

UNIVERSIDADE FEDERAL RURAL DE PERNAMBUCO

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**GEOCHEMICAL ALTERATIONS IN CONTAMINATED MANGROVE
SOILS AND EFFECTS ON THE BIOAVAILABILITY OF METALS AND
MICROBIAL COMMUNITY**

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**Geochemical alterations in contaminated mangrove soils and effects on the bioavailability
of metals and microbial community**

Dissertation presented to the Graduate
Program of Soil Science at UFRPE in partial
fulfillment of the requirements to obtain the
Master Degree

Advisor: Prof. Dr. Caroline Miranda Biondi
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Dedictory
To all minorities

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“No mangue, tudo é, foi ou será caranguejo, inclusive o homem e a lama”

Josué de Castro

Geochemical alterations in contaminated mangrove soils and effects on the bioavailability of metals and microbial community

ABSTRACT

Mangrove soils in their natural conditions are known as a sink of contamination for retaining heavy metals in solid and organic particles in non-available forms. In the northern littoral of Pernambuco, the Botafogo River estuary has a history of contamination by mercury (Hg), chrome (Cr) and zinc (Zn) but it is needed to evaluate how changes on the soil pH, redox potential, and iron (Fe) contents of these soils can affect the availability of metals and the soil microbiota. The objectives of this study were to determine Hg, Cr, Zn and Fe contents in mangrove soils and analyze changes in compartmentalization of these metals under 10 times of incubation exposing the soils to oxic conditions, as well as the interferences of geochemical alterations on microbial respiration and soil carbon biomass. Soils from three areas (A1, A2 and A3) of the Botafogo River were collected and selected for ten times of incubation (0, 5, 15, 30, 45, 60, 75, 90, 105 and 120 days). After incubation times the samples were divided in two depths (0-5 cm and 5-10 cm). Potential redox (Eh) and pH were determined on site and after every collection from incubation times. Soil particle size distribution was performed for each area. Environmental available contents of Hg, Cr, Zn and Fe were determined by the 3051A method and sequential extraction of these metals was performed. Soil microbial biomass, soil respiration and microbial metabolic quotient were also determined. These soils are classified as clay and silty clay. After 120 days of decreased humidity, all areas showed acidification and an increase in Eh from anoxic/suboxic to oxic conditions. Alterations of soil pH and redox potential did not cause significant redistribution of Hg, Cr and Fe in A1, A2 and A3. There was a decrease of Zn associated with carbonate fractions and increased association with residual fractions under incubation times for all three areas. Iron was mostly associated with the pyrite fraction and had significant contribution to holding metals in recalcitrant fractions of soils. Acidification and changes from anoxic to oxic conditions had the main effect on microbial biomass increase and decrease on soil respiration in the most contaminated area, possibly because these new conditions favored fungi communities over bacteria. Besides the changes in soil pH and Eh, there was no correlation between heavy metals and microorganismal attributes analyzed in this study. The microbial metabolic quotient remained low under different areas and times of incubation, showing little impact from the geochemical alterations on microorganisms from the Botafogo River soils.

Keywords: Heavy metals. Microorganisms. Redox potential. Wetland soils.

Alterações geoquímicas em solos de manguezais contaminados e efeitos na biodisponibilidade de metais e comunidade microbiana

RESUMO

Solos de manguezal em condições naturais são considerados drenos de contaminação por reter metais pesados em partículas minerais e orgânicas do solo em formas não disponíveis. No Litoral Norte de Pernambuco, o estuário do Rio Botafogo tem histórico de contaminação por mercúrio (Hg), cromo (Cr) e zinco (Zn), necessitando avaliação de como mudanças no pH, potencial redox e teores de Fe no solo podem afetar a disponibilidade de metais e na microbiota do solo. Os objetivos desse estudo foram determinar os teores de Hg, Cr, Zn e Fe em solos de manguezal, e avaliar as mudanças na compartimentalização desses metais sob dez tempos de incubação expondo os solos a condições oxidantes, bem como as interferências das alterações geoquímicas na biomassa microbiana e respiração do solo. Solos de três áreas (A1, A2 e A3) do Rio Botafogo foram selecionados e coletados, passando por dez tempos de incubação (0, 5, 15, 30, 45, 60, 75, 90, 105 e 120 dias). Após a incubação, as amostras foram divididas em duas profundidades (0-5 cm e 5-10 cm). O potencial redox (Eh), e pH do solo foram determinados no campo e após cada coleta dos tempos de incubação. A granulometria do solo foi determinada para cada área. Os teores ambientalmente disponíveis de Hg, Cr, Zn e Fe foram determinados pelo método 3051A e a extração sequencial dos metais foi conduzida. A biomassa microbiana, respiração do solo e quociente metabólico também foram determinados. Os solos foram classificados como argilosos. Após 120 de umidade reduzida, os solos das três áreas acidificaram e o Eh aumentou de condições anóxicas/subóxicas para óxicas. Mudanças no pH do solo e potencial redox não causaram redistribuição significativa do Hg, Cr e Fe em A1, A2 e A3. Houve diminuição de Zn associado a fração carbonato e aumento da associação com a fração residual sob os diferentes tempos de incubação nas três áreas. Ferro estava associado principalmente a fração pirita e teve contribuição significativa na retenção de metais em frações mais recalcitrantes do solo. A acidificação e mudanças nas condições oxidantes do solo demonstraram maior efeito no aumento da biomassa microbiana, e diminuição da respiração do solo na área mais contaminada, possivelmente pelas novas condições favorecerem comunidades fúngicas em relação a bactérias. Além das mudanças no pH e Eh do solo, não houve correlação entre os metais pesados e os atributos microbiológicos avaliados nesse estudo. O quociente metabólico se manteve em níveis baixos nas diferentes áreas e tempos de incubação, demonstrando limitado impacto das alterações geoquímicas nos microorganismos dos solos de manguezal do Rio Botafogo.

Palavras-chave: Metais pesados. Microorganismos. Potencial redox. Solos alagados.

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1. INTRODUCTION

Mangroves are tropical ecosystems with a high diversity of animal and plant species that play different roles in ecosystem functions to the community. In Brazil, the growth of population occupancy in coastal areas has brought various problems to the mangrove's biodiversity and its capacity to play those roles. Industrial and domestic effluents are often discharged, without treatment, on the course of rivers, sometimes containing elements like heavy metals, causing the contamination of soils and risks to the biological community existing in the ecosystem. In the northern littoral of Pernambuco, many villages are built around mangroves. The maintenance of mangroves is important to local communities for being a site of fishery production, therefore, a source of income.

Mangrove soils are known for their capacity to hold contaminants under nonexchangeable phases, preventing the release of contaminants to underlying waters. Heavy metals like mercury, chromium and zinc tend to be adsorbed by the clay fraction and organic colloids present in the soil in forms that are less available to the environment, which makes mangrove wetland soils a sink of contamination. However, anthropogenic contamination and changes in land use can alter some participative variables in the adsorption of these elements to the soil. Consequentially, these factors increasing the bioavailability of metals and can cause the soil to be a second source of contamination.

The presence of heavy metals in quantities above the natural limits associated with labile fractions of the soil can disturb the biomass and respiration of local microorganisms. Characteristics that are intrinsic to mangrove soils, such as a reductive environment, high organic matter, and the presence of Fe, are favorable to the activity of anaerobic microorganisms that act on the cycling of elements captured by the mangrove plants, keeping the whole ecosystem well-functioning. However, anthropogenic contamination and changes in land use can alter some participative variables in the adsorption of these elements to the soil. Consequentially, these factors increase the bioavailability of metals and can cause the soil to be a second source of contamination.

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organic matter, and the presence of Fe, are favorable to the activity of anaerobic microorganisms that act on the cycling of elements captured by the mangrove plants, keeping the whole ecosystem well-functioning. However, heavy metals released in these soils can interfere with the microbial communities. Thus, although there is functional redundancy in every ecosystem, it is needed to know how contaminants can affect microbial communities in mangrove soils and the consequences of environmental changes to develop ecosystem functions.

Investigating of Hg, Cr, and Zn contents and their interaction with Fe and soil microorganisms after a change in the redox condition is necessary to forecast pollution risks and know the role of mangrove soils as a sink and source of contaminants. Furthermore, the evaluation of these attributes will verify the effects of environmental variations on the bioavailability of heavy metals and interference in the microorganismal biomass, respiration, and metabolic quotient in mangrove soils.

1.1.Hypothesis

- The exposure of mangrove soils to oxidizing conditions alter the distribution and stability of mercury (Hg), chromium (Cr), and zinc (Zn) in different mineral and organic compartments of soils, and modifies the bioavailability of these metals;
- Modifications in the bioavailability of metals decrease the estimate of microorganismal Carbon biomass and soil basal respiration.

1.2.Main Objective

The aim of this research was to evaluate alterations in compartmentalization and bioavailability of Hg, Cr, and Zn in response to geochemical changes in mangrove soils and their effects on the microorganismal activity.

1.3.Specific Objectives

- To evaluate the effect of oxidizing conditions on the distribution of metals in different mineral and organic compartments of soils.

- To evaluate changes in the bioavailability of Hg, Cr, and Zn in contaminated soils originally flooded in the function of exposure time to oxidizing conditions;
- To estimate the microorganismal Carbon biomass and C-CO₂ emission after modification in the bioavailability of metals.

2. LITERATURE REVIEW

2.1. Ecosystem functions of mangrove soils

Ecosystem functions are benefits provided by the interaction between elements of nature to human society (LAYKE, 2009). These functions can contribute to human well-being by providing regulating services, provisioning services, supporting services, and cultural services in a healthy ecosystem that ultimately contributes to human well-being. Soils, in general, are known for provisioning space for different ecosystem functions to happen. The soil can develop these functions as a compartment or as the habitat for organisms that provide ecosystem functions.

Mangrove soils develop many ecosystem functions, but some of the most discussed are coastal protection, habitat for several species, a sink of contamination, and carbon storage (HIMES-CORNELL et al., 2018). In addition, hydrological processes maintain mangrove soils characteristics and drive these functions, which are sensitive to flooding changes. Because of that, it is necessary to evaluate the impacts of changing this environment.

2.1.1. Coastal protection

Mangrove vegetation is a barrier that prevents tidal waters from crossing limits into the terrestrial system, decreasing the effects of natural phenomena that might cause erosion. Consequently, this action impedes houses and villages inundation, located around the coastline, and changing the habitat of several species that live on non-flooded ecosystems close to the mangroves. Also, it can ease the climate fluctuations by stocking CO₂, which is a greenhouse gas responsible for global warming (ALONGI, 2020).

The erosion removes soil from the terrestrial ecosystems, it can also release contaminants, like heavy metals, that are adsorbed in the soil particles from the mangroves,

this process allowing the metals to be moved to the water table and contaminate the organisms living in that ecosystem and other regions through intertidal groundwater (XIAO et al., 2019).

2.1.2. Sink of contamination

Mangrove soils under anaerobic conditions enable the adsorption of heavy metals on the soil fine particles, acting as a natural filter of contaminants (DAR et al., 2016). Organic matter and clay contribute to the retention or release of heavy metals in the environment.

Humic substances present in organic matter can increase heavy metal retention by altering the affinity of ions for soil surface, enhancing the soil adsorption capacity (PITTARELLO et al., 2018).

Clay is the soil particle that has the biggest interaction with elements like chromium and zinc (CHEN et al., 2016). Heavy metals are easily associated with this fraction because of their specific surface and adsorption capacity that acts on the retention of contaminants (SHI et al., 2019). Clay and silt fractions, along with dissolved humic substances (humic and fulvic acids) act as a filter, increasing the superficial surface area and adsorbing metals to their structure, which prevents metals from getting carried out to the overlying waters of mangrove environments (CLARK et al., 1998; PITTARELLO et al., 2018).

However, when the level of contamination is high and comes from anthropogenic inputs, the difference in the accumulation of heavy metals between mangroves with higher fine-grained soils (<63 μm) and sand-size diameters (2 mm - 63 μm) becomes less significant, as the input might be constant in urban areas (TAM; WONG, 2000).

2.1.3. Carbon storage

Mangroves are blue carbon forests with a high capacity to stock this element at expressive rates even in the superficial depths, with an estimated 933 Mg C ha⁻¹ globally, a storage capacity higher than any terrestrial ecosystem (PENDLETON et al., 2012; ALONGI, 2020). These values are obtained by considering plants, soil organic matter (SOM), and the microbial community biomass. The carbon accumulation rates are approximately 200 g C m⁻² year⁻¹, on the American continent. However, it decreases with time because anthropogenic

impacts remove mangrove plants and alter the whole biogeochemistry of these soils (JENNERJHAN, 2020).

The participation of microorganisms in the C storage in mangroves goes beyond their biomass. Under anoxic and suboxic redox conditions, these organisms can decompose organic matter at a slow rate compared to oxic conditions, creating a sink of carbon as the storage is higher than the emissions of CO₂ (ALLARD et al., 2020). Human activities and climate changes can alter this regulation function and contribute to the emissions of more CO₂ into the atmosphere, increasing global warming.

Changes in flooding and anaerobic conditions of mangroves can alter the geochemistry of heavy metals and the functioning of microorganism's activity, consequently interfering in the capacity of mangrove soils to perform their ecosystem functions.

2.1.4. Heavy metals in mangrove soils

The mangrove ecosystems in Brazil have been the target of contaminants released into rivers and estuaries by industries, agricultural companies, and households due to the growth of poorly planned urbanization in coastal areas and the lack of proper treatment for effluents. Industrial and domestic waste usually contains heavy metals, increasing the content of these elements in the soil. Although they are found naturally in the soil, heavy metals can alter their input and dynamics because of anthropic activities, going from non-available forms to bioavailable forms which can cause them to become a toxic risk to living organisms (LI et al., 2016).

To better understand the behavior of these elements in the environment some approaches like sequential extraction are recommended to be used as a tool to separate the different forms in which heavy metals are found in soil, as the content of metal itself sometimes is not enough to track the risks of bioavailability. These differences are attached to changes in biogeochemical processes and environmental conditions that interfere with their solubility and toxicity to organisms (DAR et al., 2016).

Land-use change can affect the bonding between heavy metals and soil particles. For example, in China, the transformation of a mangrove area into an aquaculture pond caused the acidification of the soil and reduction of total carbon, decreasing the contents of zinc and other

metals in this mangrove compared to others nearby. This shows the capacity loss of this soil to retain metals, releasing them to labile forms that water can carry to other environments (LI et al., 2018). In New Zealand, removing part of a mangrove forest caused soil oxidation and dissolution of pyrites, which decreased pH and organic matter contents, consequently reducing the soil's ability to retain heavy metals, releasing contaminants to adjacent waters (BASTAKOTI et al., 2019).

2.1.5. Iron (Fe)

Two factors that drive the behavior of heavy metals in mangrove soils are soil pH and Fe contents. At alkaline pH conditions, dissolved Fe co-precipitate with metals in solid phases. However, when pH becomes acidic, Fe is reduced, there is a dissolution of the precipitate formed between Fe and metals, and consequent release of contaminants to the solution (MEI et al., 2020).

Mangrove pH soils are more alkaline in wet seasons than in dry seasons, making the inundation of these soils an important factor to prevent dissociation of metals from organic matter and Fe contents in solid phases to the solution where microorganisms can absorb it. (NÓBREGA et al., 2013).

The dominant forms of iron found in mangrove soils are Fe oxide, Fe hydroxide, and sulfide (pyrite), all these forms being pH-driven (MEI et al., 2020). It is essential to understand the forms of Fe in the soil because there is a high association between this metal with [cmb1] organic matter and the binding of heavy metals in mangrove soils. In anoxic conditions, Fe dissolves in reductive phases. Once the system exposes Fe to oxic conditions, it can precipitate to oxidative phases. While this process happens, the Fe can be co-precipitated with organic matter forming stable complexes and not be easily released to the solution (DICEN et al., 2019). Iron plays an important role in metal binding in mangrove soils, as it can trap organic matter coming from terrestrial environments that are brought to the ecosystem of transition because of hydrological cycles (DICEN et al., 2019).

2.1.6. Chromium (Cr)

Chromium is an element that has six stages of oxidation in the environment. Nonetheless, Cr⁶⁺ (VI) is the most discussed form regarding toxicity to humans (IARC, 1990). In soils where the redox potential is more negative, there is a greater stock of heavy metals like Cr because of the precipitation of this element within Fe and SOM compounds as a result of reduction processes that occur in anaerobic soils (BOURGEOIS et al., 2019).

In mangrove ecosystems, Cr binds to soil particles more significantly than in overlying waters, rhizosphere soil, and mangrove plant roots. This means Cr is stable in wetlands and should remain in this situation when there is no disturbance in the environment. For example, a study of seasonal variations of heavy metals contents and partitioning from dry and wet seasons showed Cr enhance in the dry season, while also decreasing contents on the residual phase to soluble phases, increasing environmental risks (HONG et al., 2021). Because these variations are common results of tidal hydrodynamics of mangrove soils, the move of Cr between mobile and recalcitrant phases is cycles, but there might be a higher risk of liberating this metal to organisms in case the drainage of soils is constant.

There is an association of Cr permanency in the soil with the presence of iron in organic matter that binds the heavy metal in forms not available to the surrounding environment. However, changes in the soil moisture and redox potential occur, there can happen solubilization of Fe as oxides and releasing of Cr to the water column around the soil (LI et al., 2016). Once in the soluble phase, this metal can be a risk to living organisms as it affects the soil microbiota, mesofauna, and macrofauna and ultimately be present in drinkable water consumed by humans.

2.1.7. Zinc (Zn)

Human inputs of Zn in mangrove areas are increasingly contributing to the rise of this metal to a contamination status. In soils, Zn can be found linked to different compartments in soil like organic matter, carbonates (ZnCO₃), sulfides (ZnS), phosphates (Zn₃(PO₄)), and iron oxides (FeO), showing morphological changes in its conformation that can cause the metal to adhere to organic particles present in the soil (MEKAPOGU et al., 2017).

In anoxic environments, Zn shows a greater correlation with iron oxides, hydroxides, and particles with small diameters in soil than with carbonates and sulfides. These soil compartments are subject to alterations related to the hydrodynamics of aquatic environments,

which expose the soil to oxygen input that favors microorganisms acting on the decomposition of organic matter, therefore, being able to release zinc to bioavailable forms (DAR et al., 2016).

The relationship between Zn and Fe is fundamental for the metal to be trapped and environmentally unavailable under anoxic conditions (KUMAR; RAMANATHAN, 2015). Soil pH does not drive the sorption of Zn, because from acidic to alkali pH values (7.5), the main form of Zn found in soils is Zn^{2+} and there is an ion exchange between the metal and negative-charged clay that compensates the deprotonation at acidic soils (WALASZEK et al., 2018).

In inundated soils, Fe oxyhydroxide phases mostly host Zn, and common seasonal variations might not change the way Zn is bound in the soil. However, it is necessary to evaluate the association of Zn to fractions that are mobile at higher exposure to dry conditions to predict the possibility of being released to the solution once the conditions of mangrove soils are changed (WALASZEK et al., 2018; HONG et al., 2021).

2.1.8. Mercury (Hg)

Mercury is one of the most toxic natural elements to human beings, and part of its biogeochemical cycle takes place in aquatic environments (MICHALKE, 2016). Great changes in environmental conditions can modify the state of mangrove soils as a mercury sink. Because of that, there is a necessity to monitor contaminated areas and prevent these changes.

There is a globally recognized affinity between mangrove soils and Hg contents, especially in soils where the clay and organic matter contents are high, increasing the stock of Hg (MA et al., 2020). The higher potential of Hg stock occurs near mangrove vegetation in comparison with bare mangrove soils. Also, soils with high sand contents have a low capacity to retain this metal. Because of that, organic matter in the way it is present under anoxic conditions is important to increase retention of Hg in mangrove soils, as anaerobic microorganisms control the mineralization of this material, contributing to the sink of contaminants in soil (DUAN et al., 2021).

The potential availability of Hg to organisms present in the mangrove areas depends on the association with mineral and organic phases, with the possibility of Hg stocks formation in the soil (ARAÚJO et al., 2018). Oxidation and reduction processes in the soil can change

Hg availability to the environment by interfering with physic-chemical states in which Hg is found (BECKERS; RINKLEBE, 2017).

Mercury in labile phases of inundated soils correlates with Fe hydroxides and pH, and the surface diffusion of Hg in these cases might go from soils up to overlaying waters (ZHANG et al., 2021). This could mean a potential risk to the organisms around contaminated mangrove soils that are affected by decreasing pH, for instance, as most mangrove soils are around 7 to alkaline values (ZHANG et al., 2021).

A load of excessive nutrients from wastewater disposal in a freshwater lake from China caused soils acidification, and the reports found a negative correlation between soil pH and Hg mobility from non-labile phases to labile phases (ZHANG, 2017). These results indicate the direct influence of pH on the solubility and mobility of Hg in inundated soils. Therefore, it is necessary to evaluate if changes in moisture in mangrove soils can interfere with Hg mobility.

2.2. Microorganisms as soil quality indicators

At some stage, all biogeochemical cycles of elements depend on the activity of microorganisms. In mangroves, this is especially true for carbon, as some groups of bacteria and fungi control the availability of nutrients for plants in a place that has low oxygen, high salinity, and neutral pH, and both plants and microorganisms make a stock carbon in these environments (ALLARD et al., 2020). Therefore, human activities that cause disturbances in the mangrove environment, like drainage and the release of contaminants, might interfere in the microbiota, directly and indirectly, affecting their roles on the biogeochemical cycle of elements, and affecting the ecosystem functions soils.

The interaction between organisms and contaminants happens both from the execution of processes related to the removal and release of metals from organic matter and the interference of heavy metals in the functionality of microorganisms. For example, in the evaluation of Zn availability, soil samples from a chronically polluted mangrove were treated with a biocide to inhibit the activity of microorganisms and compared to samples that did not undergo treatment. The results obtained showed that Zn removal from tidal waters and adsorption on soils is greater in samples where there is higher biological activity,

demonstrating the participation of microorganisms in metal retention in estuarine environments (SONDERMANN et al., 2018).

2.2.1. Soil microbial biomass (SMB)

There is an inversely proportional relationship between heavy metals and microbial abundance in mangrove soils. Therefore, these organisms can be bio-indicators of soil quality, showing some risks of heavy metal pollution to the environment (NUMBERE, 2017).

Heavy metals in flooded environments have the potential to decrease soil microbial biomass in acute short-term exposure because of their direct toxicity to microorganisms, causing either reduction of microbial communities or inhibiting specific genes responsible for key processes related to nutrient cycling and element immobilization (LI et al., 2019). However, the effects of metals on the microbial biomass are less visible in chronic long-term exposure to these contaminants, when the combination of other effects on the soil might play a bigger role on the geochemistry of metals and the dynamic with microorganisms (SONG et al., 2018).

In an experiment of long-term incubation to determine the interference of Zn and other metals in the microbiota of saturated soils, single metals alone could not explain alterations on microbial biomass when in immediate contact with the microorganisms, but the interaction of metals and soil pH had a better correlation with a biomass decrease on the long term (SONG et al., 2018).

Soil microbial biomass is a key ecological parameter to determine the functioning of ecosystems and stress to the microorganisms because it helps correlate the abundance of these organisms to activities of biogeochemical cycles (SINGH; GUPTA, 2018). Even stressed ecosystems, such as the ones contaminated by heavy metals, can show high levels of microbial biomass because of the buffering capacity of microorganisms that can adjust their population and still contribute to key roles of ecosystem functions in soils (SINGH; GUPTA, 2018).

Some properties of mangrove ecosystems can control the way microorganisms are present in the soil. For example, the fluctuation of water levels can interfere with the soil microorganisms because the shifts of tidal waters drive nutrients, contaminants and change soil potential redox, and these parameters change the conditions for microbial growth (MA et al., 2018).

When an environment is changed, a new optimal condition for microorganisms is generated, and the microbes that are adaptable to the new situation grow at higher rates compared to the ones that are not (MA et al., 2017). For instance, the restoration of a river in China affected the coastal soils changing pH and nutrient availability, which caused the fungi promotion and decrease of a bacterial community, consequently increasing soil microbial biomass because of the structures of fungi that add to the fungal-to-bacterial ratio (MA et al., 2017; CHEN et al., 2021). An explanation for this is that fungi can convert recalcitrant materials into accessible forms and expand their exploration range, which is how they increase their chances of survival in impacted mangrove soils (ALLARD et al., 2020).

2.2.2. Soil respiration (SR)

Another parameter used to understand the health of mangrove soils is the basal rate of soil respiration (SR). While soil microbial biomass might increase during a decline in water levels in soils originally inundated, it might not affect the SR as much. Different groups of microorganisms can contribute to the emissions of CO₂ at the same rates of a non-contaminated site, even after a disturbance on their abundance happens, as it can be observed in soils where fungi populations take the main control of activities and bacteria populations show a decline on biomass (MA et al., 2018).

Soil respiration is a process that contributes to the emissions of CO₂ to the ecosystem, and it can be related to microorganisms actively participating in the decomposition of organic matter at different rates depending on land use, soil moisture, and seasonal precipitation variability (SHI et al., 2020).

A study about responses on SR under redox status varying from extreme anaerobic conditions to aerobic conditions in wetlands from China showed that increasing redox potential and temperature also increased soil microbial respiration (CHEN et al., 2018).

Soils from tropical coastal areas are saturated during most of the year. The high moisture can decrease SR because it limits oxygen, nutrient availability, and diffusion of CO₂, making limited acceptor electrons such as nitrate, iron, and sulfate the ones available to be consumed by microorganisms under anaerobic conditions (HAN et al., 2018).

2.2.3. Microbial metabolic quotient (qCO_2)

It is possible to compare soil microbial biomass and soil respiration to better explain the behavior of microorganisms under contaminated soils (GEOGHEGAN et al., 2021). For that matter, microbial metabolic quotient (qCO_2), the microbial respiration per unit of biomass, is a factor that can measure how much energy is necessary for a population of microorganisms to maintain their biomass, thus making it possible to explain if the soil is under degradation that consequently puts microorganisms under stress (BASTIDA et al., 2008).

Drainage of soils from areas where there is high moisture can increase the microbial metabolic quotient, meaning higher stress to the microorganisms caused by the loss of CO_2 that is promoted at aerobic conditions (HE et al., 2020). In mangrove soils, a low qCO_2 means less energy required to maintain the microbial biomass, which can be related to no stress in the environment or a loss of carbon through respiration combined with a decline in microbial biomass caused by some disturbance to a group of microorganisms, conversely favoring another group (DINESH & CHAUDHURI, 2013).

Even though it is expected to observe a change in soil carbon biomass and respiration rates where a disturbance caused drought of naturally saturated environments, the maintenance of standard qCO_2 values in soils after drainage is possible because of the high ability of some fungi groups to develop their communities under the new conditions established (HE et al., 2020).

In contaminated mangrove soils, high humidity and neutral pH values are factors that influence the behavior of microorganisms normally present on-site. These factors set an environment that is ideal for specific groups of anaerobic microbes able to respond to contamination and participate in the decomposition of elements and emissions of CO_2 , even if the conditions are not favorable to most groups of microorganisms (GAO et al., 2019). Normally, these variables are constant in most mangroves, being altered only by anthropogenic disturbances or specific differences in the composition of these soils. Therefore, it is necessary to evaluate how the exposure of mangrove soils to changes in the redox conditions interferes

with the geochemistry of heavy metals and the relation with impacts on the microbiota and their ability to develop ecosystem functions.

2.3. Botafogo River Estuary

The Botafogo River is located on the northern coast of Pernambuco, Brazil. It provides a watershed included in the Small Coastal Basins Group (GL-1), with the greatest extension among all of them, which is approximately 51 kilometers (APAC, 2020). The Botafogo River basin combined with the GL-1 supplies water to more than six cities for a population of over 1.205.700 inhabitants in the State of Pernambuco, while also having an important socio-economic value because of the surroundings as a place of urban and industrial occupation with fishing activities and sugarcane cultivation (CPRH, 2008).

It has three main species of mangrove plants *Rhizophora mangle*, *Laguncularia racemosa* and *Avicennia schaueriana* (MEDEIROS et al., 2001), and species of crustaceans that add to the total carbon and carbonates in the soil (AZEVEDO-LINHARES; FREIRE, 2015), making this mangrove an important agent of regulating ecosystem functions of soils.

The course of the river receives non-treated effluents from domestic and industrial sources, causing the contamination of water and soil in that area that increasingly suffers from alterations on land occupation and disorganized population rise (NILSON JR et al. 2001). Among the pollutants discharged in the river, mercury pollution is the most well-known issue occurring in the estuary. The pollution of the Botafogo River has been studied for some years, but there are not yet efficient policies to prevent the area from being more damaged.

The Botafogo River has the highest concentration of mercury in soils from coastal environments in Brazil (10.44 mg kg⁻¹) because of the discharge of effluents from a chlor-alkali plant in this river for several years (ARAÚJO et al., 2019). When comparing the Hg contents found in the area over thirty years ago (CETESB, 1984) and the most recent investigation, it is evident that the metal remains in the mangrove soil, making this ecosystem a drain of contamination. However, there is a high ecological risk from exposure to Hg present in that soil in the current state of environmental conditions (ARAÚJO et al., 2020), thus making modifications in the soil a threat that could increase risks.

2.4.Environmental policies for mangroves in Brazil

The importance of mangrove ecosystems to humanity and other elements of nature is highly discussed and understood. However, there is a lack of strong environmental policies that prevent the loss of mangrove forests to other forms of land use, as well as the contamination of rivers that end up polluting mangrove soils.

Brazil has 7% of the world's mangrove areas, being the third country in this classification (GIRI et al., 2011). The Federal Law nº 12.651/2012 established by the Brazilian Forest Code legally protected mangrove areas by classifying them as Permanent Protection Areas (APPs), thus prohibiting the deforestation and land-use change of this and other coastal environments (ALBUQUERQUE et al., 2015). However, recent changes in policies weakened this law when the Brazilian Government revoked the normative that protected mangroves (CONAMA art 303), now making this ecosystem passible of being explored by human activities and entrepreneurship (BERNARDINO et al., 2021).

Anthropogenic impacts have already increasingly caused the loss of mangrove areas to the construction of houses, industries, shrimp farms, and other human activities (LACERDA et al., 2021). With the weakening of environmental protection laws, it is predicted that water quality, soil retention capacity of pollutants and food provision coming from fishery might be reduced as a consequence of higher mangrove exploration (BERNARDINO et al., 2021).

The impacts on mangrove soils come from direct and indirect actions of contamination and utilization of mangrove land for other purposes, changing the whole aspects that make this ecosystem a pool of functions that benefit the communities of macro, meso, and microorganisms, including humanity (LACERDA et al., 2021).

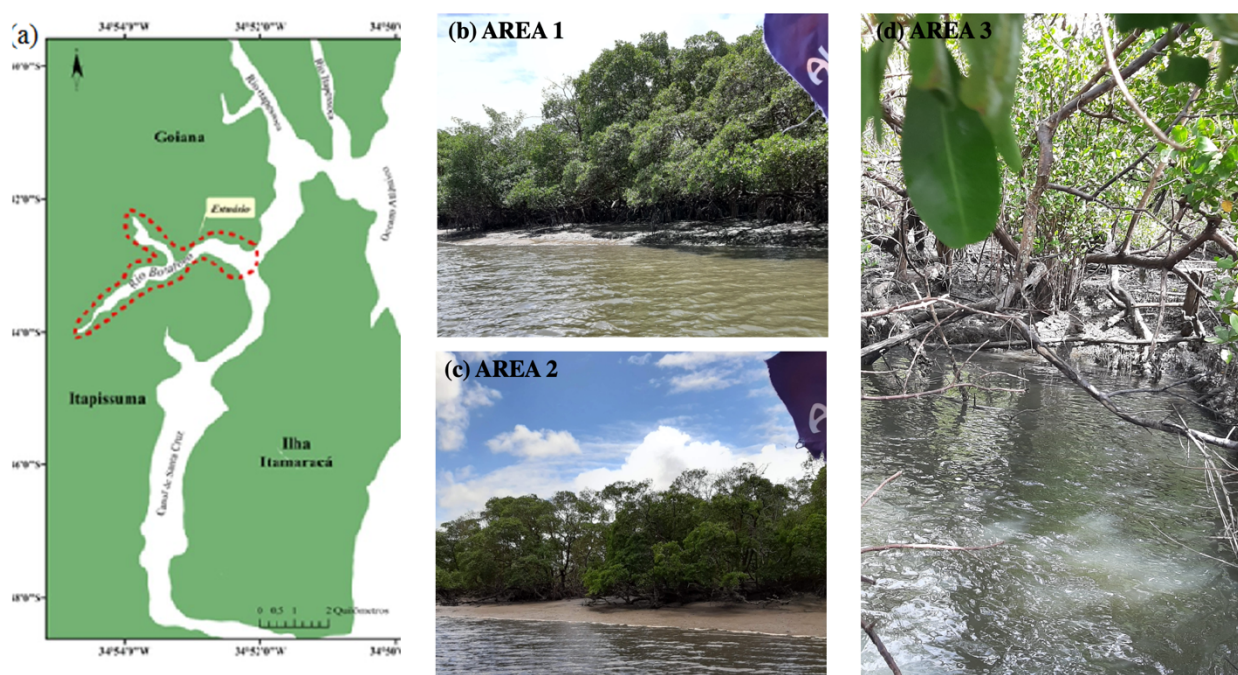
From 1990 to 2015, the north littoral of Pernambuco, Brazil, has lost approximately 10% of mangrove areas that were converted mainly to aquaculture, and this is a higher loss than the ones observed in other mangroves from PE over three decades (PELAGE et al., 2019). Because of this worrisome data, environmental policies need to be reinforced to protect the Botafogo River mangrove, an area that contributes to ecosystem functions and needs to be preserved especially after already being contaminated by heavy metals for so long.

3. METHODOLOGY

3.1. Study area and incubation of soils

The Botafogo River estuary (Figure 1) is a mangrove surrounded by industries and sugarcane crops located in the northern littoral of Pernambuco State, Brazil. Based on a previous work that evidences the contamination of this mangrove soil by Hg, three areas were selected to be studied in this research (ARAÚJO et al., 2018). On September 3rd and 4th of 2020, the soil sampling was conducted in the three areas selected, where two soil samples formed by twenty soil cores were collected in each area using PVC tubes (10 mm of diameter and 10 cm of depth) open at the upper and lower ends. After collection, the tubes were sealed and stored in a hermetically sealed thermo-box with ice to avoid chemical and biological changes in the soil samples that were further used for the incubation test.

Figure 1 - Study area of Botafogo River (a) and the sampling sites A1 (b), A2 (c) and A3 (d).

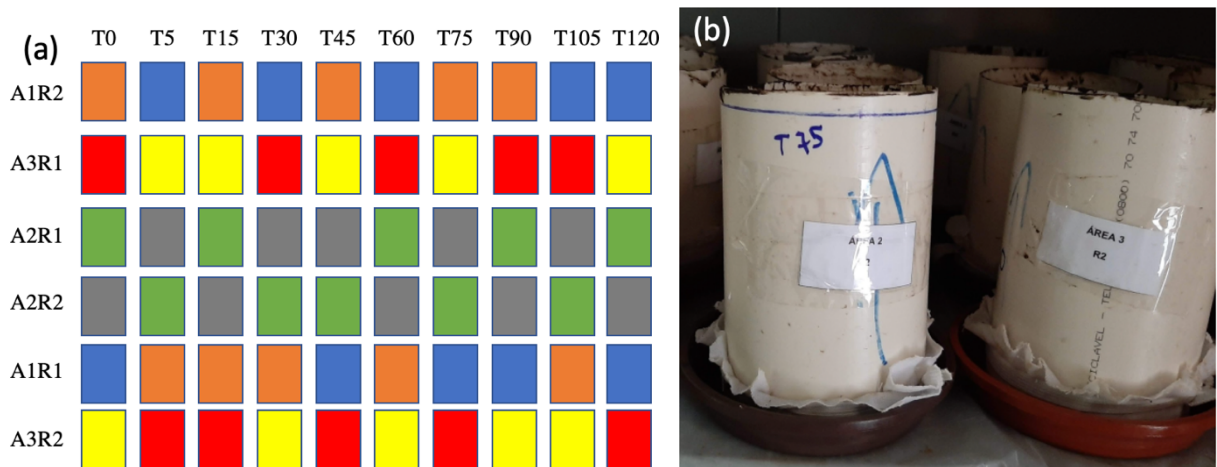


The 60 soil samples intended for incubation were kept in the PVC tubes, having the lower end sealed. Each tube represented an experimental unit (3 areas, ten incubation times, two repetitions). Incubation times were 0, 05, 15, 30, 45, 60, 75, 90, 105, and 120 days and

evaluations were performed by subtracting two soil samples per area at the end of each time (Figure 2).

The humidity of the samples was gradually decreased to approximately 50% of their calculated humidity at pot capacity, and distilled water was added when necessary. The measurement of pH and Eh (oxi-reduction condition) of the samples was performed for all collection times. After incubation, the collected samples were divided into two depths (0-5cm and 5-10cm), each one being homogenized, stored in plastic recipients, and kept refrigerated at -18°C until the time of chemical and biological analysis.

Figure 2 - Scheme of sampling set in Areas (A) 1, 2 and 3 with repetitions (R) 1 and 2 through incubation times (T) of 0, 5, 15, 30, 45, 60, 75, 90, 105 and 120 days (a); incubation recipients (b).



3.2. Soil particle-size distribution

This analysis was carried out in one sample composed of two from each area of study. First, the samples were dried and passed through a 2 mm sieve. Then the following pre-treatments were conducted:

- Removal of carbonates: 50 g of soil were put in plastic buckets and add a solution of hydrochloridric (10%) until the soil did not show effervescence;

- Removal of salts: the soil samples were put in filters and washed with a solution of 60% of ethyl alcohol until the filtrate did not show the formation of a precipitate when reacting with silver nitrate due to the formation of silver chloride;
- Removal of organic matter: the soil samples were put back into the plastic buckets, where a solution of 50% hydrogen peroxide was added until no more effervescence was observed in the material. Then, the samples were placed on filter papers and washed with distilled water until the presence of hydrogen peroxide was not observed. Afterward, the samples were dried in the oven at 60°C and homogenized.

The particle size analysis was made for the hydrometer method, according to EMBRAPA methodology (2017) with adaptations described by Almeida (2012) where 20 g of dry soil, 100 ml of water, and 25 ml of sodium hexametaphosphate as dispersant were added.

3.3. Analysis of Hg, Cr and Zn in soil

3.3.1. Environmental availability of metals

To determine the environmentally available contents, aliquots of the refrigerated soil samples were dried in the oven at 35°C, pulverized and passed through a stainless-steel 0.15 mm sieve (ABNT No. 50). Later, the samples were subjected to acid digestion 3051A (USEPA, 1998) where 0.50g of soil was added to PTFE tubes with 9 mL of nitric acid and 3 mL of hydrochloridric acid at 175°C for 4 hours and 30 minutes under closed system. The samples were then filtered with ultrapure water and stored in glass containers. Chromium, zinc and iron were detected by inductively coupled plasma atomic emission spectroscopy (ICP-OES) and Hg was determined by flow injection cold-vapor generation atomic absorption spectrophotometry (AAAnalyst 800 Perkin Elmer) with electrodeless discharge lamps and sodium borohydride 0.2% as a reducing agent.

For quality control, certified soil samples (NIST San Joaquin – 2709a) with known concentrations of all analyzed metals and blanks were used. Based on the NIST certified values, the percentage recovery for each metal studied was of 97.7% (Hg), 93.5% (Cr), 70.92% (Zn) and 87.5% (Fe).

3.3.2. Sequential Extraction of Hg

The sequential extraction of Hg was conducted following the methodology of BLOOM *et al.* (2003). For each sample 1g of humid soil was weighed and put inside of Teflon bottles. The sequential extraction of water-soluble Hg (F1), human stomach acid soluble Hg (F2), organo-chelated (F3), elemental Hg (F4), and mercuric sulfide (F5) was conducted as follow:

- Fraction 1 (F1): 25 mL of ultra-pure water was added to the bottles and the samples were put in the horizontal shaker for 18 hours. After that, the samples were put in the centrifuge for 20 minutes at 3,000 rpm then verted to quantitative filters where the extraction was collected at 50 mL volumetric flasks. The Teflon bottles were filled with 20ml of ultrapure water again then closed and put in the horizontal shaker for 15 minutes following 20 minutes at the centrifuge for 20 minutes at 3,000 rpm. This solution was filtered to the volumetric flasks where 0.5ml of 0.2M BrCl and ultrapure water was added to complete 50 mL.
- Fraction 2 (F2): 25 mL of a solution formed by 0,01 mol/L of hydrochloridric acid and 0.1 mol/L of acetic acid was added to the bottles and the samples were put in the horizontal shaker for 18 hours. After that, the samples were put in the centrifuge for 20 minutes at 3,000 rpm then verted to quantitative filters where the extraction was collected at 50mL volumetric flasks. The Teflon bottles were filled with 20ml of the 0.01 mol/L HCl and 0.1 mol/L CH₃COOH solution again then closed and put in the horizontal shaker for 15 minutes following 20 minutes at the centrifuge for 20 minutes at 3,000 rpm. This solution was filtered to the volumetric flasks where 0.5ml of 0.2M BrCl and ultrapure water was added to complete 50 mL.
- Fraction 3 (F3): 25 mL of 1M potassium hydroxide was added to the bottles and the samples were put in the horizontal shaker for 18 hours. After that, the samples were put in the centrifuge for 20 minutes at 3,000 rpm then verted to quantitative filters where the extraction was collected at 50mL volumetric flasks. The Teflon bottles were filled with 20ml of KOH again then closed and put in the horizontal shaker for 15 minutes following 20 minutes at the centrifuge for 20 minutes at 3,000 rpm. This solution was

filtered to the volumetric flasks where 5ml of 0.2M BrCl and ultrapure water was added to complete 50 mL.

- Fraction 4 (F4): 25 mL of 12M of nitric acid was added to the bottles and the samples were put in the horizontal shaker for 18 hours. After that, the samples were put in the centrifuge for 20 minutes at 3,000 rpm then verted to quantitative filters where the extraction was collected at 50mL volumetric flasks. The Teflon bottles were filled with 20ml of 12M HNO₃ again then closed and put in the horizontal shaker for 15 minutes following 20 minutes at the centrifuge for 20 minutes at 3,000 rpm. This solution was filtered to the volumetric flasks where 0.5ml of 0.2M BrCl and ultrapure water was added to complete 50 mL.
- Fraction 5 (F5): A solution of 10 mL of HCl and 3 mL HNO₃ was added to the bottles and the samples were agitated then put to rest for 12 hours. After that, the samples were centrifugated for 20 minutes at 3,000 rpm. The solution was filtered to volumetric flasks and ultrapure water was added to complete 50 mL.

Mercury contents from each fraction were determined by flow injection cold-vapor generation atomic absorption spectrophotometry (AAnalyst 800 Perkin Elmer) with electrodeless discharge lamps and sodium borohydride 0.2% as a reducing agent.

3.3.3. Sequential Extraction of Cr, Zn and Zinc

The method used was described by Tessier, Campbell, Bisson (1979); Fortin, Leppard, Tessier (1993) and Huerta-Diaz; Morse (1990), with adaptatons by Ferreira (2006). For this, 2 g of moist soil was weighed and used in the following sequential extraction steps:

- Exchangeable (F1) - 30 mL of a 1M MgCl₂ solution (pH 7.0) was added to the soil samples that were then agitated for 30 minutes and centrifugated at 6,000 rpm for 30 minutes;

- Carbonate (F2) - a 30 mL aliquot of 1M sodium acetate (pH 5.0) was added to the samples, which were shaken for 5 hours and then centrifugated at 6,000 rpm for 30 minutes;
- Ferrihydrite (F3) - a solution of 30 mL of hydroxylamine (0.04M) and acetic acid (25%) was added to the samples, which were shaken for 6 hours at 30°C and then centrifugated at 6,000 rpm for 30 minutes’
- Lepidocrocite (F4) - a solution of 30mL of hydroxylamine (0.04M) and acetic acid (25%) was added to the samples, which were shaken for 6 hours at 96°C and then centrifugated at 6,000 rpm for 30 minutes
- Crystalline Fe oxide (F5) - 20 ml of a solution of sodium citrate (0.25M), sodium bicarbonate (0.11M) and 3g of sodium dithionite were added to the samples, which were then shaken for 30 minutes at 75°C, then centrifugated at 6,000 rpm for 30 minutes
- Pyrite (F6) - 10 ml of concentrated nitric acid (HNO₃) was added to the samples, which were shaken for 2 hours at room temperature. The extracts were centrifuged at 6,000 rpm for 30 minutes and the residue was washed with 15 ml of ultrapure water. After stirring and centrifuging, it was added to the initial extract

The residual fraction (F7) was calculated by subtracting the total contents of the metals by the contents found in F1, F2, F3, F4, F5 and F6.

3.4. Soil Basal Respiration (C-CO₂ emission)

Following the methodology of Mendonça e Matos (2005), 50g of dry soil in each sample was weighed. The samples were placed in plastic recipients, and 25mL of 0.5M of sodium hydroxide solution was added to small cups that were put inside the recipients with the soil samples. The recipients were sealed, and the incubation was conducted for seven days.

The same procedure was done for blank samples. After seven days of incubation, 10 mL of the NaOH solution from each sample was taken from the cups and transferred to 125 mL erlenmeyers. In each erlenmeyer flask, 5 mL of 0.05M barium chloride solution and three drops of 1% phenolphthalein were added. The titration of samples was carried out using a solution of 0.25M hydrochloridric acid. The C-CO₂ (mg kg⁻¹ day⁻¹) was estimated by the difference between the soil samples and the blank treatment for seven days.

3.5. Microbial biomass Carbon

The procedure followed Barlett e Ross, (1988) methods. The equivalent amount of humid soil to have 10g of dry soil sample was weighed and put in 250 mL erlenmeyers. Half of the samples were submitted to microwave irradiation for three minutes, and the other half did not undergo treatment. Subsequently, 80 mL of 0.5M potassium sulfate was added to all, and the samples were shaken for 30 minutes on a horizontal shaker. After 30 minutes of rest, 2 mL of the soil sample extractions plus 3 mL of distilled water were pipetted into glass containers where, in order, 2.5 mL of working solution (sodium pyrophosphate, sulfuric acid, potassium permanganate, and sulfate manganese monohydrate) and 2.5 ml of concentrated sulfuric acid were added. The samples were manually shaken and put to rest for 18 hours. After this period, the samples were read in a spectrophotometer with wavelengths of 495 nm. The estimate of microbial Carbon biomass (mg kg⁻¹) was obtained by the difference between blank and soil samples.

3.6. Microbial metabolic quotient

The microbial metabolic quotient was measured by dividing the soil respiration rate by the soil microbial biomass.

3.7. Statistical analysis

Pearson's correlation coefficient was used for all chemical and biological attributes of soil and the statistical significance used was $p < 0.05$. The regression analysis was used for

chemical attributes and the Student's t-test was used for microbiological analysis. All statistical analysis were performed through the R software.

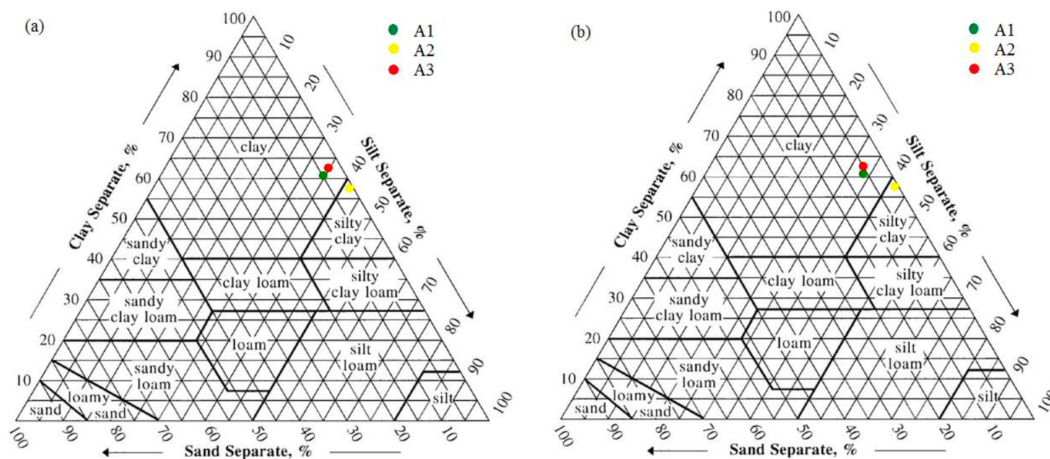
4. RESULTS AND DISCUSSION

4.1. Physical attributes

Soils from A1, A2, and A3 have over 50% of clay in both depths studied, classified as clay or silty clay (Figure 3), agreeing with the average soil texture classification in other mangroves around the world (WANG et al., 2021). There is no statistical difference between depths for clay fractions in all areas ($p > 0.05$). The high content of clays in the Botafogo River soils results from fine particles being carried by tidal waters from different points of the river and accumulating in specific areas because of the hydrodynamic conditions and high content of organic matter settled around mangrove vegetation that can hold these particles and decrease disturbance from tides (ARAÚJO, 2018; GOMES et al., 2016).

Clay and silt fractions have surfaces with an adsorption capacity much higher than sand. There is a strong correlation between silt with Cr ($r=0.91$, $p < 0.05$), and Zn ($r=0.90$, $p < 0.05$) and between clay with Cr ($r=0.65$) and Zn ($r=0.99$). Clay had also a weak correlation with Hg ($r=0.59$), while sand showed non-significant negative correlation with all metals. The major ways clays can form a sort of microaggregate with metals is by the strength of the chemical bond between metal ions and the surface of solid particles, as well as the interaction with organic compounds, both driven by pH (TOMBACZ, 2003).

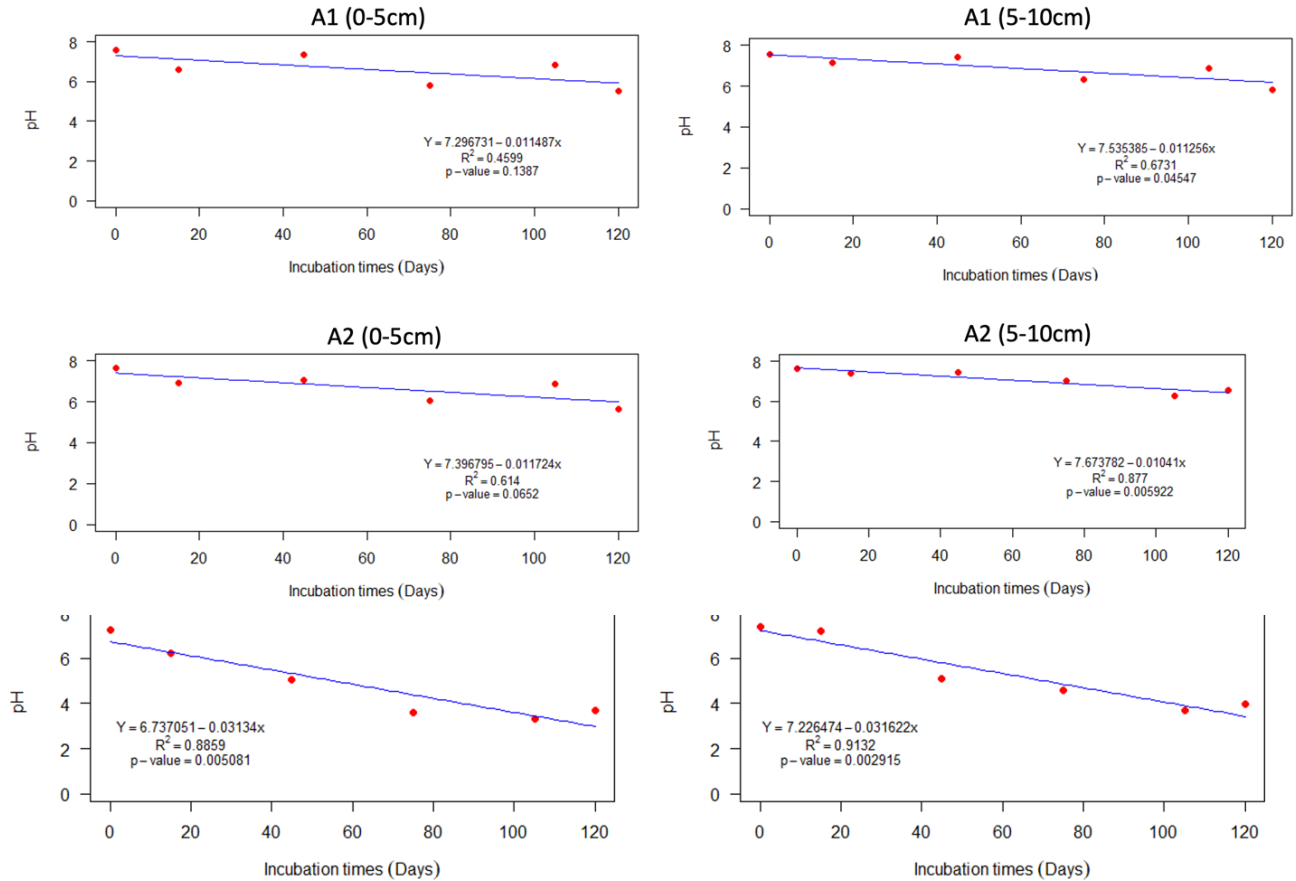
Figure 3 - Soil texture triangle of A1, A2 and A3 for the 0-5cm (a) and 5-10cm (b) depths.



4.2. Soil pH and redox potential

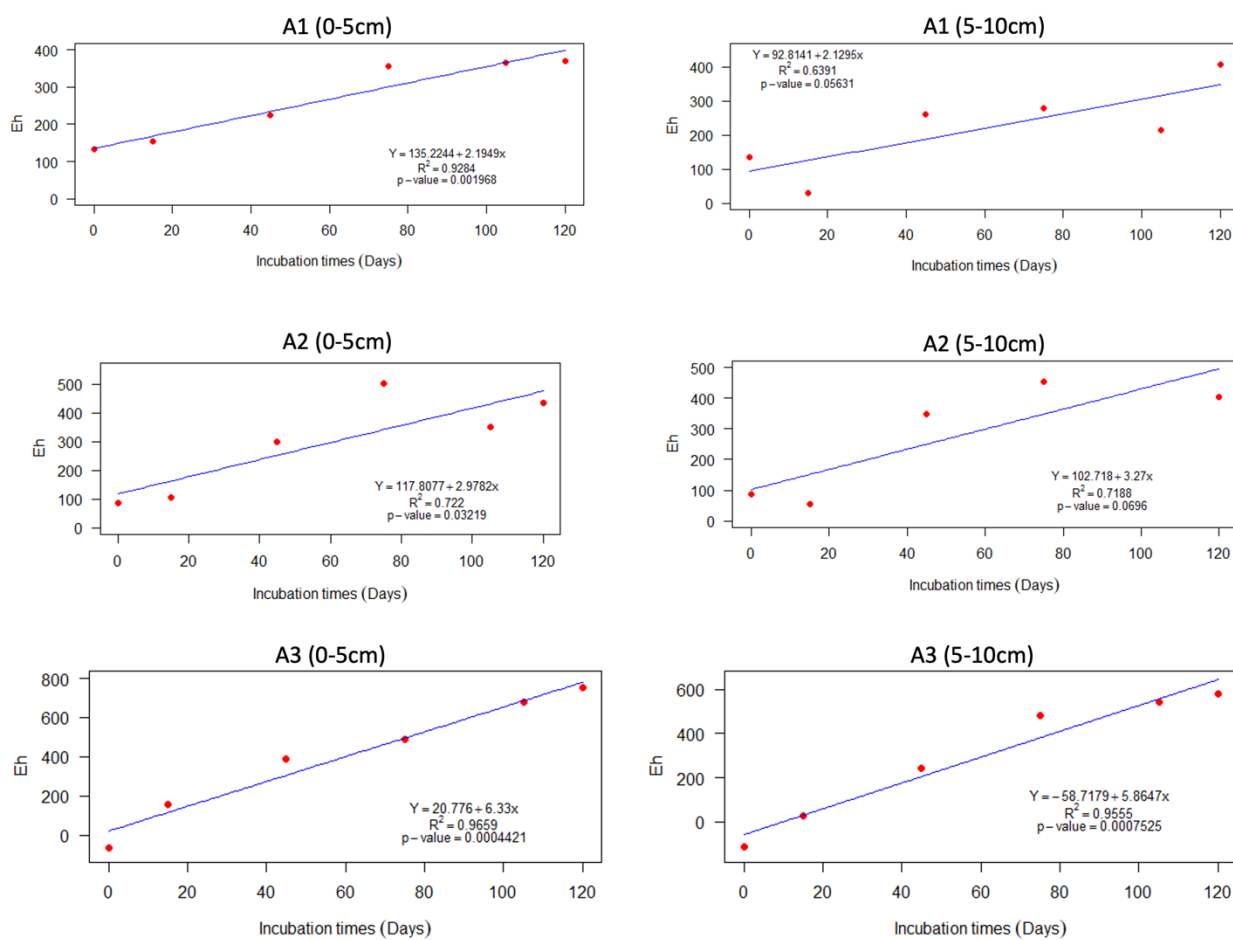
Soil pH at the moment of field sampling was approximately 7.5 (A1), 7.65 (A2), and 7.25 (A3) in the 0-5cm and 5-10cm depths (Figure 4). At the end of the 120 days of incubation, while pH became slightly more acidic on A1 (5.6) and A2 (6.5), it dropped significantly in A3 (3.8), showing no statistical difference between depths in all areas ($p < 0.05$).

Figure 4 - Soil pH A1 (0-5 cm), A1 (5-10 cm), A2 (0-5 cm), A2 (5-10 cm), A3(0-5 cm) and A3 (5-10 cm) under incubation times (days).



Soil samples from A1 and A2 reacted to the test for carbonates with HCl, confirming the presence of dissolved inorganic carbon. The presence of this material in wetlands explains the reason some soils keep the buffering capacity, preventing abrupt pH changes, while others with low levels of carbonates are more likely to acidify (GARCIA-TROCHE et al., 2021).

Figure 5 - Soil potential redox (Eh) A1 (0-5 cm), A1 (5-10 cm), A2 (0-5 cm), A2 (5-10 cm), A3 (0-5 cm) and A3 (5-10 cm) under incubation times (days).



Decreased soil moisture to half of the initial humidity resulted in redox changes from anoxic (100 - 300 mV) to oxic conditions (>300 mV) in sites A1, A2, and A3 by the end of 120 days of incubation (Figure 5).

4.3. Heavy metal contents

The following sequence shows a gradient of Zn, Cr and Hg contamination in the study areas: A3>A2>A1, where A3 is the most contaminated, A2 is of middle contamination, and A1 the less contaminated area (Table 1). These values are compared against the sediment quality guidelines set by international standards of wetland soils: threshold effect levels (TEL), the level of contamination where toxic responses of organisms start occurring; and probable effect level (PEL), where the large population of organisms shows a toxic response to the level of contamination (USEPA, 1996).

Table 1 - Mean values of mercury, chrome, zinc, and iron concentrations in A1, A2, and A3.

SD¹: Standard Deviation; TEL²: Threshold effect level; PEL³: Probable effect level

ID	Depths (cm)	Hg (mg/kg)	Cr (mg/kg)	Zn (mg/kg)	Fe (g/kg)
A1	0-5	1.34	42.87	21.78	24.91
A1	5-10	1.48	44.53	22.27	26.44
SD ¹	-	0.1	2.55	2.52	1.9
A2	0-5	2.6	45.57	24.36	29.76
A2	5-10	2.87	47.88	24.45	32.03
SD ¹	-	0.2	6.82	5.03	2.93
A3	0-5	6.3	50.21	29.22	34.41
A3	5-10	6.35	50.97	30.85	34.96
SD ¹	-	0.38	4.83	10.12	1.89
TEL ²	-	0.1	52.3	124	-
PEL ³	-	0.7	160	271	-

Mercury contents are highly above PEL in all areas, almost reaching TEL in A3 (Table 1). These results show high contamination of this mangrove, as previously stated by other studies (CPRH, 1984; ARAUJO, et al., 2019).

All three areas showed Cr contents close to TEL, increasing the necessity of monitoring these areas to prevent an elevation of Cr to polluted levels in the Botafogo River. However, mean values of Zn in A1, A2 and A3 are below the TEL and PEL, showing no contamination of this metal in the Botafogo River mangrove soils.

Zinc has a positive correlation with Fe in the 0-5cm depth ($r=0.56$, $p<0.05$) and 5-10cm depth ($r=0.6$, $p<0.05$) following the tendency of wetland soils to form strong associations between Zn and Fe oxyhydroxide fractions (WALASZEK et al., 2018).

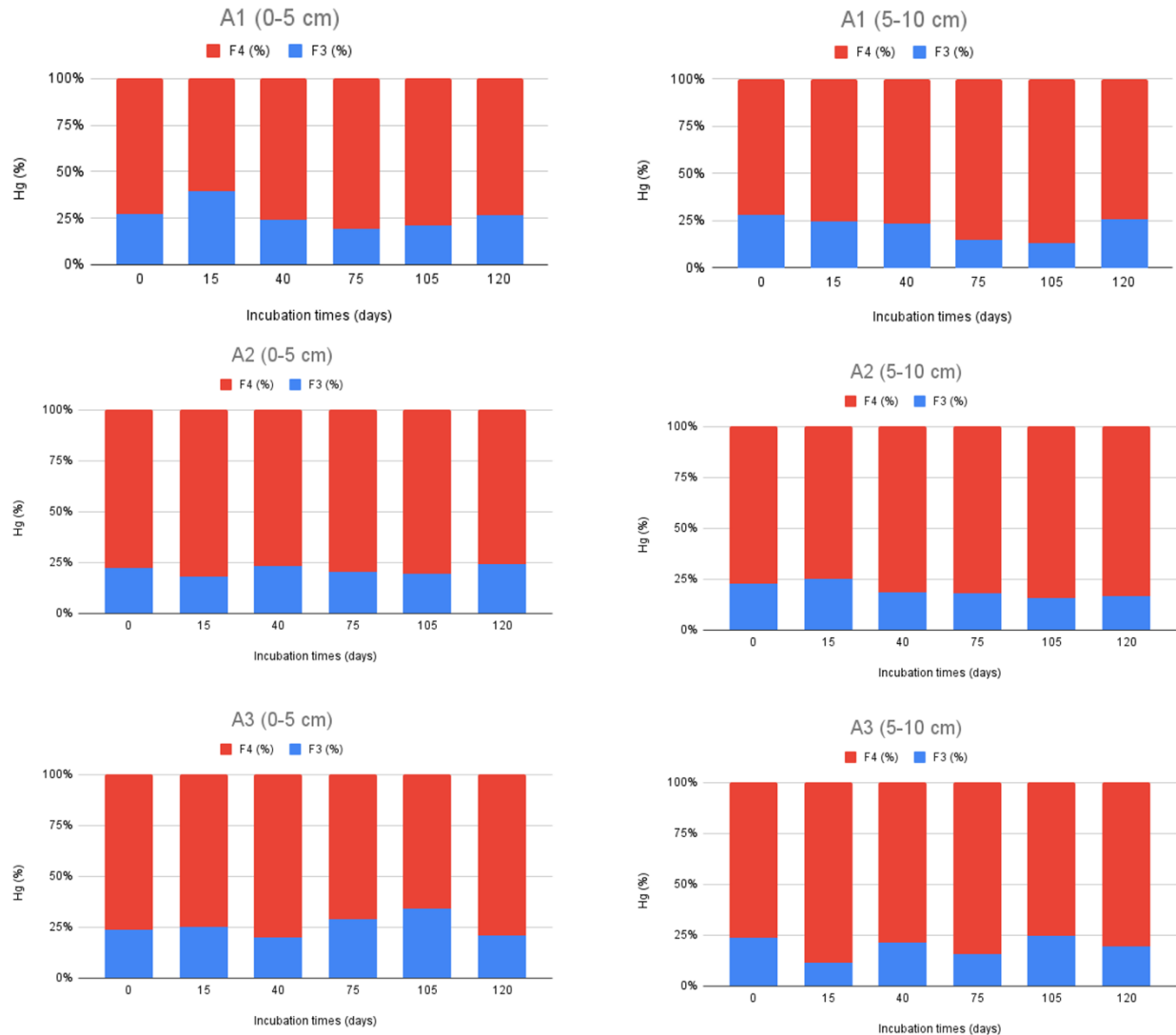
Chromium is highly correlated with Fe at both depths ($r=0.79$, $p<0.05$). There is a high correlation between Fe and Hg in 0-5cm ($r=0.86$, $p<0.05$) and 5-10cm ($r=0.87$, $p<0.05$), showing again the importance of Fe binding with metals in wetland soils. Mangrove vegetation has the potential to form Fe plaque on the rhizosphere that can trap Hg in the soil (CHAI et al., 2020) and along with the presence of clay fractions, these soils bound with metals on solid particles in non-exchangeable phases.

There is also a correlation between Cr and Zn in the 0-5cm depth ($r=0.7$, $p<0.05$) and in the 5-10cm depth ($r=0.82$, $p<0.05$) probably because of the association of Cr and Zn to organic matter and Fe in mangrove soils (MARCHAND et al., 2006).

4.4.Hg distribution in soil

The sequential extraction of water-soluble Hg (F1), human stomach acid-soluble Hg (F2), organo-chelated Hg (F3), elemental Hg (F4), mercuric sulfide (F5) was carried to understand better the behavior of Hg in these soils after alterations in the chemical characteristics (Figure 6). In this study, all Hg contents were mainly associated with F3 and F4, from time 0 to time 120 in all areas, showing a moderate to the high stability of Hg in these soils. The other three fractions (F1, F2, and F5) showed no contents or contents below the detection limit of the equipment ($0.05\mu\text{g/L}$). The water-soluble and human stomach acid-soluble Hg fractions are the most unstable fractions, allowing the release of Hg to solution and increasing availability to organisms uptake (YU et al., 2012). The organo-chelated Hg fraction is moderately stable, and it is especially important for being strongly correlated to methylation of Hg in wetland soils, increasing risks of the release of the most toxic form of Hg (BLOOM et al., 2003). Elemental Hg and mercury sulfate fractions are considered strongly complexed, thus less mobile, or available to organisms (YU et al., 2012).

Figure 6 - Sequential extraction of Hg (%) in A1 (0-5 cm), A1 (5-10 cm), A2 (0-5 cm), A2 (5-10 cm), A3 (0-5 cm) and A3 (5-10 cm) under incubation times (days).



More than 70% of Hg is associated with F4 in A1, A2, and A3 in both depths studied. The incubation of soils did not change the association of Hg with the most recalcitrant fraction. Although the levels of Hg in all areas are above minimum quality values, the majority of it is strongly bonded in a non-available fraction. There is a positive correlation between F3 and pH in A2 ($r=0.068$, $p<0.05$), while there is a negative correlation between F3 and Eh ($r=-0.65$, $p<0.05$). The opposite happens when comparing pH and Eh with F4. No correlation was found between both fractions and other soil properties of A1 and A3. Mercury associated with sulfide is largely observed in other wetland areas during dry and wet seasons, even when there are low levels of sulfide, forming a complexant that traps Hg in soil (JIANG et al., 2018).

A higher association of Hg with F3 and F4 was also found in an estuarine region of India (MOHAN et al., 2021). The presence of Hg in the organo-chelated fractions shows a higher risk of methylation, and although there was no significant change in the contents of Hg associated with this fraction, there is an average association between this metal and F3 of 20% in all areas. Because this experiment is relative to the low time of exposure, it is still necessary to know if longer exposure to oxic conditions might change the distribution of Hg in the Botafogo River.

4.5.Cr, Zn and Fe distribution in soil

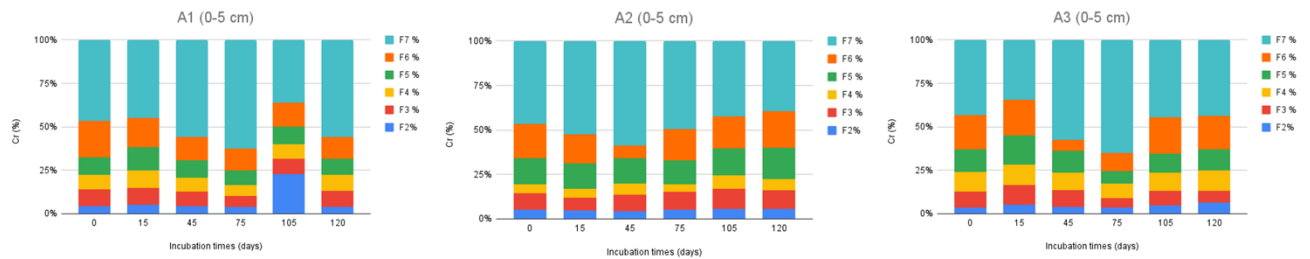
The sequential extraction of Cr, Zn, and Fe shows the association of metals in the exchangeable fraction (F1), carbonate fraction (F2), ferrihydrite fraction (F3), lepidocrocite fraction (F4), crystalline Fe oxide (F5), pyrite fraction (F6) and a residual fraction (F7). The metal mobility in soil decreases according to the associated fraction in the following order: F1>F2>F3>F4>F5>F6>F7.

Reads of contents were below the detection limit for Cr (<0.002 mg/L), Zn (<0.002 mg/L), and Fe (<0.01 mg/L) in the exchangeable fraction of A1, A2, and A3 during all times of incubation, meaning the low risk of mobility of contaminants in the less recalcitrant fraction.

4.5.1. Chromium

Chromium was mainly associated with the most stable fractions, F4, F5, especially with F7 (>40%) in A1, A2 and A3 (Figure 7). In natural soils under different pH conditions, Cr is usually associated with residual fraction, but there are studies of incubation showing that increased input of Cr in contaminated soils associated with low pH might increase the potential mobility of this metal from residual fractions to the exchangeable ones (XU et al., 2020). Because Cr contents in the Botafogo River soils are almost reaching TEL, it is necessary to prevent the increased discharge of Cr in rivers and soils to avoid potential risks of organisms uptake.

Figure 7 - Sequential extraction of Cr (%) in A1 (0-5 cm), A2 (0-5 cm) and A3 (0-5 cm) under incubation times (days).



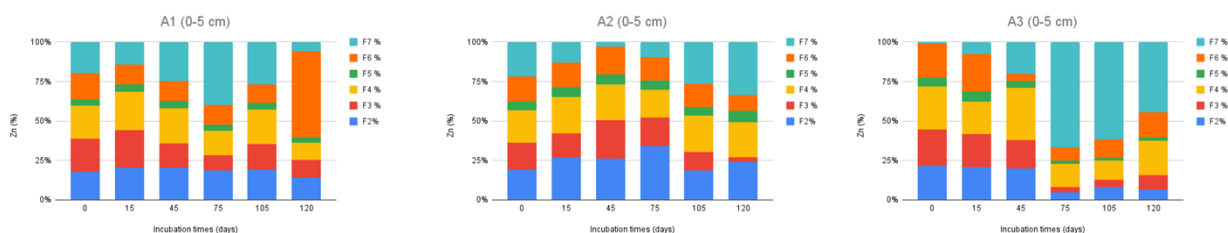
There is a positive correlation between Cr and the residual fraction in A1 0-5cm ($r=0.66$, $p<0.05$) and a negative correlation between the redox potential and the pyrite fraction ($r=-0.68$, $p<0.05$) in A1. While there is a positive correlation between F3 ($r=0.64$, $p<0.05$) and F5 ($r=0.64$, $p<0.05$) with pH in A3. No correlation was found between soil pH and Eh in A2. The conservative behavior of Cr in these soils follows tendencies observed in other mangrove soils and is higher than the rates found for metals like Zn, for example (MINU et al., 2018), and it is explained by the strong association of Cr with Fe/Mn minerals in mangrove soils (LI et al., 2016).

4.5.2. Zinc

In A1 (0-5cm), there was an association of Zinc with F2 of over 15% (Figure 8). Under anoxic conditions of wetland soils, it is common to find Zn associated with the carbonate fraction (F2), where sulfide and carbonate solids are mostly stable because of the limited exchange of gases between soil and atmosphere (BOSTICK et al., 2001). Although metals in this fraction have higher mobility in soil and increased availability to microorganisms, the low contents of Zn in A1 decrease the potential toxicity of the metal to organisms. After 75 days of incubation, there was a decrease of Zn association with F3 and F4 and increased association with F6 and F7, the most stable fractions. There is a negative correlation between F3 and Eh in these soils ($r=-0.67$, $p<0.05$) and F6 with pH ($r=-0.58$, $p<0.05$). The increased redox potential plays a role in the precipitation of Fe to oxic forms, thus changing the metal distribution in wetland soils (RATIE et al., 2018). Similar results were found in seasonally inundated soils from China, where the association of Zn with residual phases increased

compared to permanently inundated soils because of the dynamic between metals and Fe that also follows a redistribution in soils exposed to increased oxygen (YIN et al., 2020). In addition to the low contents of Zn in A1, the association of this metal with stable fractions means that there is no risk of Zn contamination in that area.

Figure 8 - Sequential extraction of Cr (%) in A1 (0-5 cm), A2 (0-5 cm) and A3 (0-5 cm) under incubation times (days).



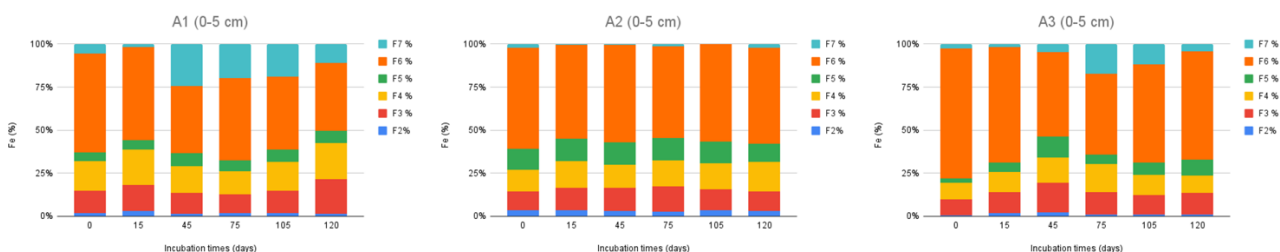
In A2 (0-5 cm), Zn distribution in the associated fractions was fairly spread out between F2, F3, F4, F6, and F7, showing no significant differences among incubation times. Accordingly, there was an initial association of Zn at similar percentages (>20%) with F2, F3, F4, and F6 in A3 (0-5 cm). The spread-out distribution of Zn associated with those fractions remained until time 45 days of incubation when the pH and Eh conditions of A3 significantly changed, and Zn association with the residual fraction increased. This redistribution did not occur in A2. Zinc in the residual fraction had a correlation strong positive correlation with pH ($r=-0.91$, $p<0.005$) and a negative correlation with Eh ($r=0.81$, $p<0.05$) in A3. The association of Zn with the residual fraction highly immobilizes the metal in soils (HONG et al., 2021), and that was the tendency in A3. The redistribution of Zn in A3 shows how changes in redox potential and soil pH might affect the association of Zn to soils.

4.5.3. Fe

The major association of Fe in soils was with the pyrite fraction in A1 (>50%), A2, and A3 (>50%) at all times of incubation (Figure 9). At lower pH, metallic cations show higher mobility in mangrove soils, and the relation between soil pH and the metal Fe can infer that response (ELTUK et al., 2019). The three major sorbent phases of Fe found in mangrove soils, Fe³⁺ oxides, FeS, and FeS₂, influence the concentration of metals, and low concentration of

Fe can explain higher mobility of metals in mangrove soils (JOHNSTON et al., 2016). The main contents of Fe in A1 (24.91 mg kg⁻¹), A2 (29.76 mg kg⁻¹), and A3 (34.41 mg kg⁻¹) are similar to the average (34.418 mg kg⁻¹) found in other mangroves from natural sources in the Northeast of Brazil (MIOLA et al., 2016).

Figure 9 - Sequential extraction of Fe (%) in A1 (0-5 cm), A2 (0-5 cm) and A3 (0-5 cm) under incubation times (days).



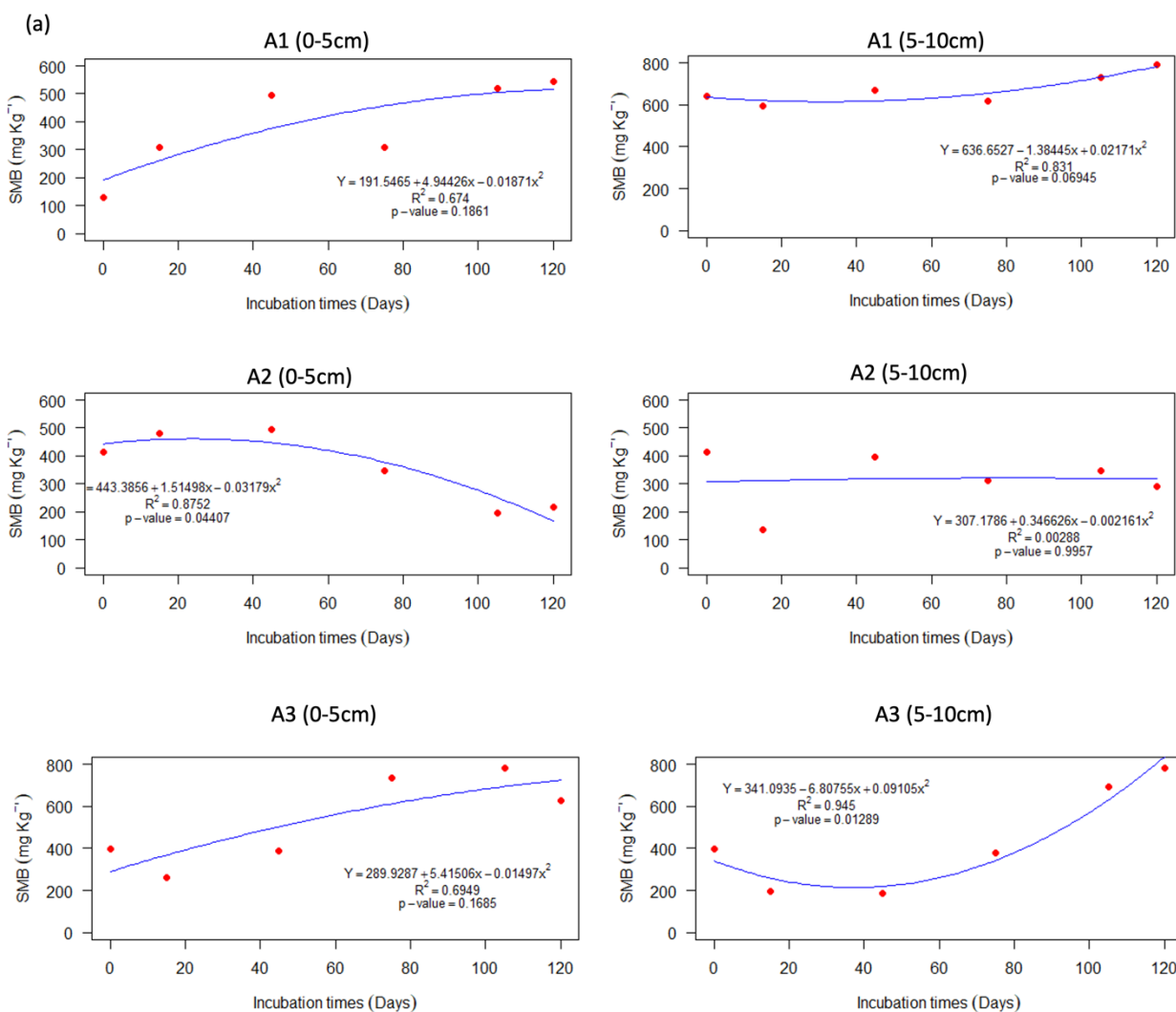
Under anaerobic conditions, Fe reduction is one of the main pathways for biogeochemical processes that form dissolved Fe³⁺, which controls Fe²⁺ production. In mangrove soils, there is weak solubilization of Fe²⁺, and because of that, labile Fe fluxes are very low in oxic soil layers (JOHNSTON et al., 2016). There was very low association of Fe with F2 in the three areas of this study and the major correlation between Fe associations was with the pyrite fraction and pH ($r=0.69$, $p<0.05$) in A3. This can explain how the contamination of heavy metals remains present in the Botafogo River mangrove soils by possibly being associated with Fe in recalcitrant phases, as there was a high correlation between the Hg, Zn, and Cr with Fe contents in both depths.

4.6. Soil microbial biomass (SMB)

Initial soil microbial biomass was of 309 mg kg⁻¹ (0-10cm) in A1, 412 mg kg⁻¹ (0-10cm) in A2, and 379 mg kg⁻¹ (0-10cm) in A3 (Figure 10). As soil pH decreased and Eh increased in function of the exposure times to oxic conditions, the microbial biomass followed increasing until 791 mg kg⁻¹ (0-10cm) in A1, and 779 mg kg⁻¹ (0-10cm) in A3, while decreasing in A2 (292 mg kg⁻¹). Even though the conditions of pH and Eh changed, the increase in microbial biomass shows the capacity of microorganismal communities to emerge through

different impacts on soil. There was no significant correlation between soil pH and Eh with microbial biomass of both A1 and A2.

Figure 10 - SMB rates for A1 (0-5 cm), A1 (5-10 cm), A2 (0-5 cm), A2 (5-10 cm), A3(0-5 cm) and A3 (5-10 cm) under incubation times (days).



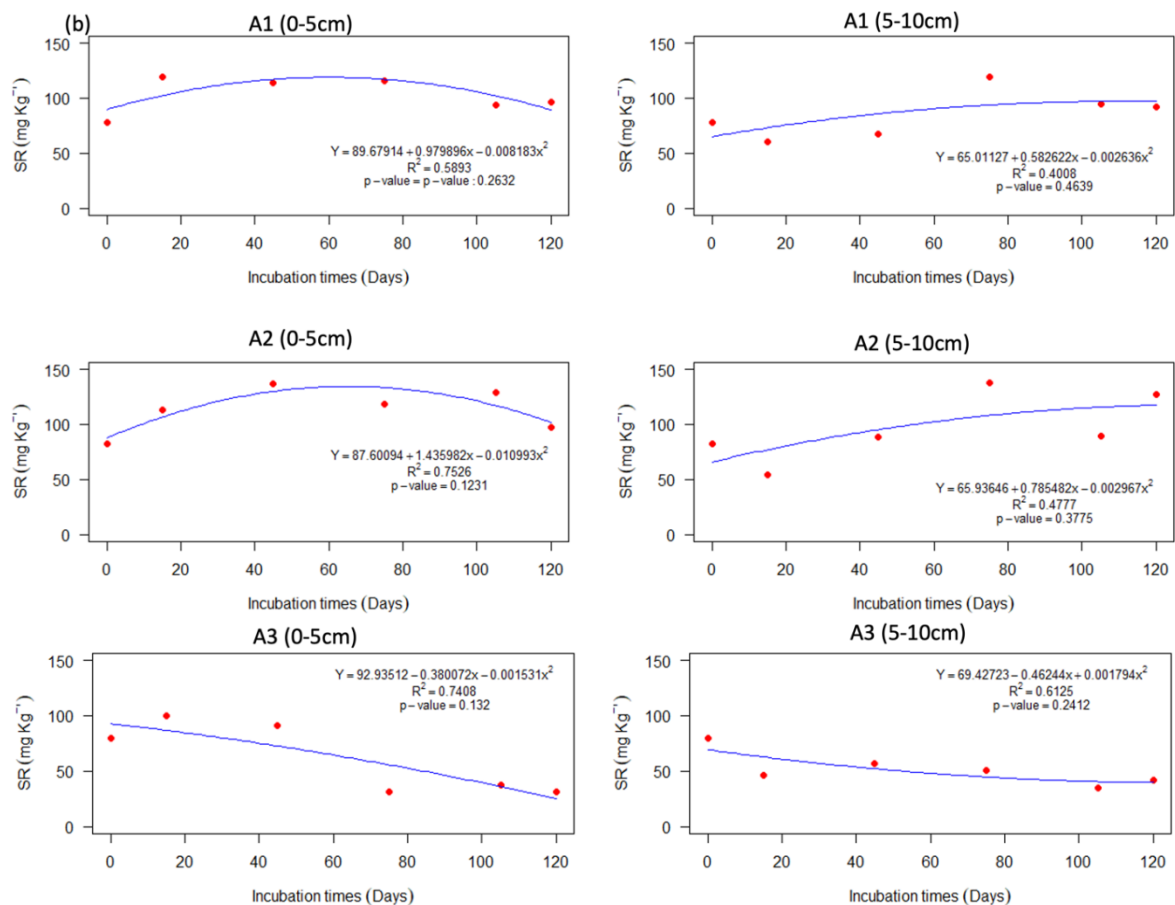
Increases in microbial biomass in A3, where pH dropped to around four might be related to a shift of communities from bacteria to fungi. There is a negative correlation between soil microbial biomass and pH ($r = -0.89$, $p < 0.05$) and a positive correlation with redox potential ($r = 0.74$, $p < 0.05$) in A3. A study monitoring a constructed mangrove that receives wastewater over ten years showed that fungi communities thrived more than bacteria under the new conditions of substrate availability in those soils, highly contributing to the total microbial

biomass (TIAN et al., 2020). Although the levels of contamination and fraction distribution varied among sites, there was no correlation between SMB with environmental contents of the metals. However, there was a positive correlation between SMB and Zn associated with carbonate fraction ($r=0.69$, $p<0.05$). Studies show that this correlation might happen because of zinc solubilizing bacteria that are present in mangrove soils, and as the levels of Zn in these soils are low and likely not toxic for microorganisms, the metal can be utilized by them (JERLIN et al., 2017).

4.7. Soil Respiration (SR)

Mangrove soils have a higher capacity to store carbon ($717 \text{ t Mg C ha}^{-1}$) and lower respiration rates ($49 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$) compared to other terrestrial ecosystems at global scales (ALONGI, 2014). The crescent exposure to oxic conditions increased soil respiration from 78.31 mg kg^{-1} (0-5cm) in A1, peaking at $122.31 \text{ mg kg}^{-1}$ after 60 days of incubation and decreasing to 96.38 mg kg^{-1} at the end of the experiment. Similarly, soil respiration in A2 started at 82.23 mg kg^{-1} (0-5cm), peaked at 60 days of incubation ($133.31 \text{ mg kg}^{-1}$), and dropped to 81.17 mg kg^{-1} at 120 days of incubation. The same tendencies were observed in the 5-10cm depth (Figure 11).

Figure 11 - Values of SR for A1 (0-5 cm), A1 (5-10 cm), A2 (0-5 cm), A2 (5-10 cm), A3(0-5 cm) and A13(5-10 cm) under incubation times (days).



Ma et al. (2020) found similar trends in mangrove soils from south China. The authors monitored the fluxes of CO₂ during four seasons and observed a decrease in emissions in the field and in incubated soils. In that study, CO₂ fluxes increased during Summer and Fall, peaking between 450 e 300 CO₂ mg m⁻² h⁻¹ respectively, while the peaks decreased to less than 100 CO₂ mg m⁻² h⁻¹ during Spring and Winter. The maintenance of lower respiration rates in inundated tropical soils is possible because of the constant water table levels that contribute to low decomposition rates and sub-oxic redox conditions (CHIMMER et al., 2004). Mangrove soils can capture CO₂ from the atmosphere and have lower rates of soil respiration (POUNGPARN et al., 2009), but this study confirms that alterations in the redox conditions can speed up the production of this greenhouse gas through microbial respiration.

There is a negative correlation between SR with Cr ($r=-0.64$, $p<0.05$) and Zn ($r=0.59$, $p<0.05$) associated with the residual fraction in A2.

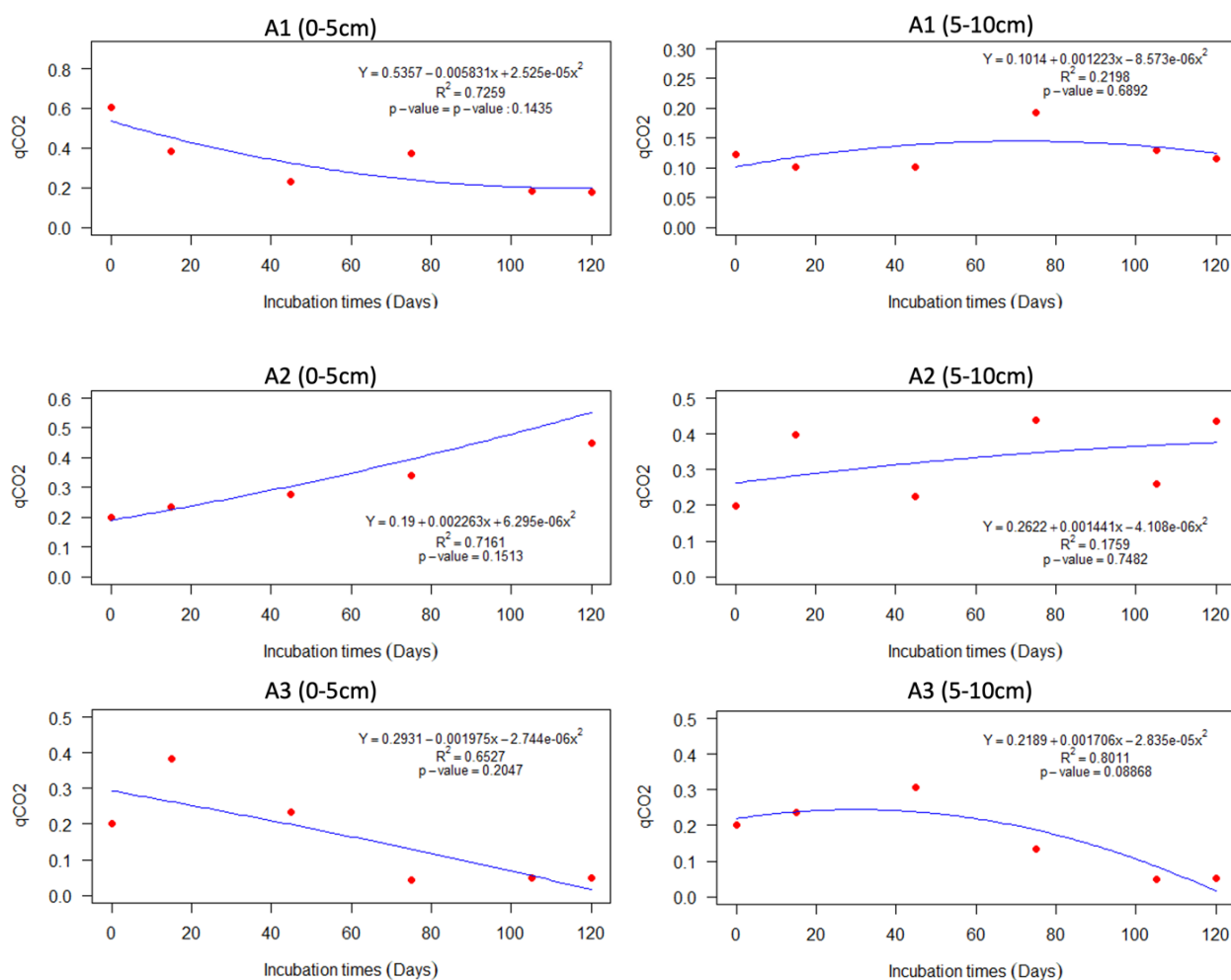
Compared to A1 and A2, SR In A3 has the lower levels and decreased from 79.62 mg kg⁻¹ (0-5cm) and 46.36 mg kg⁻¹ (5-10cm) to 31.17mg kg⁻¹ (0-5cm) 41.64mg kg⁻¹ (5-10cm) after 120 days of incubation. Mercury contamination might have influenced the initial lower soil respiration, but the decrease along incubation times is likely because of the changes in pH in that area, dropping from 7 to 4. There is a negative correlation between C-CO₂ with pH ($r=-0.6$, $p<0.05$) and Eh ($r=-0.47$, $p<0.05$) in the first 5cm of the depth of soil. Considering that salinity and soil pH mostly control mangrove microorganisms, especially bacteria and archaea, changes in these conditions decreased soil respiration in the most contaminated area (CECCON et al., 2019).

4.8.Metabolic Quotient

The microbial metabolic quotient (qCO₂) for all areas is relatively low (Figure 12) compared to other results found in mangrove soils contaminated by heavy metals, with average values ranging between 0.4 and 1.6 qCO₂ (JAISWAL; PANDEI, 2018). A1 had an average 0.27 qCO₂ (0-5cm) and 0.12qCO₂ (5-10cm), A2 had an average 0.38 qCO₂ (0-5cm) and 0.35 qCO₂ (5-10cm), while A3 had qCO₂ of 0.17 (0-5cm) and 0.14 (5-10cm). This means the contamination and crescent acidity of soils did not affect the respiration/biomass ratio of microorganisms, meaning their capacity to spend energy and sustain biomass. There was a negative correlation between qCO₂ with Zn in A2 ($r=-0.61$, $p>0.05$) and A3 at ($r=-0.81$,

$p > 0.05$), Cr in A2 ($r = -0.88$, $p > 0.05$) and A3 at ($r = -0.66$, $p > 0.05$), and Fe with A2 ($r = 0.86$, $p > 0.05$) at 0-5cm. However, there is a positive correlation between $q\text{CO}_2$ and Zn associated with the carbonate fraction in A2 ($r = 0.82$, $p < 0.05$) and A3 ($r = 0.82$, $p < 0.05$). Zinc solubilizing bacteria might be utilizing this available Zn (JERLIN et al., 2017).

Figure 12 - $q\text{CO}_2$ rates in A1 (0-5 cm), A1 (5-10 cm), A2 (0-5 cm), A2 (5-10 cm), A3(0-5 cm) and A3 (5-10 cm) under incubation times (days).



It was expected that changes in soil characteristics would cause stress in the microorganisms of the Botafogo River mangrove soils, elevating the metabolic quotient. Instead, they showed similar behavior from the least contaminated area to the most contaminated. There was no correlation between $q\text{CO}_2$ with Hg in any of the areas. He et al.

(2020) found the same tendency in wetland soils under the drying process. The authors reported that the maintenance of low $q\text{CO}_2$ rates in wetland soils under stress could happen because of a community shift between fungi and bacteria, as fungi have a stronger capacity to conserve soil organic carbon under drier conditions. This is especially relatable to the most contaminated and acid area, A3, where the soil microbial biomass increased with incubation times while soil respiration decreased. A higher ratio between fungi: bacteria might explain the lowest $q\text{CO}_2$ in A3 among the three areas studied.

5. CONCLUSIONS

Increased exposure of mangrove soils from the Botafogo River to oxidizing conditions caused the acidification of soils and changes in redox conditions from anoxic/suboxic to oxic. These changes did not interfere significantly in the redistribution of Hg and Cr in the three areas studied, which remained similar throughout the incubation experiment. Zinc association with carbonates decreased and were redistributed to residual fractions in all areas. The association of metals with Fe were positively correlated with the retention of metals in the mangrove soils. Soil acidification and redox potential played a bigger role in the increased microbial biomass and decreased soil respiration especially in the most contaminated area. The low microbial metabolic quotient showed that contamination of these soils by heavy metals and geochemical alterations did not disturb the microbial communities from the least to the most contaminated area.

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