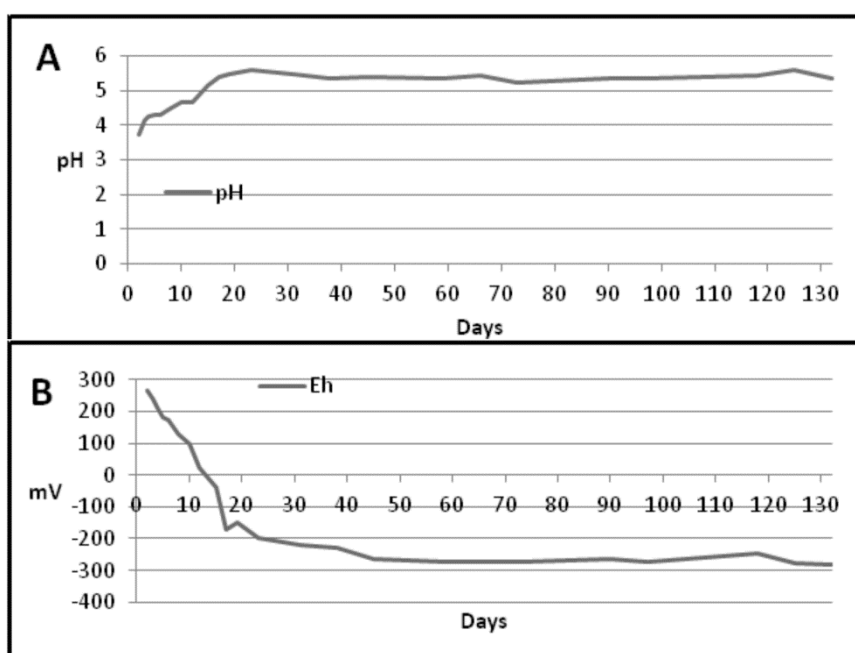


Figure 4. Variation in the mean pH (A) and Eh (B) values recorded during the 132 days of immersion

The Eh readings fell drastically over the first 15 days, in direct contrast with the pH values, reaching negative levels by the 15th day, and remaining at between -200 and -300 mV from the 17th day onwards (Table 3, Figure 4-B). These values contrast considerably with those recorded for the haplic gleisol of the Guamá estuary, in which the values fell more rapidly to much lower levels, of between -300 and -400 mV (Silva *et al.*, 1996; Silva, 2008; Silva & Costa, 2011). According to Sahrauat (2003), values of Eh of this level indicate the absence of electron acceptors, which impedes the oxidation of organic matter and would account for the accumulation of this material in the mangrove.

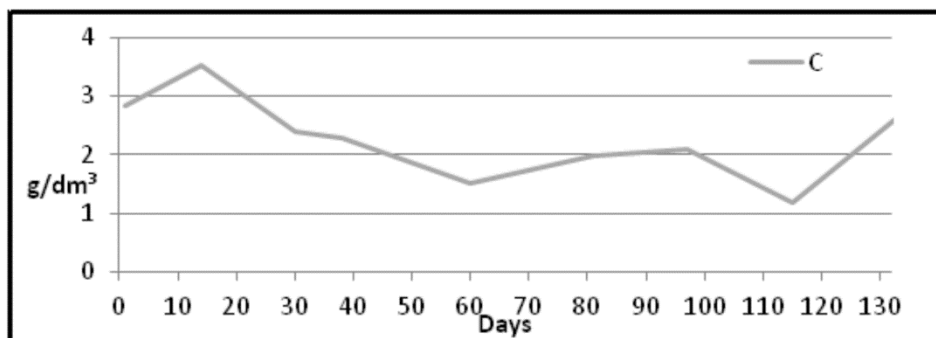


Figure 5. Variation in the mean concentrations of dissolved organic carbon over the 132 days of immersion

The positive Eh values recorded during the first few days are reflected in an increase in dissolved carbon (from 2.84 to 3.52 g/dm³) during the initial 15 days of the study, which then decreased linearly until the 60th day, when it increased again until the 97th day, declining again until the 115th day (Table 3, Figure 5). After the 14th day, the concentration of dissolved carbon stabilized at a level of around 2.0 g/dm³. The pattern of variation in this component was roughly parallel to that observed in the Eh values, that is, as this parameter stabilized, so did the carbon concentrations, a pattern also seen in the pH readings. Overall, then, the conditions of the experiment remained relatively stable from the 15-17th day onwards, with a general tendency for an anoxic environment.

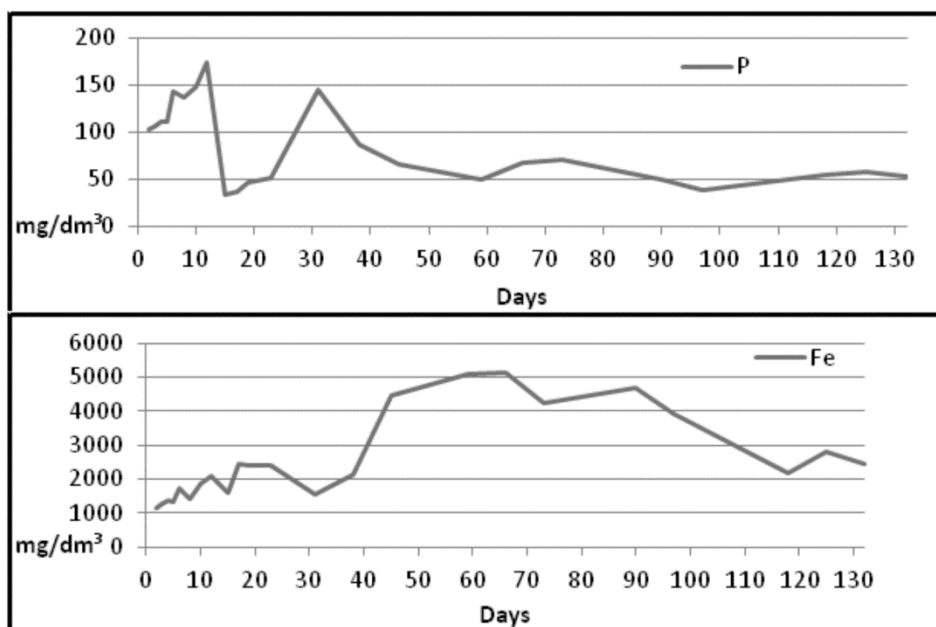


Figure 6. Variation in the mean concentrations of iron and available phosphorus over the 132 days of immersion

The dissolved carbon concentrations recorded in the present study were relatively high in comparison with those recorded in yellow latosol 1.08 g/dm³ from the municipality of

Tomé-Açu, also in the Brazilian state of Pará (Vieira, 1988), although they were generally lower than the concentrations recorded in haplic (2.4 g/dm^3) and salic gleisols (6.6 g/dm^3) in Salvaterra and Bragança, respectively, also in Pará. Overall, then, salic gleisol tends to present the highest levels of dissolved carbon.

The mean concentration of phosphorus increased considerably over the first 10 days, from 103.18 mg/dm^3 to 148.36 mg/dm^3 , but then fell rapidly until the 23rd day, reaching 50.77 mg/dm^3 , and then increasing sharply again to 114.05 mg/dm^3 by the 31st day, and finally stabilizing at between 50 and 75 mg/dm^3 until the end of the study period (Table 3, Figure 6). In general, this pattern is consistent with those of the Eh values and concentrations of dissolved carbon which, together with the pH, define the environment. It seems likely that the phosphorus liberated was derived from ferrous oxy-hydroxides, which became more unstable as the environment became increasingly reducing, neutralizing the consumption of organic material.

A similar pattern was recorded for the phosphorus content of haplic gleisols from the same region in a similar experiment (Silva *et al.*, 1996, Mattar *et al.*, 2002, Silva, 2008). Mello *et al.* (1992) recorded the presence of this element in ferrous oxy-hydroxides, such as ferrihydrite, lepidocrocite, and goethite, and Lima *et al.* (2005) found larger quantities of phosphorus liberated in 11 different soils containing these minerals in reducing conditions in the Amazon basin. These minerals were not detected by XRD, although this does not mean that they were completely absent. In an analysis of the mangrove soil of the Marapanim River, in the same region (Salgado zone), Silva (2006) only observed oxy-hydroxides covering the quartz in the form of a thin film. The immobilization of the phosphorus may occur through its co-precipitation as ferrous phosphate, that is, vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Chancon, 2006).

The diagrams of binary dispersal (Figure 7) and the Pearson correlation coefficients (Table 5) indicated that the phosphorus content correlated in a linear fashion with that of iron only at the lower P values ($20\text{-}70 \text{ mg/dm}^3$) and higher Fe values (Figure 7), which corresponds to the period of the experiment when the environment appeared to have stabilized (Figures 4, 5, and 6). Overall, the correlations tended to be negative, while there was no correlation with Ca and Mn (Table 5). Silva & Costa (2011) recorded positive correlations between phosphorus and soluble Ca, Fe, and Mn in the haplic gleisol of the Guamá River. This suggests that the phosphorus is being liberated by the ferrous minerals, when decomposed in the anoxic environment, as shown previously. The chemical analyses of the soluble fraction of the suspended material indicated that the available phosphorus is relatively abundant (Table 1), which indicates that the suspended material may be contributing to the

introduction of soluble phosphorus into the mangrove during the high tide, as a periodic contribution to this system.

Table 4. Pearson's linear correlation coefficients for the concentrations of P, Ca, Mn, and Fe recorded in the gleisol immersed during the present experiment (n = 40).

	P	Ca	Mn	Fe
P	1	-0.3688*	-0.0855 ^{ns}	0.4209*
Ca	0.3164*	1	0.5450*	0.5450*
Mn	0.3164*	-0.2766*	1	-0.2762*
Fe	-0.8201*	-0.0835*	-0.0342*	1

*Significant ($p < 0.01$; ^{ns} = not significant ($p > 0.05$)).

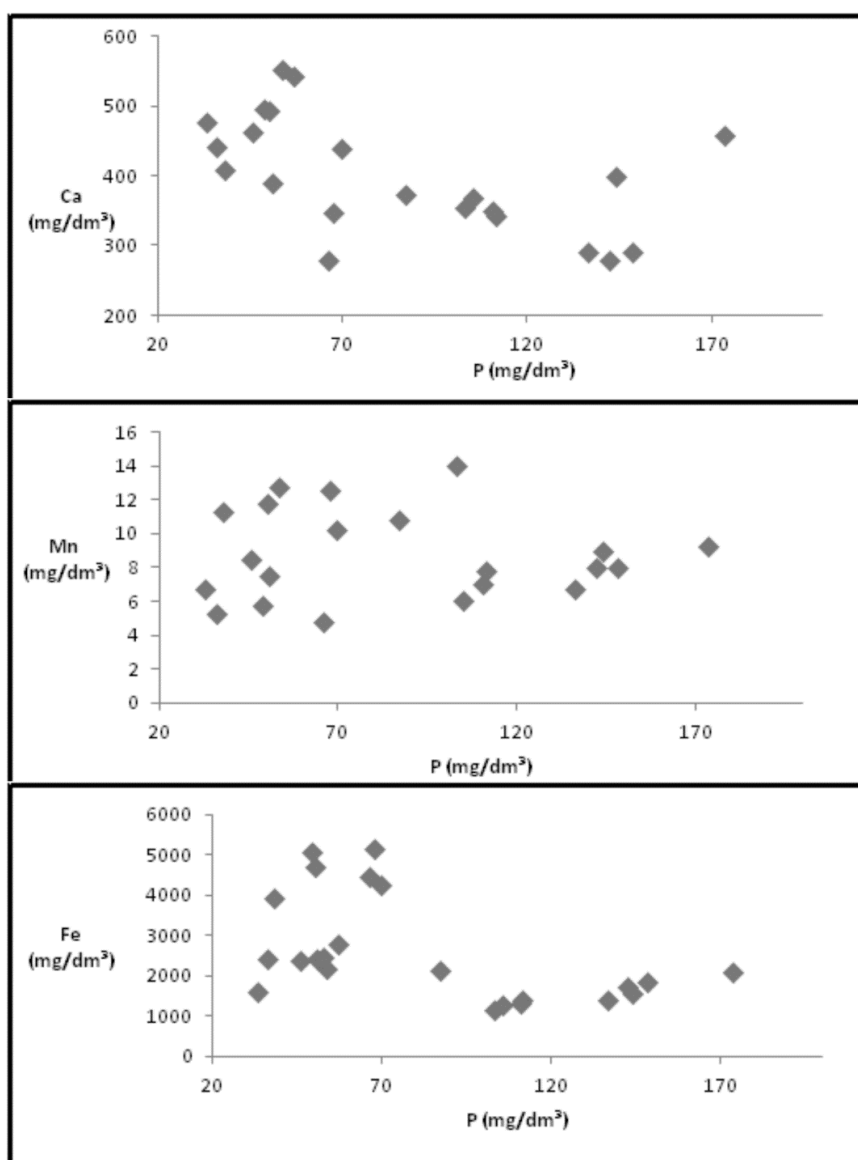


Figure 7: Binary dispersal diagrams for the soluble concentrations of P and Fe, P and Ca, and P and Mn.

In broad terms, the concentrations of soluble iron increased steadily until the 90th day, but reached a maximum value of 5136.5 mg/dm³ on the 66th day, decreasing abruptly to 1549 mg/dm³ on the 31st day (Table 3, Figure 6). Between the 90th day and the end of the experiment, the values decreased to 2451 mg/dm³. This pattern is practically the opposite of that of the Fe, as shown above. This indicates that Fe was solubilized continuously throughout most of the experiment, suggesting that the oxy-hydroxide minerals of this element become unstable in the anoxic environment, and probably only begin to precipitate as sulfides from the 95th day onwards, or when the oxy-hydroxides were exhausted. The dissolution of the iron oxy-hydroxides in anoxic environments, such as mangroves and freshwater swamps, has been well documented (Silva *et al.*, 1988; Silva *et al.*, 1996; Ferreira *et al.*, 1998; Ferreira & Botelho, 1999; Mattar *et al.*, 2002; Silva, 2008) as has the consequent precipitation of iron sulfides (Costa *et al.*, 1984; Vilhena *et al.*, 2010; Sherman *et al.*, 1988; Prada Gamero *et al.*, 2004). The levels of soluble iron recorded in this study may be considered toxic for most plants, for which concentrations of over 600 mg/dm³ may be deleterious (Fageria, 1984).

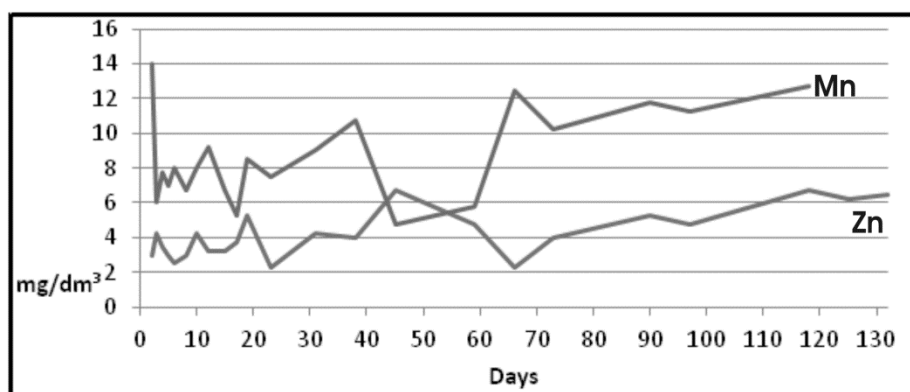


Figure 8. Variation in the mean concentrations of exchangeable manganese and zinc made available during the 132 days of immersion

The levels of soluble Mn recorded during the experiment were relatively low (Table 3, Figure 8), indicating the absence of manganese minerals or the presence of stable Mn minerals in the natural environment. However, Mn minerals were not identified by XRD, and the levels of total MnO in the samples analyzed were below mean crustal values (0.01%). Clearly, then, no manganese minerals were present in the soil investigated in the present study. Despite these extremely low values of soluble Mn, it was possible to identify a gradual increase during the course of the experiment, following an abrupt decrease on the second day of observation, with values of around 10 mg/dm³ until the 31st day, with abrupt reductions on the 45th and 59th days, followed by a gradual, but oscillating increase until the end of the experimental, reaching a maximum value of 12.75 mg/dm³ by the 118th day. These relatively

low quantities may have been liberated by the ferrous oxy-hydroxides. The reduction observed between the 45th and 60th days may represent the precipitation of MnCO_3 (rhodochrosite) or as FeCO_3 , siderite (Sanches, 1981), but the extremely low values do not support this conclusion. The concentrations of dissolved manganese (6-14 mg/dm^3) are considerably lower than those observed in the haplic gleisol of the Guamá River, in the Amazon estuary, which ranged from 100 to 300 mg/dm^3 (Silva & Costa, 2011).

In general, the concentrations of soluble zinc were distributed in a manner similar to those of Mn, but with much lower values, which were expected, given that this is a trace element and is thus much less abundant in the Earth's crust. The only distinction was observed in the period between the 45th and the 59th days, when, in contrast with Mn, there was an abrupt increase in the values, but then a marked reduction on the 66th day, when it reached 2.25 mg/dm^3 . Overall, the values for Zn were between 2.25 mg/dm^3 and 6.75 mg/dm^3 (Table 3, Figure 8). Ponnampuruma (1972), Neue & Mamaril (1985), and Fageria *et al.* (2011) all observed the exactly opposite pattern, that is, a reduction in the availability of Zn with increasing pH, which favors the precipitation of Zn(OH)_2 (wülfingite) and/or ZnCO_3 (smithsonite) through the accumulation of CO_2 resulting from the decomposition of organic material. Alternatively, the precipitation of ZnS would be favored under highly reducing conditions. In the present case, the extremely low values recorded for zinc (<6.75 mg/dm^3) would be insufficient for the formation of these compounds, especially in the anoxic environment that prevailed during most of the experiment. The low levels of available zinc may indicate the absence of minerals containing this element that are unstable in this type of environment. As in the case of Mn, the overall levels of Zn in the soil (10 ppm) are lower than crustal values, that is, they are of reduced significance. Silva & Costa (2011) recorded a similar pattern for Zn in the haplic gleisol of the Guamá River.

Like phosphorus, calcium and potassium are primary macronutrients, and are thus required by plants in relatively large quantities. In this immersion experiment, the concentrations of these two elements varied in a similar fashion until the 45th day, that is, increasing erratically until the 20th day and then decreasing until the 45th day. From this point onwards, the availability of Ca increased erratically, whereas K varied less, with a slight tendency to decrease overall. The levels of Ca (278-552 mg/dm^3 : Table 1, Figure 9) are approximately 200 times greater than those of K (0.15-2.92 mg/dm^3 : Table 1, Figure 9). However, these levels, even those of K, are adequate for plant nutrition (Lopes & Guilherme, 2005).

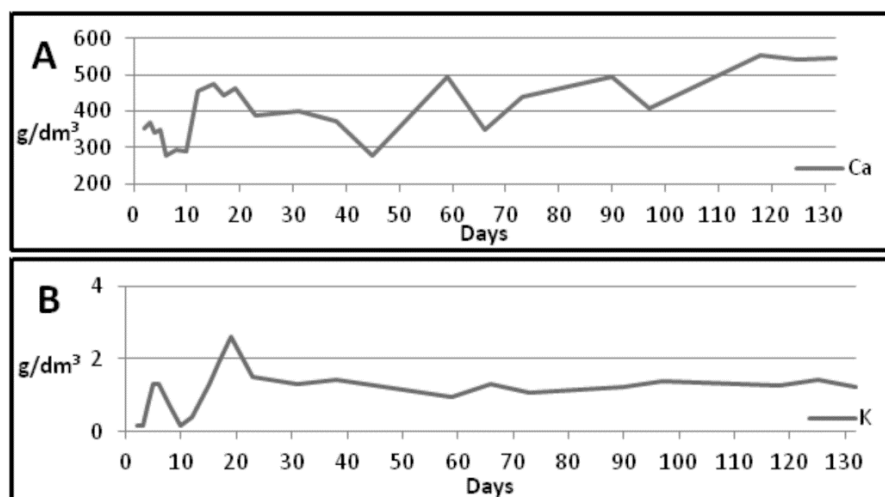


Figure 9. Variation in the mean concentrations of calcium (A) and exchangeable potassium (B) released during the 132 days of immersion.

Potassium was nevertheless only available during the first 19 days of the experiment, when it increased from 0.15 mg/dm³ to 2.62 mg/dm³ (Table 1, Figure 9). The total concentration of K₂O in the soil was 0.72%, although this reduced availability reflects the presence of the principal potassium-bearing mineral identified by XRD, illite-muscovite, which is of reduced solubility in soils (Loughnan, 1969; Mohr et al. 1972; Plas & Schuylenborgh, 1970).

The reduction in the availability of Ca in the first 10 days, when Eh was positive, that is, oxidizing, and the pH was acidic, may reflect the consumption of Ca for the formation of the carapaces of the crustaceans found in this environment. In the specific case of the present experiment, the absence of these organisms from the environment, may have led to the precipitation of this element as inorganic CaCO₃. The increasing availability of this element after the 45th day, when Eh was already negative, and the environment was reducing and less acidic, may represent the solubilization of the Ca carbonates, either precipitated or found in the carapace fragments. The oscillations towards lower values may represent the variations in the environment indicated by the fluctuating values for Eh, pH, and dissolved carbon. The total level of CaO in the soil was comparatively high (0.72%) and the available concentration was also relatively high, reaching 552 mg/dm³, which indicates that the element may be derived from minerals of high solubility, such as Ca carbonates, calcite or aragonite, the principal components of mangrove organisms, which were solubilized during the course of the experiment, which provided environmental conditions favorable to this process (Suguio, 1980; Chou *et al.*, 1988; Liang *et al.*, 1996).

4. CONCLUSIONS

The salic gleisol of the Bragança region is highly fertile, with a predominance of negative charges, which are mostly occupied by elements that are plant nutrients. The high CCE and high levels of base saturation recorded in the study indicate the presence of a eutrophic environment for plants. In addition, the reduced participation of aluminum in the exchange complex is confirmed by the saturation of extremely low levels of this element (0.26%). This permits the occupation of the exchange sites by the cations essential to plant nutrition. The mineralogical composition of the soil, with high concentrations of smectite and illite, which are also found in the suspended material, favors increased CEC.

In comparison with the haplic gleisol of the tidal floodplain of the Guamá River in the vicinity of the city of Belém (Silva & Costa, 2011), the samples analyzed in the present study were characterized by their higher fertility, and features such as the stabilization of the pH following immersion, moderate acidity, and high levels of organic material in the soil profile, much higher than those recorded in the haplic gleisols (Silva *et al.*, 1996, Mattar *et al.*, 2002, Silva, 2008). The Eh of this salic gleisol was also 100 mV lower than that of the haplic gleisol of the Guamá indicating that the reduction is interrupted at a certain point, leading to an accumulation of organic carbon. While this does not favor an increase in the pH towards neutrality, the presence of this organic material is advantageous in terms of the fertility of the soil.

The organic material must also be contributing to the formation of the CEC and thus providing the available phosphorus for this mechanism. However, the principal source of phosphorus appears to be the unstable ferrous oxy-hydroxides present under the dominant anoxic conditions.

The experiment showed that the soil responded to the addition of distilled water through modifications in the environment and its fertility. While the pH values stabilized at between 5 and 6, which are acidic values, this permits the decomposition of the minerals that form soils, making the elements essential to plant growth available. The quantities liberated into the soil were beneficial, even in the case of potassium, which was available in the smallest, but nevertheless adequate quantities. The concentrations of Mn, which responds to reductive processes in anoxic environments, were relatively low in comparison with those recorded in haplic gleisol (Silva and Costa, 2011), but once again, at adequate levels, considering that plants require extremely small quantities of this element.

Overall, the organic material and 2:1 clay minerals present in this mangrove environment constitute important determinants of the soil's fertility. The solubilized ferrous oxy-hydroxides were equally important as a source of P, M, and Zn. The primary source of the inorganic components of the salic gleisol is the suspended material of the Caeté River, which are fed into the mangroves on the tide.

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6 COMPARISON OF METHODS FOR THE EVALUATION OF THE FERTILITY OF GLEYSOLS IN NORTHERN BRAZIL (Submetido a Geoderma)

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ABSTRACT

The predominant soils of the Amazon estuary are haplic and salic gleysols, which are found over wide areas. The fertility of these soils is modified by their periodic flooding, which results in the exclusion of the air contained in the soil, and its modification into an environment appropriate for the development of anaerobic micro-organisms, which decompose the organic matter contained in the soil, using its elements and compounds to capture electrons, converting the soil into a reducing environment. This reduction provokes alterations in the fertility of the soil, but once the substrate is dried, these modifications revert to those of the oxidized environment. This pattern of modification constitutes a problem for the chemical analysis of these soils, given that the procedure usually employed for the processing of samples, which involves their pre-drying, produces results different from those likely found under the original field conditions. Given this, a number of researchers have analyzed the soil solution, which nevertheless introduces certain difficulties for the interpretation of the results, especially given the lack of control over the dilution of the samples. In order to provide more easily interpreted criteria for the assessment of the fertility of the soil, many scientists have analyzed humid soil samples, rather than pre-dried ones. The present study was based on the comparison of the results obtained from the analysis of the humid soil with those of the pre-dried samples, for which the results of the humid samples were adjusted using a conversion factor. Samples representing the soils of two different areas of the Amazon estuary in northern Brazil were compared here – haplic gleysol from the várzea swamps of the Guamá River in the estuary of the Pará River, and salic gleysol from the estuary of the Caeté River. The soil samples were analyzed in the laboratory, where they were immersed experimentally under distilled water (four replicates for each soil type) over a 132-day period, with observations being conducted over the first 52 days. Samples were taken at regular intervals and their chemical composition – P, Fe, Mn, Ca, K, Zn, and Cu – was analyzed using the two methods (humid and pre-dried). The results indicate that both procedures were able to detect the variation in the concentrations of the different elements over immersion time. Statistical analyses indicated significant differences in the results obtained for the two soil types. The results obtained by the two procedures for phosphorus, potassium, manganese, and zinc in the salic gleysol, and calcium in the haplic gleysol were virtually the same. The elements P, Mn and Cu in the haplic gleysol, and Ca in the salic gleysol presented significantly higher values in the analysis of the pre-dried samples. The values for the majority of the other elements – Fe, K, and Zn in the haplic gleysol and Fe and Cu in the salic gleysol – were higher for the humid samples. These samples also provided a more detailed analysis of the variation of these elements, which occurred at relatively low concentrations, primarily during the initial immersion period. The increased sensitivity of the humid soil approach in these specific cases represents a major advantage for the determination of the chemical characteristics of the soils found in the environments analyzed.

Key-Words: soil analysis, floodplain, surface geochemistry, mangrove.

1. INTRODUCTION

In Brazil, the chemical analysis of soils began in the 1960s, accompanying the expansion of industrialized agriculture in the country (Vetori, 1969; Guimarães *et al.*, 1970; Bloise & Moreira, 1976; EMBRAPA, 1979). Initially, analytical approaches were adapted from those used internationally (Jackson, 1958; Chapman & Pratt, 1961, Black, 1965). These procedures were eventually standardized by the Brazilian Agricultural Research Enterprise, EMBRAPA (EMBRAPA, 1979; EMBRAPA, 1997). In 1975, the Brazilian Society for Soil Sciences (SBCS) recommended the application of units of the international system (SI), with the aim of standardizing the terminology used for the analysis of chemical composition and fertility.

Scientists have long recognized the need to standardize procedures in order to guarantee the systematic interpretation of results. This preoccupation begins with the preparation of the samples, and includes the drying of the soil, which must be carried out in a stove or the air, which is then sieved through a 2 mm mesh. The material of less than 2 mm in size is referred to as the active fraction of the soil, and is sent to one of the existing soil laboratories for analysis (Camargo *et al.*, 1986; EMBRAPA, 1997). Such simple procedures facilitate the interpretation of the results, and have been adopted universally by the laboratories, with minor modifications in some cases, which should be informed together with the results.

However, some soils suffer alterations which affect their fertility when they are in contact with water, which changes once again when they dry out. Specifically, the presence of water fills the pores, and excludes the air. A few hours after flooding, the aerobic microorganisms contained in the soil use all the oxygen dissolved in the water, creating an oxygen-free environment, which is then occupied by facultatively aerobic or strictly anaerobic microorganisms, which multiply very rapidly and decompose the organic matter in the soil using the oxidized compounds in the soil to capture electrons, converting the substrate to a reductive condition (Ponnamperuma, 1972; Camargo *et al.* 1999, Inglett, *et al.*, 2012).

This process is characterized by a number of different alterations (Ponnamperuma, 1972, Sanches, 1981; Camargo *et al.*, 1999; Tan, 2011), which include the liberation of Fe and Mn following the reduction of the minerals that contain these elements. This affects indirectly the availability of phosphorus and other elements such as calcium, magnesium, potassium, and sodium, which, while not being reduced, may be displaced to the solution

through the production of soluble ions. The pH is also altered by the reduction reaction processed in the iron and manganese oxy-hydroxides, which produces hydroxyls, which make the medium less acidic (Catling, 1992, Lima *et al.*, 2005). After drying, however, the oxygen returns to the soil and oxidizes the reduced substances, provoking a reversion of the chemical and electrochemical transformations caused by the flooding (Ponnamperuma, 1972; Fageria, 1984; Assis *et al.*, 2000; Lima *et al.*, 2005).

A number of studies have analyzed the soil solution obtained from experimental samples for the evaluation of the effects of water on the soil pores. In this case, the solution is removed from the samples by suction or gravity, and the analysis is conducted without the application of a chemical extractor, although weak acids may be used in some cases (Silva *et al.*, 1988; Melo *et al.*, 1991; Silva *et al.*, 2003; Silva & Ranno, 1995, Lima *et al.*, 2005). The lack of published tables for the interpretation of the adjusted results of this approach and the absence of standards for the dilution of the experimental samples, which must be irrigated in order to maintain the water level, hampers the regular use of this procedure for the analysis of soils affected by inundation.

The measurement of the available elements through the evaluation of the adsorbed portion in the soil has a number of advantages. The analysis of the exchangeable cations and the non-exchangeable acidity (H^+) provides an estimate of the capacity of the soil for the exchange of cations according to the quantity of these charges, which corresponds to the total of negative charges in the soil. It is possible to assess the saturation of alkalis and aluminum in the soil in a similar fashion. These data, together with the availability of a large number of tables for the interpretation of soil analyses, established for agricultural purposes, facilitate the interpretation of the results of the analysis of these soils (Souza & Lobato, 2004; Jones Jr., 1984; Oleynik, 1984, Lopes & Guilherme, 2004).

Given these considerations, a number of authors (Silva, 1995; Silva *et al.*, 1996; Ferreira *et al.*, 1998; Ferreira & Botelho, 1999; Mattar *et al.*, 2002; Silva, 2008) have used the humid soil approach, that is, without drying the samples prior to analysis, in order to maintain the characteristics of the samples observed at the moment they were collected. As the results and the interpretation tables are designed for the volume or weight of dry samples, these authors have used a humidity factor to convert the results into values equivalent to those of dry samples. Given this, each humid sample is collected in duplicate, and while one sample is reserved for chemical analysis, the other is dried in a stove and then dehydrated in a dessicator prior to being weighed. The ratio of dry to humid weight provides a correction factor for the adjustment of the results. However, while this approach has been used in a number of

different studies, it is necessary to standardize the procedure by comparing the results of this method systematically with those of the traditional approach, based on the analysis of dry samples. This will amplify perspectives for the collection and routine analysis of hydromorphic soils.

The humid-soil approach developed by Silva, (1995), Silva *et al.* (1996), Ferreira *et al.* (1998), Ferreira & Botelho (1999), Mattar *et al.* (2002), and Silva (2008) is especially relevant to the environments of the northern coast of Brazil, where hydromorphic soils dominated by gleysols are common. Haplic gleysols predominate along the whole of the Brazilian state of Amapá, the estuary of the Amazon River, and the coast of Pará state as far east as the mouth of the Pará River. Salic gleysols predominate along the coastline between this river and the mouth of the Gurupi River on the border of Maranhão state, to the east (Lima & Tourinho, 1995; Lima *et al.*, 2001). This belt of salic gleysol, known as the macrotidal mangrove coast, underlies the World's largest continuous tract of mangrove forest (Souza Filho, 2005). Haplic gleysols can be found in the rivers that flow into this mangrove system. The constant saturation of these soils caused by the tidal cycle provokes alterations in their fertility, which are generally beneficial (Catling, 1992).

The objective of the present study was to compare the results of the analysis (macro- and micronutrients) of humid samples of soils from the várzeas of the Amazon estuary, which were immersed over a 52-day period, with those of pre-dried samples. Subsequently, these procedures were tested for the comparison of the samples of haplic and salic gleysols.

- Characteristics of the soils analyzed

Both types of soil belong to the same pedological category, which is characterized by the presence of water in the soil profile. The principal difference between these soils is the exposure of the salic gleysol to seawater, which determines the saline characteristics of this substrate, to which the overlying vegetation must be adapted. The mineralogical identification of these soils by X-ray diffraction indicated the presence of quartz, illite, kaolinite, smectite, goethite and anatase in the haplic gleysol, and quartz, kaolinite, illite, smectite, and anatase in the salic gleysol (Silva & Costa, 2011). However, while these soils are very similar in mineralogical terms, they present major differences in fertility (Figure 1). Surrounded by weathered and leached soils, the gleysols are relatively fertile by local standards (Vieira & Santos, 1987). The haplic gleysol is less fertile than the salic gleysol, with base saturation close to 50%, although the salic gleysol is characterized by a saturation of 88.64%, reflecting its eutrophic status.

The presence in the soil of 2:1 clay minerals and organic matter contributes to the high fertility of the substrate, in contrast with the soils of the surrounding area, which have no 2:1 clay minerals and only low concentrations of organic matter. The concentration of organic matter in the soil, which was medium in the salic gleysol and low in the haplic gleysol, increased markedly with the depth of the profile (Silva & Costa, 2011, Silva & Costa, 2012), partly because of the slower oxidation of this material in comparison with the aerobic environment, given that the oxygen functions as an electron acceptor (Scholz, 2011), partly because of the intense biological dynamic of these environments, as well as the absence of electron acceptors for the development of the reductive process. These soils also presented relatively high levels of available phosphorus and reduced saturation of aluminum (Lopes & Guilherme, 2004).

The two types of soil also present distinct granulometric characteristics. The haplic gleysol can be characterized as a silty loam according to the classification system of Vieira & Vieira (1983), with 743 g/kg of silt in the samples, whereas the salic gleysol was a clayey-sandy loam, with 634.1 g/kg of sand. These differences in texture are reflected in distinct patterns of water retention and penetration of the soil profiles.

Table 1. The pH, concentrations of elements and available compounds, and granulometry of the samples EXP-GH and EXP-GS, for the analysis of the fertility of the respective soils (adapted from Silva & Costa, 2011, and Silva & Costa, 2012)

Sample	pH		C	M.O	P	Ca	Mg	K	SB	H	Al	T	V	m
	H ₂ O	KCl	g/kg		mg/dm ³	cmol/ dm ³								%
EXP-GH	4.69	3.59	3.9	6.72	2.52	1.52	2.48	0.08	4.08	3.94	1.60	9.62	42.41	28.67
EXP-GS	6.80	5.55	10.52	18.14	20.76	3.81	12.85	2.10	18.74	2.35	0.05	21.14	88.64	0.26

Sample	Coarse sand		Fine sand		Silt	Clay
	g/kg		g/kg		g/kg	g/kg
EXP-GH	2.90		28.00		743.00	226.3
EXP-GS	105.80		528.30		76.60	298.30

2. MATERIALS AND METHODS

The present study was based on two simultaneous experiments conducted in the Chemical Analyses Laboratory of the Geosciences Institute of the Federal University of Pará (UFPA), which analyzed samples of the gleysols collected from the várzea swamps of the Guamá River in the city of Belém and the mangrove forests of the estuary of the Caeté River, in the vicinity of the town of Bragança, both located in the Brazilian state of Pará (Figure 1).

The samples from the Guamá were collected 10 km from the mouth of the river, 500 m from the right bank of the river, while those from the Caeté were collected in the mangrove neighboring Bragança, 5.2 km from the mouth of the river.

Samples were taken up to a maximum depth of 20 cm, corresponding to the A₁ horizon. In order to guarantee a representative sample, 65 separate subsamples of approximately 1.5 kg each were collected at Bragança, and 63 from the Guamá, using a manual auger. The subsamples were homogenized to produce a single compound sample for each site, denominated EXP-GH (haplic gleysol) and EXP-GS (salic gleysol of the Caeté).

The várzeas of the EMBRAPA campus, on the right bank of the Guamá River, are typical of this type of forest, with plant species such as the acapurana (*Campsiandra laurifolia*, Benth.), ubim (*Geonoma baculifera*, K.), mamorana (*Pachira aquatic*, Aubl.), ananim (*Symphonia globulifera*, L.), palheteira (*Clitoria arbores*, Benth.), and ucuúba (*Virola sebifera*, Aubl.). The mangrove forest of the Caeté is characterized by the presence of the red (*Rhizophora mangle*, L.), white (*Laguncularia racemosa*, L.), and black mangroves (*Avicennia sp.*, L.).

The fertility of the soils was determined by the standard methods, following EMBRAPA (1997), for both the haplic gleysol of the Guamá River and the salic gleysol of Bragança (Silva & Costa, 2012). The experimental procedure consisted of placing four samples of each type of soil in 7-liter Styrofoam boxes, which were then immersed in distilled water and maintained underwater for 132 days, when the procedure was halted. The present study focuses on the first 52 days only. A modified syringe was used to obtain duplicate 10 ml samples of the soil, which were immediately weighed. One of the duplicate samples was used for a soil analysis (EMBRAPA, 1997) while the other was dried in a stove, dehydrated in a desiccator, and then weighed. The ratio between the weights of the dry and humid samples was used as the correction factor for the evaluation of the results of the analysis of the humid soil samples. The dry sample was then fractioned for chemical analysis, following EMBRAPA (1997).

Aliquots were obtained daily for the first five days, in order to accompany the rapid changes that occur during this initial period, then every second day during the second week, and at weekly intervals during the rest of the experimental period. The chemical analysis determined the concentrations of available and exchangeable phosphorus, potassium, and calcium, as well as the micronutrients iron, manganese, zinc, and copper (EMBRAPA, 1997).

The variation in the concentrations of the different components of the soil samples were represented graphically for the 52-day study period. The results were evaluated

statistically using the Analysis of Variance (ANOVA), for the two treatments, T_1 – analysis of the humid soil, and T_2 – analysis of the dry soil, run in the SISVAR application (Ferreira, 2007). The results of these analyses were compared using the Tukey post-test.

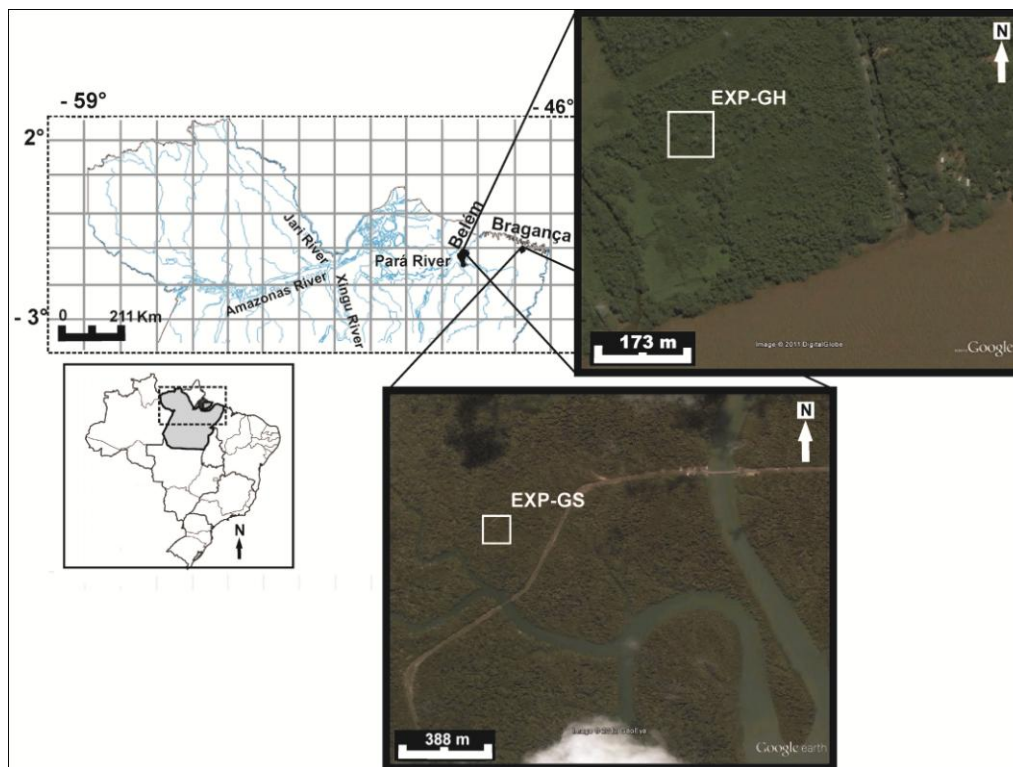


Figure 1. Location of the study sites in the várzea of the Guamá River ($1^{\circ}27'32.50''$ S, $48^{\circ}25'33.89''$ W), where the samples of haplic gleysol were obtained, and the mangrove of the Caeté Estuary ($0^{\circ}50'38.38''$ S, $46^{\circ}38'51.67''$ W), where the samples of salic gleysol were collected.

3. RESULTS AND DISCUSSION

3.1. Results of the experiment

The immersion of the samples resulted in considerable modifications of the fertility of the soil, as indicated by the variation in the concentrations of available and exchangeable elements recorded over the 52 days of the study in both the humid and the dry samples (Tables 2 and 3). The results of the ANOVA indicate significant variations in the concentrations of all the elements in both experiments (Tables 4 and 5). Significant differences were also found between the humid and dry samples for the majority of the elements analyzed. However, no significant variation was found for calcium, in the haplic gleysol, or for phosphorus, potassium, zinc or manganese, in the salic gleysol, reflecting specific differences in the two types of soil.

Table 2. Variation in the mean concentrations of available P, Ca, K, Zn, Cu, and Fe in the samples of haplic gleysol (horizon A₁) over the 52 days of immersion under distilled water.

Días	P úmido	P seco	Fe úmido	Fe seco	Mn úmido	Mn seco	K úmido	K seco	Ca úmido	Ca seco	Cu úmido	Cu seco	Zn úmido	Zn seco
1	7,77	55,6	1048	1662	151,5	293,75	1,28	0,19	225,25	276,5	1,25	2	6,75	12
2	8,91	54,48	1179,25	1844	227	298,5	1,11	0,18	395,25	404,75	3,75	3,25	11,25	12,5
3	10,58	61,17	1479,75	1343	226,75	243	0,71	0,15	346	356,75	1	1	12	11,25
4	13,15	51,63	1787,25	2286,25	309,25	338,25	0,13	0,17	249,25	352,75	1	2	11,25	13,25
5	11,102	73,55	2799,5	1753,25	340,75	322,75	0,37	0,18	243,75	325,37	2	2	13,75	11,25
8	20,63	84,58	2628	2475,5	373,75	349,75	1,39	0,18	270,25	298,87	2	2,25	13,25	12,5
10	15,42	63,03	2886,25	2586,75	367	359,25	1,06	0,19	285	351,25	2	2,5	16	15
12	16,46	82,6	5330	1991,5	324,75	343	0,17	0,18	496,75	472,87	2	2	14,5	10,25
15	23,12	83,84	5806,25	3595	360	354,5	0,18	0,14	456,5	455,5	1,25	2	14,5	11,75
17	20,96	76,65	6203,25	4522,5	316,25	347	0,48	0,16	404	409,5	1,75	2	15,25	14,25
19	18,6	97,59	6952	3857,75	355,75	356,75	1,01	0,16	446,25	430,12	2,25	3	18	11,5
23	38,62	91,27	7165	2556,25	334,5	317,5	1,24	0,14	434,75	417,5	2,25	2,25	14,75	10
25	48,66	156,4	6690,25	7644,25	346	321,5	1,04	0,17	426	380	0,75	2	14	21
31	119,15	139,45	2539	2221	365	351,5	0,15	0,18	390	362,62	3,75	6,25	10	6,75
38	72,32	124,95	3887,75	3051,25	343,75	394,25	0,15	0,17	338,5	364,75	1,75	4,25	15,25	11,25
45	75,3	22,75	8136,25	8147,25	331,75	368,25	0,16	0,16	352,5	383	1,25	2,77	24,25	16,5
52	111,47	40,37	7919,5	7333	526	304	0,16	0,13	353,5	388,75	5	2	20	27,25

*humid: result obtained for the humid sample; **dry: result obtained for the pre-dried sample.

Table 3. Variation in the mean concentrations of available P, Ca, K, Zn, Cu, and Fe in the samples of salic gleysol (horizon A₁) over the 52 days of immersion under distilled water.

Días	P úmido	P seco	Fe úmido	Fe seco	Mn úmido	Mn seco	K úmido	K seco	Ca úmido	Ca seco	Cu úmido	Cu seco	Zn úmido	Zn seco
1	103,18	124,48	1168,25	1590,5	14	9,25	0,15	1,15	353	432,75	1	1	3	3,75
2	105,28	144,18	1284	1513,75	6	6,5	0,15	1,13	369,25	389,75	1	1,25	4,25	4
3	111,49	122,62	1387,75	1288,75	7,75	6,75	0,67	0,88	342,25	364,5	1	1	3,5	3
4	110,62	140,5	1311,5	1934	7	8,75	1,31	1,12	348,5	373,5	1	1	3	3,5
5	142,4	212,98	1720,25	1118,8	8	7	1,31	0,98	279	300,75	1	1	2,5	1,75
8	136,31	74,43	1408,75	1833	6,75	6,25	0,67	1	291,25	317,75	1	1	3	4
10	148,36	36,89	1850	1920	8	1,5	0,15	1,03	289,75	338	1	1	4,25	4
12	173,43	34,44	2084,5	1683	9,25	8,25	0,39	0,87	456,75	411	1	2,75	3,25	3
15	33,04	33,79	1606,25	1493	6,75	7,5	1,29	1	476,25	447,5	1	1	3,25	3,75
17	35,89	39,61	2429,75	2474,25	5,25	6	1,92	1,21	442	447,5	1	1	3,75	4,5
19	45,63	32,67	2386	1892	8,5	7,75	2,62	1,05	461,5	441,5	4	1	5,25	3,5
23	50,77	141,82	2410	1763,5	7,5	7,5	1,51	1,3	389	390,75	4	1,25	2,25	1
25	62,41	75,92	2134,25	3565	6,5	7,5	1,22	1,09	398	455	1	2,25	2,75	4,5
31	144,05	121,87	1549	1438,77	9	8,25	1,29	1,15	400	471	1	1,5	4,25	5
38	87,2	151	2133,75	1560,25	10,75	12	1,43	1,36	373	437,25	1	1	4	4
45	66,12	37,5	4450,5	3130,5	4,75	5,75	1,28	1,2	278	440,75	1	1	6,75	6,5
52	54,35	62,05	4644	3514,25	5	5	1,3	1,43	388	421	1	1	5	5

*humid: result obtained for the humid sample; **dry: result obtained for the pre-dried sample.

Table 4. Results of the ANOVA for the effects of immersion with distilled water on the haplic gleysol samples over time (days) and the two treatments.

VF	DF	P	Ca	K	Zn	Mn	Cu	Fe
Day	16	12.598**	9.644**	7.61**	20.73**	16.086**	8.177**	125.335**
Treatment	1	126.096**	2.384 ^{NS}	111.188	5.711*	8.899*	12.501**	78.259**
Treatment Vs Day	16	7.671**	3.149**	6.885**	6.801**	3.781**	2.328**	18.204**
Repetition	3	0.51	1.829	0.650	0.968	0.450	3.105	0.865
CV (%)	-	37.98	12.44	64.66	17.02	9.61	40.43	14.00

N.S.- Not Significant; * - Significant at $P < 0.05$; ** - Significant at $P < 0.01$.

V.F. Variation factor; D.F. Degree of freedom; C.V. coefficient of variation.

Table 5. Results of the ANOVA for the effects of immersion with distilled water on the salic gleysol samples over time (days) and the two treatments.

VF	DF	P	Ca	K	Zn	Mn	Cu	Fe
Day	14	16.911**	10.714**	8.096**	6.478**	4.137**	7.792**	100.103**
Treatment	1	0.104 ^{NS}	8.298**	0.252 ^{NS}	0.818 ^{NS}	0.005 ^{NS}	12.142**	15.658**
Treatment Vs Day	12	9.639**	-1.213 ^{NS}	5.750**	1.074 ^{NS}	-0.501 ^{NS}	10.769**	13.586**
Repetition	3	0.422	1.793	0.683	1.067	1.241	1.130	1.216
CV (%)	-	26.34	12.44	36.71	28.08	39.77	47.44	10.19

N.S.- Not Significant; * - Significant at $P < 0.05$; ** - Significant at $P < 0.01$.

V.F. Variation factor; D.F. Degree of freedom; C.V. coefficient of variation.

The element phosphorus showed a significant difference between treatments in Haplic Gleysol. For Salic Gleysol this difference did not exist. The Tukey test indicated that the dry treatment provided significantly higher estimates of the phosphorus content, indicating that the availability of this element was affected by immersion. These modifications were due to the hydrolysis of the iron and aluminum phosphates, which liberated phosphorus in the exchange positions in the clays and oxy-hydroxides of iron and aluminum, as well as the reduction of Fe^{3+} to Fe^{2+} , with the subsequent liberation of the phosphorus linked to these

minerals (Fageria, 1984; Lima *et al.*, 2005), although the results of the experiment indicated that this did not occur uniformly in the two soils tested (Figure 2).

In the case of the salic gleysol, which had the highest concentrations of phosphorus, the liberation of this element occurred at high levels at the beginning of the experiment, decreasing over time, but still remaining at relatively high levels. Given this, significant differences were not found between the two analytical procedures. The haplic gleysol presented relatively slow rates of increase of the phosphorus content, with the humid procedure detecting minor variations at the beginning of the process, as observed in previous studies (Silva *et al.* 1988, Lima *et al.*, 2005), but with both procedures identifying variations from the 30th day onwards, as well as a reduction in the concentration on the 45th day of immersion. Overall, then, the results of the analysis of the humid samples appear to represent the known behavior of this element in this type of environment, which starts with the initiation of the oxy-reduction processes, which influence the liberation of phosphorus at increasing rates during the first few days of immersion, as well as the anomalous pattern observed in the salic gleysol. It is important to remember that the high levels recorded for both types of substrate are a distinct characteristic of these soils. In Asia, Peng & Senadhira (1998) found that flooded soils used for the cultivation of rice were mostly deficient in phosphorus and zinc.

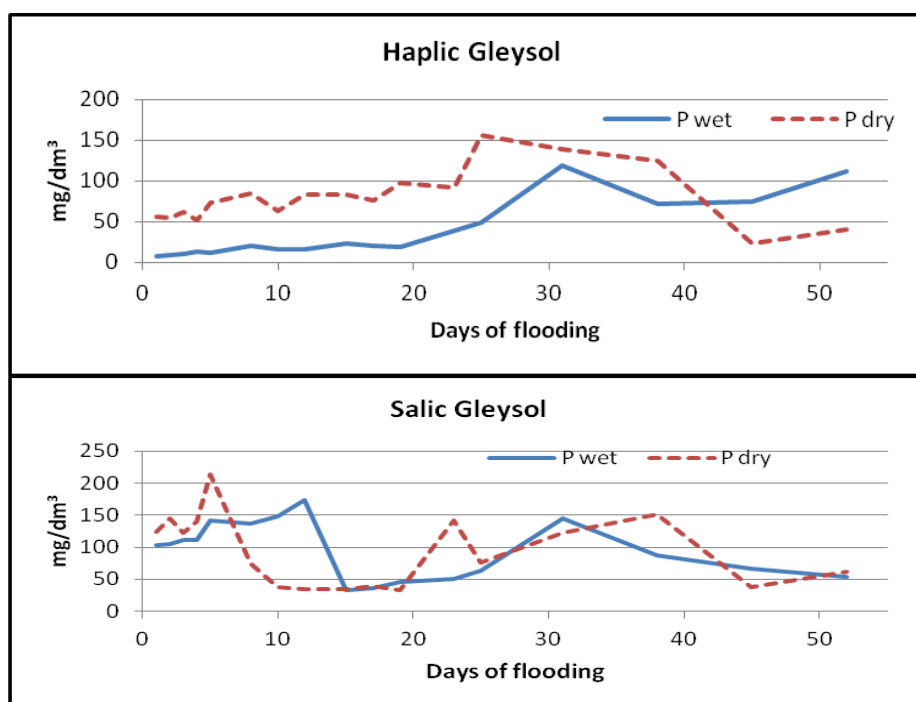


Figure 2. Variations in the concentration of phosphorus over time, according to the results of the two analytical procedures (humid and pre-dried soil).

In the case of iron, a micronutrient, the two treatments followed relatively similar patterns in the haplic gleysol, with larger amounts being liberated in the pre-dried samples over the first 23 days, but subsequently a tendency to decrease, whereas in the humid soil treatment, a tendency to increase was observed (Figure 3). This confirms the tendency for iron concentrations to increase, reaching relatively high levels (Silva *et al.*, 1988; Lima *et al.*; 2005). The ANOVA returned a significant difference (1%), with the Tukey test indicating that the humid sample was the better treatment for the analysis of the iron content. Iron suffers dynamic change in this environment (Schwertmann & Taylor, 1989), reaching abnormally high levels in both soils and treatments, which may be toxic for some cultivated plants (Fageria, 1984). While both analytical procedures indicated a progressive increase in the availability of this element (Figure 5), although the analysis of the humid samples indicated slower rates of change at the beginning of the immersion period, a pattern recorded in previous studies (Ponnanperuma, 1972; Ferreira *et al.*, 1998). This initial increase in the availability of iron was not detected with the same intensity in the analysis of the pre-dried samples.

The salic gleysol presented a similar significant difference (1%) between treatments, with the Tukey test indicating the pre-dried sample as the best treatment. The variation in iron levels observed in the salic gleysol during the initial days of immersion in both treatments indicated higher values in the humid soil samples from the 31st day onwards.

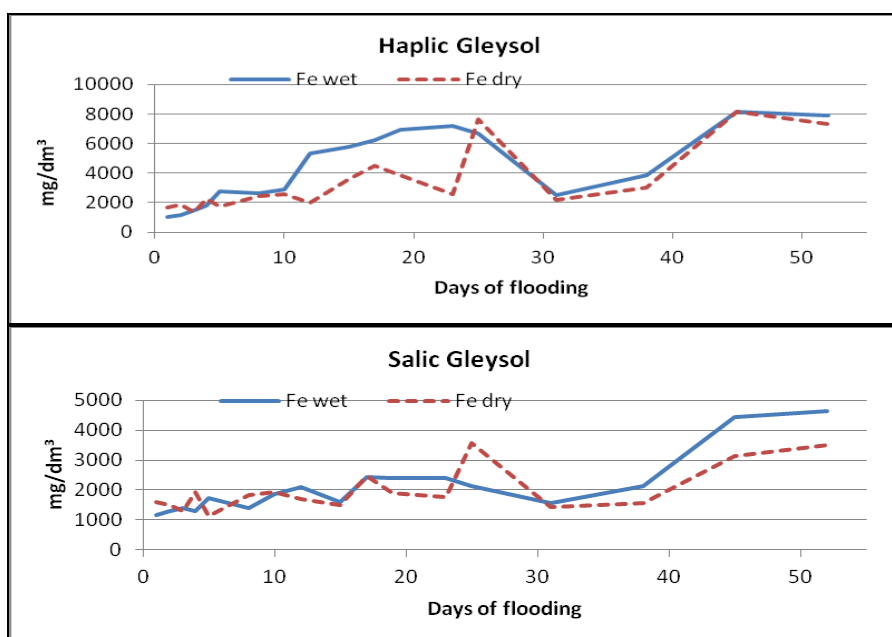


Figure 3. Variations in the concentration of iron over time, according to the results of the two analytical procedures (humid and pre-dried soil).

Manganese was affected directly by the modification in the environment, with a reduction in the first few days of immersion, when it was converted into the available form. The experiments indicate that this occurred in different ways in the two soils (Figure 4, Tables 2 and 3). In the haplic gleysol, concentrations varied from 151.5 g/dm³ (humid soil analysis) to 293.75 mg/dm³ (pre-dried soil) on the first day of immersion, reaching maximum values of 526 mg/dm³ by the 52nd day in the case of the humid sample, and 394.25 mg/dm³ by the 38th day for the pre-dried sample. Overall, then, relatively high values were recorded throughout the experiment in both types of analytical procedure. The ANOVA for the haplic gleysol indicated a significant difference between treatments, with the Tukey test confirming significantly higher values in the analysis of the pre-dried samples. In the case of this soil, however, the rapid reduction of the manganese was observed in both treatments. Lower values were recorded for the humid soil samples at the beginning of the immersion period, although the difference between treatments disappeared from the fifth day of immersion onwards.

The concentrations of manganese in the salic gleysol were very low in comparison with the haplic soil, and decreased over the course of the study period. On the first day, the values were 14 mg/dm³ for the humid soil analysis and 9.25 mg/dm³ for the pre-dried samples, decreasing to 5 mg/dm³ by the 52nd day of immersion in both analytical procedures. Given this, the ANOVA found no significant difference between treatments for the salic gleysol.

Both analytical procedures confirmed high concentrations of manganese throughout the 52 days of immersion of the haplic gleysol, and low values in the salic gleysol. In the specific case of the haplic gleysol, however, the pattern presented by the analysis of the humid samples returned lower values, increasing rapidly over the first seven days, and then up to the 20th day of immersion, a period sufficient for the reduction of this element, with an increase in the concentration still observed on the 45th day. In the case of the salic gleysol, by contrast, similar low values were recorded throughout the study period by the two analytical procedures.

Calcium was liberated at similar levels in both soils, with similar results being obtained in both treatments, although once again, lower levels were recorded in the humid soil samples over the first 10 days of immersion, in both types of soil (Figure 5). This may have occurred because the calcium had not yet been dissolved in the soil solution. There was no significant difference (ANOVA) in the levels of exchangeable calcium recorded in the different treatments for the haplic gleysol. Significant differences (1%) were recorded between treatments for the salic gleysol, however, with higher values being recorded for the

pre-dried samples, which returned higher values in comparison with the humid soil samples from the 25th day of immersion onwards.

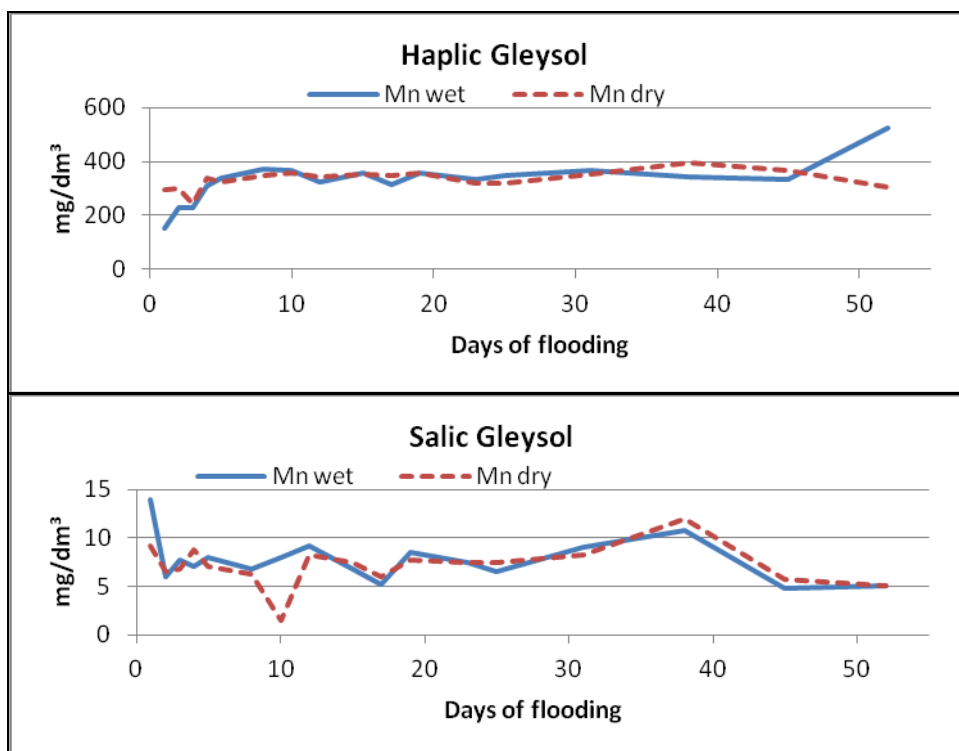


Figure 4. Variations in the concentration of manganese over time, according to the results of the two analytical procedures (humid and pre-dried soil)

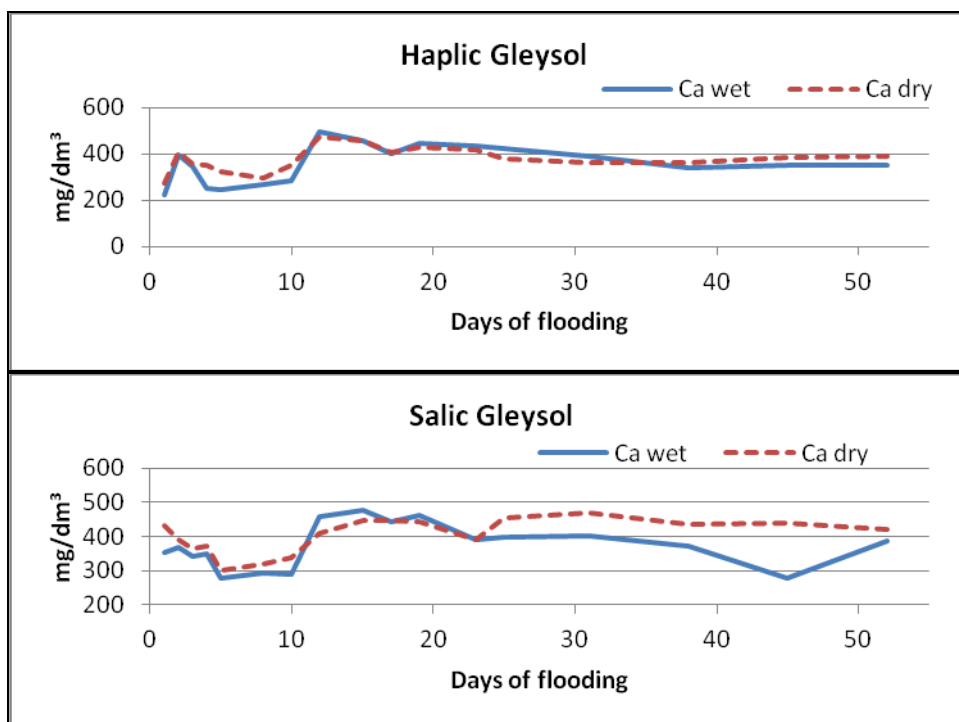


Figure 5. Variations in the concentration of calcium over time, according to the results of the two analytical procedures (humid and pre-dried soil)

Potassium levels in the salic gleysols were similar in the two treatments tested, with no significant difference found in the ANOVA, whereas significant variation was recorded for the haplic gleysol. The liberation of the potassium can be observed at each stage in the analysis of the humid soil, although medium values were recorded from the pre-dried samples throughout the study period. While no significant differences were recorded in the case of the salic gleysols, the same pattern was recorded for the humid soil analyses. In this analysis, it was also possible to confirm stability in the exchange of cations from the 23rd day onwards in the haplic gleysol, and from the 31st day onwards in the case of the salic gleysol (Figure 6). The Tukey test indicated that this treatment was the most effective for the analysis of the haplic gleysol.

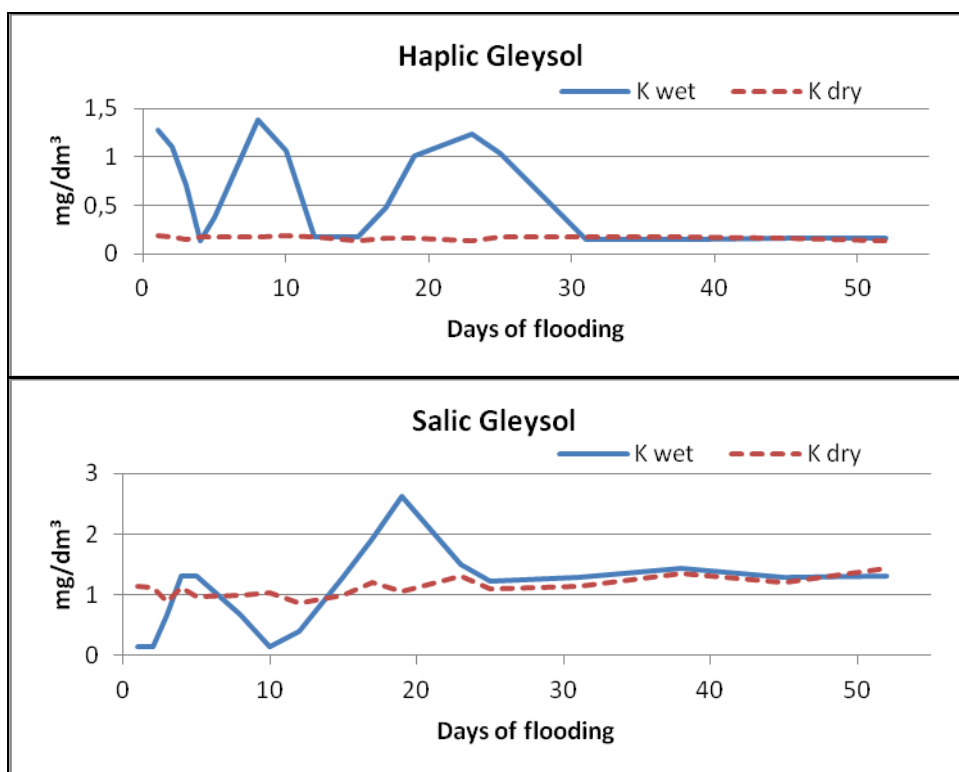


Figure 6. Variations in the concentration of potassium over time, according to the results of the two analytical procedures (humid and pre-dried soil)

Zinc and copper concentrations are not normally affected by the oxy-reduction reactions that occur typically in these soils (Fageria, 1984), but they are altered indirectly by the migration to the soil solution occurring after the substantial production of other elements, such as iron and manganese, and the alteration of the pH, which reduces the availability of these elements at higher values, or even results in their fixation in neoformed minerals (Ponnamperuma, 1972; Sanches, 1981; Fageria, 1984; Brinkman, 1985). However, while zinc did not become unavailable, it occurred at low concentrations, especially in the salic gleysol,

in which it was liberated in reduced amounts, with a similar pattern being observed in the two treatments, which did not differ significantly (ANOVA). Higher values were recorded in the haplic gleysol, with a significant difference (1%) being recorded being treatments, with much higher values being recorded in the analysis of the humid samples (Figure 7, Tables 4 and 5).

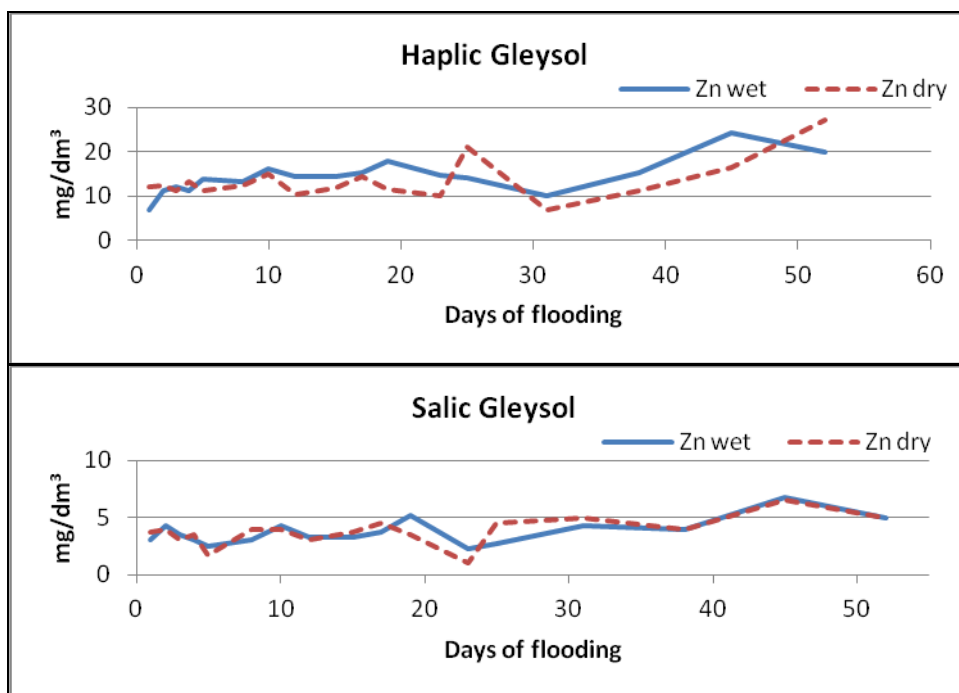


Figure 7. Variations in the concentration of zinc over time, according to the results of the two analytical procedures (humid and pre-dried soil)

Copper behaves in a similar way to potassium, increasing its contents, with these elements being liberated through discrete exchange events. In this closed system, with no external influence, copper should have decreased as pH values increased (Bertoni *et al.*, 1999; Mattar *et al.*, 2002; Silva, 2008). On the other hand, a small increase should have occurred due to production of other ions, such as those of iron and manganese, which may migrate to the soil solution. However, the concentration of this element continued to decrease over time, over a longer period than that analyzed here, but without its complete elimination, given that the pH stabilized at approximately 6.5 in the haplic gleysol (Silva & Costa, 2011) and 5.5 in the salic gleysol (Silva & Costa, 2012).

In the haplic gleysol, variations in the concentration of copper over time were very similar in the two treatments (Figure 8). The concentrations of copper recorded in the humid samples ranged from 1 to 2.25 mg/dm³ up to the 25th day, increasing to 5 mg/dm³ by the 31st day of immersion, followed by a decrease. A similar pattern was observed in the results of the analysis of the pre-dried samples, with values of 1-3.25 mg/dm³ recorded prior to the 25th

day, increasing subsequently to 6.25 mg/dm³. The Tukey test indicated significantly higher values for the dry samples, even though the humid samples indicated an increase in concentrations from the 45th day onwards, inverting the overall tendency recorded by both analytical procedures.

While the values recorded for the salic gleysol were very similar during the later part of the immersion period, significantly higher values (1%) were recorded overall in the analysis of the humid soil samples. Despite the similarities in the results, the analysis of the humid samples returned much higher values between the 19th and 23rd days, whereas the analysis of the pre-dried samples revealed much lower peaks on the 12th, and 23-25th days.

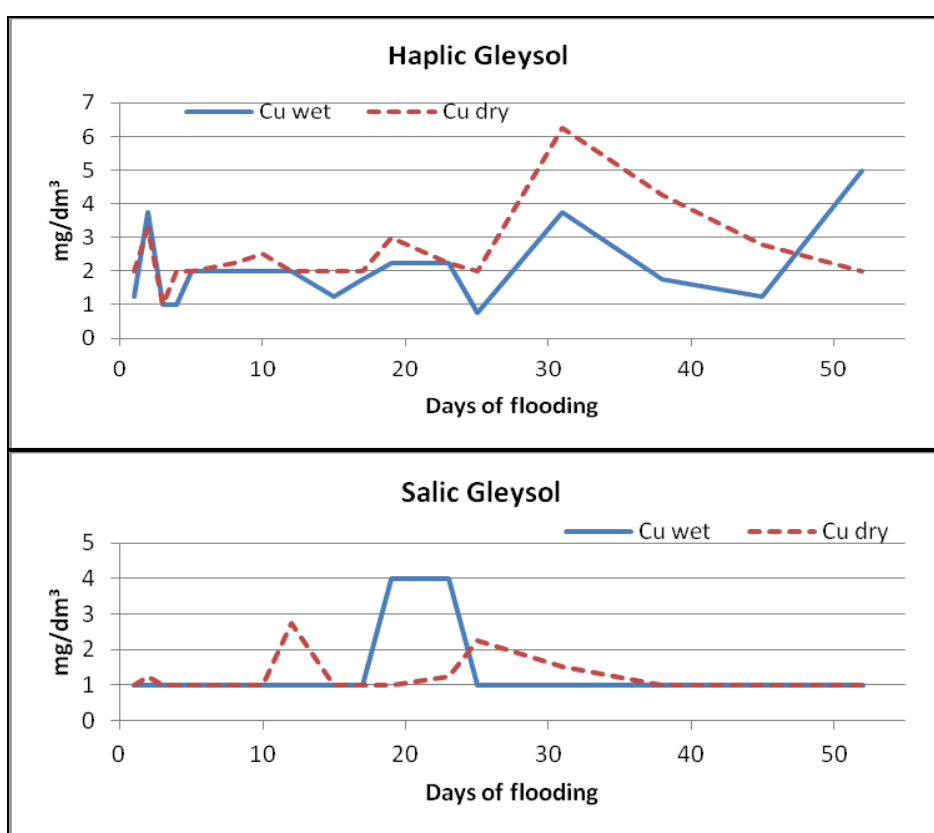


Figure 8. Variations in the concentration of copper over time, according to the results of the two analytical procedures (humid and pre-dried soil)

Significantly higher values were recorded for phosphorus, manganese, and copper in the analysis of the pre-dried samples of haplic gleysol, whereas iron, potassium, and zinc were more abundant in the humid samples. Calcium was the only element tested that did not vary significantly between treatments in the analysis of this soil type. A distinct pattern was recorded in the case of the salic gleysol, however, with no significant difference being found between treatments for phosphorus, potassium, manganese or zinc. Significantly higher values for iron and copper were recorded in the analysis of the humid samples, whereas

calcium was higher in the pre-dried samples (Tukey test). This variation in the experimental response is important because it implies that specific responses in the fertility of the soil may be interpreted differently according to the analytical procedure employed.

Overall, then, while the analysis of the dried samples provided significantly higher values in some cases, suggesting more reliable results, the values recorded by the analysis of the humid samples were more similar to those reported in previous studies (Silva *et al.*, 1988; Lima *et al.*, 2005). This suggests that this approach is more sensitive to minor changes in the concentrations of the elements analyzed. Given this, the analysis of the humid samples appears to be a reliable approach to the assessment of the fertility of these inundated soils.

4. CONCLUSIONS

The analysis of the fertility of inundated soils based on the chemical assessment of the dried samples may produce results that are invariably the same or closely similar. This may occur because the drying process reverts the characteristics of the samples to those of the aerobic soil, prior to reduction, altering the availability of the nutrients present in these substrates. As the fertility of the dry soil is not altered, the results will invariably be similar.

The present study indicates that this difference is not universal or consistent, given that some variation was observed in relation to the values recorded for the humid samples, with very similar concentrations being found in some cases. However, there were no absolutely divergent results between the two approaches. Where the two treatments produced values completely different in size, such as those recorded for manganese, both techniques recorded similar patterns of variation, in particular with regard to the differences between the types of gleysol, with relatively high concentrations being recorded for the haplic soil and lower values for the salic soil.

Both procedures also identified the same specific patterns of variation in the two types of soil analyzed. The liberation of elements by each soil type follows a distinct pattern related to its inherent characteristics, such as its vegetation and mineralogy. The values recorded for manganese are a good case in point. This element was present at high concentrations in the haplic gleysol, but occurred at very low concentrations in the salic gleysol, a result confirmed by both approaches.

Specific patterns of alterations to fertility were also recorded for each soil type. In particular, the analysis of calcium levels in the haplic gleysol did not vary significantly between treatments, while those for phosphorus, potassium, manganese, and zinc were also

similar for the salic gleysol, independently of the procedure used. This indicates that the choice of procedure did not affect the results obtained for these elements.

Statistically, the analysis of the pre-dried samples returned significantly higher values for the elements phosphorus, manganese, and copper in the haplic gleysol, and for calcium, in the salic gleysol. However, the variation observed in the dried samples may have been more favorable, given the observation of higher values (Tukey test). In the case of manganese and phosphorus, however, the humid samples appeared to be more detailed, revealing subtle variation in the relatively low concentrations during the first few days of experimental immersion. The results from calcium and copper were similar, however, in both treatments, and were within the same fertility class.

The analysis of the humid soil samples appeared to provide more reliable results for the concentrations of potassium, zinc, and iron (in the haplic gleysol) and copper and iron (in the salic gleysol). Together with the results that found no significant difference between analytical procedures, this comparison indicates that the analysis of the humid samples was at least as reliable as that of the pre-dried samples in approximately 71% of the cases.

Overall, then, the analysis of the humid soil samples was considered to be satisfactory for the evaluation of the fertility of the haplic and salic gleysols tested under anaerobic conditions. The positive results and the lack of significant differences between procedures for many of the elements analyzed indicate that this approach can be used reliably. In particular, the analysis of the humid samples appears to be better for the identification of patterns of variation at relatively low concentrations. This supports the conclusions of the research, which indicate that soils subject to natural inundation present distinct characteristics in the field and the laboratory, following the drying process. These findings are especially important in the context of the Amazon region, given the vast area covered by várzea soils.

5. ACKNOWLEDGMENTS

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7 CONCLUSÕES E CONSIDERAÇÕES FINAIS

Os estudos realizados nos Gleissolos do estuário Amazônico apresentaram atributos importantes, a influenciar diretamente em sua CTC, com relação direta para a fertilidade destes solos. Destacam-se a presença de argilominerais 2:1 e a existência de altos teores de matéria orgânica. Uma importante comprovação é relacionada ao fato, de apesar de pertencerem à mesma ordem em sua classificação, e serem geograficamente próximos, os solos e ambientes estudados apresentam características próprias, as quais influenciam os resultados referentes à disponibilidade de nutrientes.

Em ambos os solos foi demonstrado que a inundação com água destilada, promoveu alterações na fertilidade, com efeito benéfico para a disponibilidade dos elementos nutritivos. Esta liberação, entretanto, ocorreu de forma distinta para cada solo estudado, demonstrando que características individuais presentes nos solos, proporcionaram resultados diferenciados. Entre os principais resultados individuais dos solos estudados está a estabilização do pH, com valores ácidos no Gleissolo Sáfico e levemente ácidos no Gleissolo Háplico, juntamente com a variação no Eh, que ocorreu acentuadamente negativa no Gleissolo Háplico e com menor intensidade no Gleissolo Sáfico. O comportamento na liberação de fósforo nos solos testados, atípico, com valores decrescentes, embora altos no Gleissolo Sáfico, e altos e crescentes no Gleissolo Háplico, assim como do manganês com valores muito baixos no Gleissolo Sáfico, e bastantes elevados no Gleissolo Háplico, se incluem entre os resultados mais específicos a cada solo estudado.

As características após a inundação, embora distintas, se apresentaram benéficas para a formação de fertilidade favorável ao desenvolvimento vegetal. No Gleissolo Háplico, a redução ocorreu de forma intensa, para valores próximos de -400 mV, gerando reações que elevaram o pH para valores próximos de 7, favorecendo assim a disponibilização de macronutrientes e micronutrientes. Ocorreu ainda a alteração no teor disponível de fósforo, ferro e manganês para valores elevados e pequenas alterações alteração nos teores de cálcio, potássio, cobre e zinco. O zinco apresentou comportamento específico de liberação, no qual não ocorreu sua indisponibilidade, relatada em outros locais, provavelmente devido ao valor levemente ácido adquirido pelo pH, ao se estabilizarem as reações de redução. O Gleissolo Sáfico sofreu redução de forma lenta, sem atingir os valores apresentados no Gleissolo Háplico, tendo atingido o valor máximo de - 281 mV, e dessa forma, acumulando matéria orgânica em quantidade elevada ao longo do perfil do solo estudado. Da mesma forma, o pH se alterou, sem entretanto, ultrapassar o valor 6 durante o longo período de inundação. Estes

valores se relacionam à faixa em que a maioria dos elementos nutritivos se encontra disponível aos vegetais. Este solo apresentou valores muito baixos para o potássio, assim como para o manganês, e valores elevados para o fósforo, que decresceu no período estudado. Este resultado está de acordo com o exposto por Silva & Costa (2012), que neste solo o fósforo é provavelmente liberado da decomposição de oxi-hidróxido de ferro, e no entanto os valores muito baixos de manganês refletem a ausência de minerais que o forneçam, que pode, portanto estar sendo liberado dos oxi-hidróxido de ferro. A disponibilidade do potássio reflete a baixa solubilidade em solos do mineral identificado por DRX, a illita-muscovita.

Diversos rios que deságuam na região do estuário Amazônico, apresentam água branca, característica também presente aos rios Guamá e Caeté, correspondentes às várzeas deste estudo. A coloração de suas águas é inerente à presença do suspensato, que depois de depositado, contribui para a formação destes solos. Sua caracterização apontou a presença de argilominerais 2:1 e presença elevada de cátions trocáveis e fósforo disponível, atribuindo ao suspensatos estudados a propriedade de apresentar riqueza maior que a dos próprios solos estudados. Entre seus atributos, a CTC e a porcentagem de saturação de cátions (V%) é elevada conferindo caráter eutrófico em ambos os suspensatos estudados. Em razão da existência de inundação periódica nestes ambientes, que ocorre em cada maré, repõe nutrientes, que são empregados na manutenção da floresta encontrada nos dois locais, assim como contribui na manutenção de culturas empregadas pela população que tradicionalmente habita estas várzeas.

Os argilominerais dos solos da Amazônia são predominantemente do tipo 1:1, em razão de integrarem solos de antiga constituição (Vieira, 1983; Vieira & Santos, 1987). Dessa forma, é rara ou inexistente a presença de argilominerais como esmectita ou illita na superfície de solos. A presença destes minerais encontrados nestes solos pode indicar a presença de condições para a neoformação destes minerais ou o seu transporte de zonas escavadas de vales à montante dos rios, que depois de erodidos e transportados, são depositados, à jusante, na superfície destes solos. Trata-se, no entanto, de condição específica, em relação aos outros solos da região.

Os solos estudados apresentam ainda condição para promover o acúmulo de matéria orgânica humificada em seu perfil. A decomposição mais lenta da matéria orgânica e a ausência de captadores de elétrons no solo, interrompendo as reações de oxi-redução, podem colaborar para este acúmulo, em especial no Gleissolo Sáfico, com valores muito altos em todo o perfil do solo. Esta característica também se apresenta de forma benéfica, considerando a possibilidade de contribuir no aumento da CTC e fornecimento de nutrientes ao solo.

As características distintas destes solos também refletiram nos resultados referentes ao método de determinação da fertilidade do solo, em que foi comparada a análise na amostra ainda úmida e a análise na amostra seca. Ambos os métodos testados perceberam as alterações que ocorrem com o tempo de inundação em ambos os solos, e em virtude de suas características próprias apresentaram resultados diferentes em relação à aplicação dos métodos. No entanto, por perceber transformações em pequenas quantidades que ocorrem no início do processo reutivo, a análise no solo úmido foi recomendada, associado ainda em razão da indiferença para escolha do método, em grande parte dos elementos nos solos testados.

Os solos estudados no estuário Amazônico possuem características próprias e apresentam boa fertilidade. Como ocupam grande extensão, apresentam grande importância socioambiental. A manutenção da fertilidade pela deposição periódica de suspensato, e sua qualidade de retenção destes nutrientes, se apresentam como aspecto fundamental para que os nutrientes não sejam exauridos pela vegetação e pelo manejo adotado por algumas comunidades locais, que neste ambiente constantemente lavado pelos rios e pela alta pluviosidade local, certamente os empobreceriam com o tempo.

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ANEXOS

**ANEXO A - CONFIRMAÇÃO DA SUBMISSÃO DO ARTIGO DO CAPÍTULO IV
PARA APPLIED GEOCHEMISTRY**

Article Title: WATER AS A RELEASING AND FERTILIZING FOR
THE VÁRZEA SWAMP SOILS OF THE GUAMÁ RIVER IN THE AMAZON
ESTUARY COMPLEX

Corresponding Author: Mr. Sérgio Brazão e Silva

Dear Mr. Silva,

Your submission entitled "WATER AS A RELEASING AND
FERTILIZING FOR THE VÁRZEA SWAMP SOILS OF THE GUAMÁ
RIVER IN THE AMAZON ESTUARY COMPLEX" has been received
by Applied Geochemistry.

Thank you for submitting your work to the journal, and
if you have any questions, please do not hesitate to
contact me.

Yours sincerely,

Applied Geochemistry

**ANEXO B - CONFIRMAÇÃO DA SUBMISSÃO DO ARTIGO DO CAPÍTULO V
PARA GEODERMA**

Dear Mr. Silva,

Your submission entitled "GEOCHEMICAL INTERACTIONS
BETWEEN THE WATER AND SOIL OF THE MANGROVE FOREST AS A
PROCESS OF FERTILIZATION IN BRAGANÇA, NORTHERN BRAZIL"
has been received by Geoderma

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Kind regards,
Geoderma

**ANEXO C - CONFIRMAÇÃO DA SUBMISSÃO DO ARTIGO DO CAPÍTULO VI
PARA GEODERMA**

Dear Mr. Silva,

Your submission entitled "COMPARISON OF METHODS FOR THE
EVALUATION OF THE FERTILITY OF GLEYSOLS IN NORTHERN
BRAZIL" has been received by Geoderma

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Thank you for submitting your work to this journal.

Kind regards,
Geoderma



UNIVERSIDADE FEDERAL DO PARÁ
INSTITUTO DE GEOCIÊNCIAS
PROGRAMA DE PÓS-GRADUAÇÃO EM GEOLOGIA E GEOQUÍMICA

PARECER

Sobre a Defesa Pública da Tese de Doutorado de SÉRGIO BRAZÃO E SILVA

A banca examinadora da tese de doutorado de **SÉRGIO BRAZÃO E SILVA** intitulada "**INTERAÇÕES GEOQUÍMICAS NA SUPERFÍCIE DE GLEISSOLOS NO ESTUÁRIO AMAZÔNICO**" composta pelos Professores Doutores Marcondes Lima da Costa (Orientador-UFPA), George Rodrigues da Silva (UFRA), Maria de Lourdes Pinheiro Ruivo (MPEG), Vanda Porpino Lemos (UFPA) e José Augusto Martins Corrêa (UFPA), após a apresentação oral e arguição do candidato, emite o seguinte parecer:

O candidato apresentou contribuição relevante ao conhecimento sobre as características geoquímicas e pedológicas dos gleissolos na região do estuário do Rio Amazonas, utilizando técnicas analíticas clássicas e propondo novas metodologias. A apresentação oral foi clara, bem estruturada e de conteúdo relevante, demonstrando conhecimento da literatura e discussão dos dados apresentados. Na arguição o candidato defendeu sua tese e respondeu as várias questões gerais e específicas apresentadas. O documento está estruturado na forma de três artigos científicos submetidos a periódicos internacionais.

Com base no exposto, a banca examinadora decidiu por unanimidade aprovar a tese de doutorado.

Belém, 29 de junho de 2012.


Prof. Dr. Marcondes Lima da Costa (UFPA)


Prof. Dr. George Rodrigues da Silva (UFRA)


Prof.ª Dr.ª Maria de Lourdes Pinheiro Ruivo (MPEG)


Prof.ª Dr.ª Vanda Porpino Lemos (UFPA)


Prof. Dr. José Augusto Martins Corrêa (UFPA)