University of São Paulo
"Luiz de Queiroz" College of Agriculture

Iron biogeochemistry in mine tailing impacted soils: from risk assessment to enhanced bioremediation strategies

Amanda Duim Ferreira

Thesis presented to obtain the degree of Doctor in Science. Area: Soil and Plant Nutrition

Piracicaba
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Às minhas sobrinhas Luisa, Carolina e Manuela. Um passo de cada vez e tornaremos este mundo um lugar melhor para as novas gerações.

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Commit to the Lord whatever you do,

and he will establish your plans.

Proverbs 16:3

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RESUMO

Biogeoquímica de ferro em solos impactados por rejeitos de mineração: da avaliação de risco às estratégias de biorremediação aprimoradas

O “Desastre de Mariana”, um dos maiores desastres ambientais do mundo, liberou na Bacia do Rio Doce mais de 50 milhões de m³ de rejeitos de mineração de ferro (Fe), que tem como destino o estuário, localizado no município de Linhares, Espírito Santo. Solos estuarinos são fortemente influenciados pelas oscilações redox, que controlam a dinâmica de Fe, um dos principais componentes do rejeito. Além disso, o Fe, tem grande influência na dinâmica de elementos potencialmente tóxicos (EPTs). Nesse sentido, este estudo teve como objetivos: i) estudar os controles biogeoquímicos da dinâmica do Fe e EPTs nos solos estuarinos; ii) determinar possíveis riscos associados ao consumo de alimentos produzidos nos solos impactados pelos rejeitos; iii) realizar o levantamento de espécies vegetais apropriadas para biorremediação de Fe e EPTs; iv) estudar estratégias para aumentar a eficiência da biorremediação. Para isso, solos e plantas do estuário do Rio Doce foram amostrados em 2019, 2020 e 2021, além da condução de quatro experimentos em laboratório e um experimento à campo. Observamos um forte controle sazonal sob a biogeoquímica de Fe nos solos do estuário do Rio Doce. A dissolução dos óxidos de Fe durante a transição das estações chuvosa para a seca resultou em uma perda substancial de Fe. Isto levou a um aumento notável na disponibilidade de elementos potencialmente tóxicos (Mn, Cr, Cu, Ni e Pb), representando riscos ambientais elevados, especialmente durante a estação seca. A modelagem dos dados coletados durante duas estações secas (2019 e 2021) e uma estação úmida (2020) revelou que o fator climático (i.e., precipitação acumulada) foi responsável por 48% da biodisponibilidade de EPTs nos solos. Quanto aos parâmetros físicos e químicos de solo, pH e teor de matéria orgânica foram os principais controladores, respondendo por 29% da biodisponibilidade de EPTs. Quanto ao fator geoquímico, óxidos de ferro de cristalinidade curta (e.g., ferridrita e lepidocrocita), foram responsáveis por 23% da biodisponibilidade de EPTs. Já a análise de riscos associados ao consumo de alimentos produzidos no estuário do Rio Doce revelou que a associação entre EPTs e óxidos de Fe, que muitas vezes atuam na redução da biodisponibilidade dos EPTs, pode não ser um mecanismo eficiente em ambientes redox-ativos, como solos estuarinos, visto que as concentrações de Cd, Cr, Cu, Ni e Pb excederam os valores limite nas partes comestíveis (i.e., frutos e tubérculos) de todas as culturas estudadas. Contudo, as taxas de ingestão diária (ADI) desses elementos permaneceram abaixo da ingestão diária tolerável estabelecida pelas organizações internacionais. Já o índice de perigo total (THI), que estima a probabilidade de efeitos adversos de EPTs à saúde, revelou potencial risco à saúde de crianças devido ao consumo de frutos de banana produzidos no estuário. Para adultos, há um baixo risco tanto para o consumo de frutos quanto para o de tubérculos das espécies cultivadas estudadas. Diante dos riscos apontados neste estudo, identificou-se a necessidade de reduzir as concentrações de Fe e EPTs do estuário, adotando-se diferentes técnicas de remediação: i) remediação química através da indução da piritização; ii) biorremediação iii) biorremediação assistida. O levantamento de espécies no estuário mostrou que a macrófita *Typha domingensis* foi a espécie com maior potencial para fitoextração, devido as altas extrações de Fe (3,7 ton ano^{-1}), Mn (75,7 ton ano^{-1}), Cr (169,7 kg ano^{-1}) e Ni (107,8 kg ano^{-1}). Este potencial esteve correlacionado com o menor pH do solo rizosférico (4.73), bem como a predominância de óxidos de ferro de baixa cristalinidade (i.e., ferridrita e lepidocrocita), que são mais susceptíveis a dissolução. Apesar da espécie *Hibiscus tilliaceus* demonstrar potencial para fitoestabilização de Cu e Pb, outras estratégias foram testadas para a auxiliar a remediação destes EPTs. O uso de gesso agrícola ($CaSO_4$) como fonte de sulfato para remediação química resultou em maiores taxas de dissolução de óxidos de ferro, aumento nas concentrações de Fe^{2+} e sulfetos (HS^- e H_2S) na solução, o que resultou em maiores taxas de piritização de Pb (+40%), reduzindo os teores biodisponíveis de Pb no solo. Quando o uso do gesso agrícola foi combinado à aplicação de um consórcio microbiano

(*Azospirillum sp.*, *Pseudomonas sp.*, *Saccharomyces sp.*, e *Rhizobium sp.*), houve um significativo decréscimo nos teores de Fe e Mn associados a óxidos e aumento dos teores biodisponíveis desses elementos. O consórcio microbiano também diminuiu os teores pseudo-totais de Cr (-85%), Cd (-61%), Cu (-49%) e Pb (-55%) no rejeito de mineração de ferro e aumentou as concentrações de Fe, Mn, Cd, Cr e Pb na solução, o que pode ser útil para estratégias de fitorremediação assistida. Já para Cu, houve uma redução dos teores na solução, indicando um possível potencial de biossorção de Cu pela biomassa microbiana. A adubação, tanto isolada quanto aplicada em conjunto com agentes quelantes e consórcio de microrganismos, promoveu significativas mudanças geoquímicas no rejeito de mineração de ferro (diminuição do pH e Eh, aumento do carbono orgânico total e dissolvido, aumento de ferro biodisponível), o que resultou em maiores extrações de Fe pelas plantas de *T. domingensis*. Dessa forma, demonstramos que a biorremediação de áreas afetadas por rejeitos de mineração pode ser realizada com o uso de espécies vegetais nativas. Esse estudo traz uma nova abordagem na biorremediação de Fe e EPTs ao modular a geoquímica de Fe em rejeitos de mineração para incremento da biorremediação utilizando plantas não-hiperacumuladoras e microrganismos benéficos.

Palavras-chave: Saúde humana, Fitorremediação, Agromineração, Recuperação de áreas degradadas, Geoquímica do solo

ABSTRACT

Iron biogeochemistry in mine tailing impacted soils: from risk assessment to enhanced bioremediation strategies

The "Mariana Disaster," one of the world's largest environmental disasters, released over 50 million m³ of iron ore mine tailings (Fe) into the *Rio Doce* Basin. The mine tailings reached the estuary in the municipality of Linhares, Espírito Santo. Estuarine soils are strongly influenced by redox fluctuations, which control the dynamics of Fe, a primary component of the tailings. Additionally, Fe plays a significant role in the dynamics of potentially toxic elements (PTEs). In this context, this study aimed to: i) investigate the biogeochemical controls on the dynamics of Fe and PTEs in estuarine soils; ii) determine potential risks associated with consuming food produced in areas impacted by tailings; iii) identify suitable plant species for Fe and PTEs phytoremediation; iv) study strategies to enhance phytoremediation efficiency. To achieve these objectives, soils and plants from the Rio Doce estuary were sampled in 2019, 2020, and 2021, and four laboratory experiments and one field experiment were conducted. Seasonal controls on Fe biogeochemistry in Rio Doce estuarine soils were observed. The dissolution of Fe oxides during the transition from the rainy to dry seasons resulted in a substantial Fe loss, leading to a notable increase in the availability of PTEs (Mn, Cr, Cu, Ni, and Pb), posing elevated environmental risks, especially during the dry season. Data modeling for two dry seasons (2019 and 2021) and one wet season (2020) revealed that climatic factors (i.e., accumulated precipitation) accounted for 48% of PTEs bioavailability in soils. Regarding soil physical and chemical parameters, pH and organic matter content were the primary controllers, explaining 29% of PTEs bioavailability. Geochemical factors, specifically short-crystallinity iron oxides (e.g., ferrihydrite and lepidocrocite), accounted for 23% of PTEs bioavailability. Risk analysis associated with consuming food from the Rio Doce estuary indicated that the association between PTEs and Fe oxides, often reducing PTEs bioavailability, may not be efficient in redox-active environments like estuarine soils. Concentrations of Cd, Cr, Cu, Ni, and Pb exceeded limit values in edible parts (i.e., fruits and tubers) of all studied crops. However, daily intake rates (ADI) for these elements remained below internationally established tolerable daily intake levels. The total hazard index (THI), estimating the probability of adverse effects of PTEs on health, indicated potential health risks for children consuming bananas from the estuary. For adults, there was low risk for both fruit and tuber consumption of the studied crops. Given the identified risks, there is a need to reduce Fe and PTE concentrations in the estuary. For this, we tested different remediation techniques: i) chemical remediation through pyritization induction; ii) bioremediation; iii) assisted phytoremediation. The survey of species in the estuary revealed that the macrophyte *Typha domingensis* exhibited the highest potential for phytoextraction, extracting high amounts of Fe (3.7 tons year^{-1}), Mn (75.7 tons year^{-1}), Cr (169.7 kg year^{-1}), and Ni (107.8 kg year^{-1}). This potential correlated with the lower rhizospheric soil pH (4.73) and the prevalence of short-range ordered Fe oxides (i.e., ferrihydrite and lepidocrocite), which are more susceptible to dissolution. Although the plant species *Hibiscus tilliaceus* showed potential for Cu and Pb phytostabilization, other strategies were tested for these PTEs remediation. The use of agricultural gypsum ($CaSO_4$) as a sulfate source for chemical remediation resulted in increased dissolution rates of iron oxides, elevated concentrations of Fe^{2+}, and sulfides (HS^- and H_2S) in the solution, leading to enhanced Pb pyritization (+40%) and reduced bioavailable Pb in the soil. When agricultural gypsum was combined with the application of a microbial consortium (*Azospirillum sp.*, *Pseudomonas sp.*, *Saccharomyces sp.*, and *Rhizobium sp.*), significant decreases in Fe and Mn associated with oxides contents and increased bioavailable concentrations of these elements were observed in the soils. The microbial consortium also reduced total Cr (-85%), Cd (-61%), Cu (-49%), and Pb (-55%) contents in the iron ore mining tailings and increased concentrations of Fe, Mn, Cd, Cr, and Pb in the solution, which could be useful for assisted phytoremediation strategies. In In addition, there was a reduction in solution concentrations for Cu, indicating potential Cu biosorption by microbial biomass. Fertilization, either alone or combined with chelating agents and microbial consortium, induced significant geochemical changes in iron mine tailings (decreased pH and Eh, increased total and dissolved organic carbon, increased bioavailable Fe), resulting in higher Fe extractions by *T. domingensis* plants. Thus, this study demonstrates that remediation of areas affected by mine tailings can be achieved using native plant species. This research introduces a novel approach to Fe and PTEs phytoremediation by modulating Fe geochemistry in mine tailings to enhance bioremediation using non-hyperaccumulator plants and beneficial microorganisms.

Keywords: Human health, Phytoremediation, Agromining, Recovery of degraded areas, Soil geochemistry

2. SEASONAL DRIVES ON POTENTIALLY TOXIC ELEMENTS DYNAMICS IN A TROPICAL ESTUARY IMPACTED BY MINE TAILINGS

Abstract:

This study investigates the impact of seasonality on estuarine soil geochemistry, focusing on redox-sensitive elements, particularly Fe, in a tropical estuary affected by Fe-rich mine tailings. We analyzed soil samples for variations in particle size, pH, redox potential (Eh), and the content of Fe, Mn, Cr, Cu, Ni, and Pb. Additionally, sequential extraction was employed to understand the fate of these elements. Results revealed dynamic changes in the soil geochemical environment, transitioning between near-neutral and suboxic/anoxic conditions in the wet season and slightly acidic to suboxic/oxic conditions in the dry season. During the wet season, fine particle deposition (83%) rich in Fe (50 g kg^{-1}), primarily comprising crystalline Fe oxides, occurred significantly. Conversely, short-range ordered Fe oxides dominated during the dry season. Over consecutive wet/dry seasons, substantial losses of Fe (-55%), Mn (-41%), and other potentially toxic elements (Cr: -44%, Cu: -31%, Ni: -25%, Pb: -9%) were observed. Despite lower pseudo-total PTE contents, exchangeable PTEs associated with carbonate content increased over time (Cu: +188%, Ni: +557%, Pb: +99%). Modeling indicated climatic variables and short-range oxides substantially influenced PTE bioavailability, emphasizing the ephemeral Fe oxide control during the wet season, and heightened ecological and health risks during the dry seasons.

Keywords: seasonal dynamics; PTE fate; PTE bioavailability; risk modeling.

2.1. Introduction

Seasonal flooding drives changes in the redox conditions of estuarine soils and sediments [1,2], which influences ecosystem structure and function [3–6]. During the wet season, the combined effects of suspended sediment deposition, increasing dissolved organic carbon content, and freshwater input can promote more reducing conditions, which may affect the dynamics of potentially toxic elements (PTEs) in estuaries [3–6]. Conversely, suboxic to oxic conditions may be established during seasonal droughts, which may also affect the bioavailability of PTEs [7,8]. For example, the low water content in wetland soils during dry periods may favor the oxidation of sulfides, which potentially releases PTEs [7,8]; these conditions may promote the formation of short-range Fe and Mn oxyhydr oxides, which can act as a sink for PTEs [9]. Furthermore, in estuarine systems, physicochemical conditions, such as pH, Eh, and salinity, and biogeochemical processes, such as adsorption, complexation, precipitation, and chelation, are affected by seasonal hydraulic changes like rainfall variations and water flow, which ultimately control the differentiation and mobility of PTEs [6,10–12].

3. RISK ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS IN EDIBLE CROPS CULTIVATED IN MINE TAILING IMPACTED SOILS

Abstract

The deposition of mine tailings in natural and agricultural ecosystems raises concerns about risks to human health, particularly in estuarine environments where the dissolution of Fe oxides, the primary component of the mine tailings, can release potentially toxic elements (PTEs). Soils and crops cultivated in the Rio Doce estuary were collected in August 2021. We evaluated the total levels of PTEs in different parts of the plants grown in the estuarine soils. We estimated the risks of consuming these products by the local population by calculating the Hazard Quotient (HQ), Hazard Index (HI), and Total Hazard Index (THI). Our results showed Cd, Cr, Cu, Ni, and Pb concentrations in edible parts of the plants exceeding the threshold values in all the crops studied. Also, there is a possible non-carcinogenic risk associated with the consumption of banana fruits by children. For adults, there are no risks of consuming the products from the studied plants. In conclusion, the association between PTEs and Fe oxides, which often act to reduce PTEs' phytoavailability, was not an efficient mechanism in redox-active environments such as estuarine soils, which increased the risk of food production in this environment.

Keywords: crop; metal pollution; human health; iron oxides.

3.1. Introduction

Over 600 million people have experienced health problems due to unsafe food, resulting in 420,000 deaths annually [1]. In this sense, food security is one of the most important challenges. Food contamination by potentially toxic elements (PTEs) such as Cd, Cr, Cu, Ni, and Pb represents one of the most significant challenges in the realm of food safety [2,3].

To ensure food safety, international organizations such as the Codex Alimentarius and the Joint FAO/WHO Expert Committee on Food Additives (JECFA) rigorously regulate the intake of various PTEs. These regulations aim to establish maximum allowable limits for specific contaminants in food products, safeguarding public health and preventing adverse effects of excessive exposure to PTEs [4]. By setting standards and guidelines, these organizations contribute to harmonizing international food safety practices, fostering consumer confidence in the quality and safety of the global food supply [4].

Since PTEs are non-biodegradable, they are biomagnified into body tissues, causing severe health risks, including gastric, neurological, hematological, renal, and cardiac disorders [5] as well as the disruption of the central nervous system, reproductive failure, and

4. IRON HAZARD IN AN IMPACTED ESTUARY: CONTRASTING CONTROLS OF PLANTS AND IMPLICATIONS TO PHYTOREMEDIATION

Abstract

Due to its abundance and role as a micronutrient for plants iron (Fe) is rarely perceived as a contaminant. However, in redox active environments, Fe bioavailability increases sharply representing an environmental risk. In this study, a recent catastrophic mining dam failure is used as a field framework to evaluate the role of wetland plants on Fe biogeochemistry and assess their potential for phytoremediation programs. To achieve these objectives, a Fe geochemical partitioning and the concentration of Fe in different plant compartments (iron plaque on root surfaces, roots, and leaves) were determined in two sites vegetated by different wetland species. Soils exhibited contrasting Fe biogeochemical dynamics. Lower pseudo-total contents and more reactive Fe oxides were observed in the soil vegetated by *Typha domingensis*. Iron plaque was present on both species but more concentrated in Fe in *T. domingensis*. *T. domingensis* showed Fe shoot concentrations (3,874 mg kg^{-1}) 10-fold higher than in *Hibiscus tiliaceus*, which prevented Fe absorption through iron plaque formation and root accumulation. In conclusion, contrasting biogeochemical effects on Fe (e.g., rhizosphere acidification) lead to different phytoremediation abilities. *T. domingensis* showed a high potential for Fe phytoremediation on sites affected by Fe-enriched wastes and should be tested in assisted phytoremediation approaches.

Keywords: mine tailings, biogeochemistry, *T. domingensis*, *H. tiliaceus*, phytoextraction.

4.1. Introduction

Iron (Fe) is the fourth most abundant element in the crust and is mainly found in soils as Fe oxyhydroxides, which are among the most thermodynamically stable mineral phases at the earth's surface conditions [1]. Despite its abundance, only minimal amounts of Fe are required by plants, with rarely reported toxicities that hide its potential as a contaminant [2,3]. In fact, under the geochemical conditions of well-aerated soils, its bioavailability usually remains below the nutritional threshold for plants [4] because Fe oxyhydroxides are the dominant sources of the element for plants. In these cases, terrestrial plants may use different strategies to acquire Fe; e.g., Fe^{3+} chelation and reduction or secretion of phytosiderophores [5].

In contrast, in poorly aerated soils (e.g., under anoxic/suboxic conditions; redox potentials, Eh < 100 mv; [6], such as those commonly found in wetlands and estuarine soils, the solubility of Fe oxyhydroxides is sharply increased because of the reductive dissolution of

5. SCREENING FOR NATURAL MANGANESE SCAVENGERS: DIVERGENT PHYTOREMEDIATION POTENTIALS OF WETLAND PLANTS

Abstract

Manganese is a potentially toxic micronutrient with great ecological risk. In wetland soils, Mn bioavailability increases sharply with contamination hazards. Wetland plants may have different effects on Mn mobility and reactivity in soils, affecting their phytoremediation potential. This study evaluated the role of three naturally occurring wetland plants (i.e., *Hibiscus tiliaceus*, *Eleocharis acutangula*, and *Typha domingensis*) in Mn biogeochemistry and screened their potential for phytoremediation in an Mn-contaminated estuary (*Rio Doce* estuary; SE-Brazil). Shoots, roots, and soils (0–40 cm) of each plant species were sampled. Soil physicochemical parameters (i.e., pH, rhizospheric pH, and redox potentials) were measured, and Mn concentrations were determined in the plant tissues, root iron plaques, and soils. In addition, Mn geochemical fractionation was performed on the studied soils. Our results reveal that *T. domingensis* is highly efficient at Mn phytoremediation. *T. domingensis* showed unprecedented Mn shoot concentrations (6,858 mg kg^{-1}), translocation (TF; 99.5), and bioconcentration factors (BCF; 11.7). We revealed that rhizospheric acidification promoted by *T. domingensis* significantly altered the soil Mn geochemistry, favoring its acquisition from iron plaques and short-range-ordered Mn oxides. In contrast, despite the high Mn bioavailability, *E. acutangula* and *H. tiliaceus* showed Mn concentrations 13- and 10-fold lower than those recorded for *T. domingensis*. Naturally growing *T. domingensis* is able to phytoextract 147 tons of Mn (~19,000 m^2), which represents a removal of 75.7 ton ha^{-1}. The Mn phytoextraction potential of *T. domingensis* should be assessed in association with different phytotechnologies and agronomic practices to maximize its phytoextraction efficiency.

Keywords: estuary; Mn contamination; mining tailings; macrophytes; Mariana's mining disaster.

5.1. Introduction

Manganese (Mn) is one of the most abundant elements in natural terrestrial environments and an important micronutrient for all living organisms; thus, it is rarely perceived as a contaminant (Queiroz et al., 2021a; Shao et al., 2017). However, in the last century, human activities, such as mining, industrial processes, and agriculture, have increased Mn levels in soils, sediments, and coastal and continental waters (Gabriel et al., 2021a; Sitko et al., 2021; Summer et al., 2019) compromising the health of humans and other living organism (Blamey et al., 2018; Pragnya et al., 2021; Queiroz et al., 2021a; Rajpoot et al., 2020). High daily Mn intake, inhalation, and dermal contact may cause different diseases in humans (Levy and Nassetta, 2013; Sandilyan and Kathiresan, 2014). Soil Mn concentrations >

6. CONTRASTING PLANT-INDUCED CHANGES IN POTENTIALLY TOXIC ELEMENTS DYNAMICS: IMPLICATIONS FOR PHYTOREMEDIATION STRATEGIES IN ESTUARINE WETLANDS

Abstract

Wetland plants affect soil geochemical conditions, regulating the fate of potentially toxic elements (PTE). We hypothesized that the different estuarine plants control soil geochemistry and will affect PTE speciation, bioavailability, and uptake, thus affecting phytoremediation potential. We evaluated the soils (pH, redox potential, rhizospheric pH, PTE total concentration, and geochemical fractionation), plant parts (shoot and root), and iron plaques of three plants growing in an estuary affected by mining tailings. *Typha domingensis* accumulated the highest Cr and Ni contents in their shoots (> 100 mg kg^{-1}). In contrast, *Hibiscus tiliaceus* accumulated more Cu and Pb in their roots (> 50 mg kg^{-1}). The differences in rhizospheric soil conditions and root bioturbation explained the different potentials between the plants by altering the soil dynamics and PTE's bioavailability, ultimately affecting their uptake. This study suggests that *Eleocharis acutangula* is not suitable for phytoextraction or phytostabilization. Otherwise, *Hibiscus tiliaceus* is a wood species promising for Cu and Pb phytostabilization, whereas *Typha domingensis* shows potential for Cr and Ni phytoextraction.

Keywords: metal biogeochemistry; macrophytes; sea hibiscus; phytoextraction, phytostabilization

6.1. Introduction

Estuarine soils are commonly impacted by potentially toxic elements (PTEs) because they may receive contaminant loads from upstream watersheds transported by rivers and accumulate within estuaries [1,2]. In estuarine ecosystems, PTEs may have several fates: they may be retained and accumulated in the soils, absorbed by plants, released into estuarine waters, or concentrated in the tissues of aquatic organisms [3]. Thus, PTEs may be transferred along the food chain, thus posing serious risks to human health [4,5].

In these environments, estuarine plants may differ in their impact on estuarine soil geochemistry [6,7], ultimately affecting PTE bioavailability and, thus, the plant's ability to promote phytoremediation. The removal of PTEs from soils can be influenced by various plant traits and plant-mediated soil processes, such as evapotranspiration [16], biomass production [17], root system architecture [18], root uptake kinetics [19], translocation mechanisms (e.g., metal transporters; [20]). These processes alter soil geochemical conditions allowing plants to access PTEs from the soil solution and other soil fractions. For example, plants may enhance the reductive dissolution of Fe (oxyhydr)oxides through the input of labile organic matter

7. GYPSUM AMENDMENT INDUCED RAPID PYRITIZATION IN Fe-RICH MINE TAILINGS FROM *RIO DOCE* ESTUARY AFTER FUNDÃO DAM COLLAPSE

Abstract

Mine tailings containing trace metals arrived at the *Rio Doce* estuary, after the world's largest mine tailings disaster (the Mariana disaster) dumped approximately 50 million m3 of Fe-rich tailings into the *Rio Doce* Basin. The metals in the tailings are of concern because they present a bioavailability risk in the estuary as well as chronic exposure hazards. Trace metal immobilization into sulfidic minerals, such as, pyrite, plays a key role in estuarine soils; however, this process is limited in the *Rio Doce* estuarine soil due to low sulfate inputs. Thus, to assess the use of gypsum amendment to induce pyritization in deposited tailings a mesocosm experiment was performed for 35 days, with vinasse added as a carbon source and doses of gypsum (as a sulfate source). Chemical and morphological evidence of Fe sulfide mineral precipitation was observed. For instance, the addition of 439 mg of S led to the formation of gray and black spots, an Fe2+ increase and sulfides decreased in the solution, an increase of pyritic Fe, and a greater Pb immobilization by pyrite at the end of the experiment. The results show that induced pyritization may be a strategy for remediating metal contamination at the *Rio Doce* estuary.

Keywords: sulfidation; pyrite; lead sulfide; soil remediation; chemical immobilization.

7.1. Introduction

The mineral pyrite (FeS_2) is widely known for its potential for metal immobilization in coastal wetland soils [1–4]. The formation of pyrite in soils is controlled by edaphic factors such as iron (Fe) and sulfide concentration in soil solutions, soil organic matter, microbial activity, redox potential (Eh), pH, soil moisture [5–8]. The formation of pyrite in coastal wetland soils results from anaerobic metabolic pathways for the degradation of organic matter using electron acceptors other than O_2 under reducing conditions (e.g., Eh < 100 mV) [5]. Accordingly, due to the high abundance of Fe and sulfate (SO_4^{2-}) from the ocean, the microbial reduction of Fe^{3+} and SO_4^{2-} is the most important anaerobic process for organic matter degradation in coastal wetlands soils [9,10]. In this sense, inducing the pyritization in soil has been identified as a strategy for increasing metal immobilization [11,12].

Since 2015, when the Fundão tailings dam in Brazil collapsed (the largest dam failure of the world, known as "Mariana disaster"), metal contamination has been identified as one of the most concerning phenomena along the Brazilian Coast [13–17]. After the Mariana disaster, a huge amount of Fe-rich mining tailings entered the *Rio Doce* estuary increasing the trace metal content in the soil [14]. Furthermore, the biogeochemical conditions of the

8. ASSESSMENT OF THE POTENTIAL OF MICROBIAL CONSORTIUM FOR THE RECLAMATION OF MINE TAILINGS CONTAINING POTENTIALLY TOXIC ELEMENTS

Abstract

Bioremediation using microorganisms is an emerging green technology for the remediation of potentially toxic elements (PTEs) in soils and sediments. However, such technology can differently impact PTEs dynamics (e.g., immobilization and mobilization), ultimately affecting the efficiency of the remediation programs. In this study, we aimed to assess different microbial remediation mechanisms triggered by a microbial consortium to bioremediate Fe-rich mining tailings. The tailings were incubated in a mesocosm system for 35 days with increasing colony-forming units (CFU) of a specific microbial consortium (*Azospirillum sp*., *Pseudomonas sp*., *Saccharomyces sp*., and *Rhizobium sp*.). At the end of the experiment, we determined the geochemical fractionation of Fe and PTEs in the solid phase to assess the effect of treatments on PTE's bioavailability. Increasing the CFU resulted in higher Fe (15%) and Mn (37%) reductive dissolution compared to the control. As a result, the Fe and Mn concentrations in water increased by 9-fold. In addition, microbial consortium decreased the contents of Fe and Mn associated with oxides (-59% and -79%, respectively) and increased the more bioavailable solid fractions. The microbial consortium also efficiently decreased PTEs pseudo total contents in the mine tailings (Cr: -85%, Cd: -61%, Pb: -55%, and Cu: -49%). In addition, lower CFUs increased PTEs dissolved in the drainage water, indicating a potential for assisting other remediation strategies. Lower CFU also induced high Cr biomineralization (94%). In conclusion, our work provides novel evidence of a microbial consortium for remediating Fe mine tailings through different strategies (biodissolution and biomineralization). In view of the effects of the microbial consortium over Fe and Mn oxyhydroxide dissolution rates, further research should test it on microbially assisted phytoremediation protocols.

Keywords: bioavailability; biodissolution; biosorption; biomineralization; microbially assisted remediation.

8.1. Introduction

Reclamation of geochemically complex ecosystems (e.g., redox-active environments) is challenging, and thus different strategies must be considered to combine the strengths and avoid the weaknesses of individual remediation approaches. In Brazil, the Rio Doce estuary has been widely studied because of the large amounts of Fe-rich tailings deposited in a redox-active environment after the "Mariana disaster", which is considered the world's largest mining dam collapse (Bernardino et al., 2019; Gomes et al., 2017; Queiroz et al., 2018). The arrival of tailings was marked by an increase in different potentially toxic elements (PTEs) associated mostly with Fe oxyhydroxides, which under the estuarine physicochemical

9. BIOGEOCHEMISTRY APPLIED TO MINE TAILINGS MODULATION: FARMING FOR METALS USING NON-HYPERACCUMULATOR PLANT SPECIES

Abstract

The economic exploration of Fe mining tailings is an alternative to their disposal in dams, which are structures that are at risk of rupture. *Typha domingensis* is widely known for accumulating several metals, being a potential Fe accumulator from mining tailings. Therefore, the present work aimed to evaluate the effect of treatments in modulating the geochemical environment of Fe mine tailings (IMT) to enhance *T. domingensis* Fe accumulation. The experiment was conducted for 360 days, with six treatments (three repetitions each) distributed in randomized blocks. The effects of adding a consortium of beneficial microorganisms (Fe-reducing microorganisms), a chelating agent (citric acid), and fertilizers on Fe accumulation by the species *T. domingensis* were evaluated. The results indicate that *T. domingensis* cultivation associated with fertilizers influenced the development of plants, carbon accumulation, and Fe biogeochemistry in the IMT. In conclusion, this work set up a successful soil decontamination protocol and established the foundation for using *T. domingensis* for agromining.

Keywords: phytomining, agromining, constructed wetlands, *Typha domingensis*

9.1. Introduction

Iron (Fe) mining is recognized as one of the most crucial economic activities [1]. In addition, the global population increase, average income rise, and energy source shifts have escalated the demand for metals [2]. However, the metal content in mineral resources has decreased, leading to substantial volumes of waste, commonly disposed of in dams [3]. Brazil, the world's second-largest producer of Fe ore, harbors a total of 928 Fe mine tailing dams, with 36% categorized as "high risk" or having a "high potential for associated damage," posing a significant threat of dam failure and environmental harm [4]. The 2015 rupture of the Fundão dam in Mariana (MG) marked the largest environmental disaster in the global mining industry, both in terms of the released waste volume (> 50 million m^3) and the extent of geographical damage, spanning 668 km of watercourses [5–7].

In this context, nature-based solutions involving the protection, restoration, and/or management of natural and semi-natural ecosystems have garnered significant attention in mitigating mining-induced damages [8]. Cultivating hyperaccumulator plants emerges as a nature-based solution for revegetating areas affected by mine tailing and soils rich in

10. FINAL CONCLUSIONS

Iron (Fe) mining is an essential economic activity worldwide, especially in Brazil, the second-largest producer of Fe ore. However, the disposal of Fe mine tailings in dams poses significant human, social, and environmental risks, considering the recent catastrophic dam failures (e.g., the Mariana and Brumadinho disasters). Iron is one of the most common elements on the Earth's crust, a major element in soils, and a micronutrient for all life forms. Conversely, this work revealed environmental and human risks associated with Fe mine tailings deposited in an estuary. Understanding Fe biogeochemistry is crucial to recognizing estuarine soils as an environment where Fe bioavailability can sharply increase, turning Fe into a hazardous element.

In this sense, this work showed that the seasonal dynamics of potentially toxic elements (PTEs) in the estuarine soils were controlled by Fe biogeochemistry. The dissolution of Fe oxides during the transition from the rainy to the dry seasons resulted in a substantial loss of Fe and a notable increase in Mn, Cr, Cu, Ni, and Pb availability.

The analysis of risks associated with the consumption of food produced in the impacted estuary revealed that the association between PTEs and Fe oxides, which often act to reduce the bioavailability of PTEs, may not be an efficient mechanism in redox-active environments, as estuarine soils. The total hazard index (THI), which estimates the probability of adverse health effects from PTEs, revealed a potential risk to children's health due to the consumption of banana fruits produced in the estuary. Adults have a low risk of consuming fruits and tubers of the cultivated species studied.

Given the risks highlighted in this study, we explored techniques to remediate Fe mine tailings-impacted environments and options to reuse these mine tailings. The survey of species in the estuary showed that the macrophyte *Typha domingensis* had the highest potential for phytoextraction due to the high Fe, Mn, Cr, and Ni extractions in the aerial biomass.

The use of agricultural gypsum ($CaSO_4$) as a source of sulfate for chemical remediation resulted in higher dissolution rates of Fe oxides, increased concentrations of Fe^{2+} and sulfides (HS^- and H_2S) in the solution, which resulted in higher pyritization rates of Pb. When the use of agricultural gypsum was combined with the application of a microbial consortium (*Azospirillum* ssp., *Pseudomonas* ssp., *Saccharomyces* ssp., and *Rhizobium* ssp.), there was a significant decrease in the contents of Fe and Mn associated with oxides and an increase in the levels bioavailable of these elements.

In an enhanced bioremediation experiment, our results showed that the fertilization, either isolated and applied with chelating agents and a microbial consortium, promoted significant biogeochemical changes in Fe mine tailing, leading to greater Fe extraction by *T. domingensis* plants.

In conclusion, grounding the risk assessment and bioremediation studies on Fe biogeochemistry, this study explored new approaches for Fe mine tailings remediation and reuse, contributing to the development of the geochemistry applied to Soil Science and Environmental Science.