UNIVERSIDADE FEDERAL DE LAVRAS

MARINA MONTEIRO FEITOSA

RISK ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS IN AREAS WITH ARSENIC ANOMALIES

LAVRAS-MG
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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Ciência do Solo, área de concentração em Recursos Ambientais e Uso da Terra, para a obtenção do título de Doutor.

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Orientador

Prof. Dr. Marco Aurélio Carbone Carneiro
Coorientador

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Dedico

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RESUMO

Agricultura e mineração são atividades importantes no cenário econômico global. No entanto, podem causar impactos adversos no ambiente e na saúde humana ao mobilizar elementos potencialmente tóxicos (EPTs) para solos e águas. Entre os principais EPTs, arsênio (As) e chumbo (Pb) têm alto potencial para causar danos à saúde. No entanto, a determinação apenas dos teores pseudototais desses EPTs nos solos pode ser inadequada para prever os reais efeitos adversos, uma vez que a biodisponibilidade pode ser influenciada por diversas propriedades físicas e químicas do solo. Dessa forma, o objetivo desse estudo foi avaliar os riscos ambientais e à saúde humana em solos com níveis anormais de As em áreas agrícolas irrigadas de Paracatu (MG), Brasil. Além disso, avaliamos os riscos potenciais de As e Pb à saúde em solos amostrados de duas áreas contrastantes com diferentes origens e usos da terra, uma em áreas agrícolas de Paracatu (MG), Brasil, e outra em áreas de uma mina de ouro abandonada, em Marmora e Lake (ON), Canadá, usando testes de bioacessibilidade oral de As e Pb desenvolvido pelo *Solubility Bioaccessibility Research Consortium* (SBRC). No Brasil, amostras de solo e tecidos vegetais foram coletados em dez áreas agrícolas e de referência. Enquanto no Canadá, foram coletadas amostras de solo em dez áreas de uma mina de ouro abandonada e suas áreas adjacentes. Em geral, os teores pseudototais de As e Pb nos solos foram superiores aos limites regulatórios de qualidade do solo do Brasil e do Canadá. No entanto, os teores de As nos tecidos vegetais na área agrícola foram abaixo do limite de detecção. Os teores pseudototais de As dos solos agrícolas não diferiram entre as profundidades do solo, indicando que provavelmente a fonte de As nesses solos é natural. Em geral, a bioacessibilidade de As e Pb nos solos foi baixa, com valores de 5,57% para As_{IVBA} e de 17,19% para Pb_{IVBA} em solos agrícolas e de 31,53% para As_{IVBA} e de 20,58% para Pb_{IVBA} em solos de mina. Houve correlação positiva significativa entre os teores bioacessíveis de As e Pb e algumas das propriedades do solo, principalmente, os teores totais e extraíveis de ferro (Fe). Os teores bioacessíveis de As e Pb, pelo método SBRC, foram utilizados nos cálculos de avaliação de risco para ingestão acidental de solo. Para áreas agrícolas, em geral, os riscos ocupacionais não são preocupantes. No entanto, para áreas da mina abandonada, houve um alto nível de risco carcinogênico de As para adultos e crianças. Em ambas as áreas, não houve risco associado à exposição de Pb. Concluímos que a avaliação baseada apenas nos teores totais de As e Pb não é suficiente para prever os efeitos adversos à saúde humana, superestimando a exposição crônica a esses elementos. Por isso, sugerimos um fator de correção de 10% de bioacessibilidade de As para solos agrícolas brasileiros com altos teores de Fe. Este estudo fornece *insights* valiosos para avaliações de risco localizadas e orienta futuras pesquisas sobre a biodisponibilidade oral de As e Pb.

Palavras-chave: bioacessibilidade oral; biodisponibilidade; mineração de ouro; agricultura irrigada.

ABSTRACT

Agriculture and mining are important activities in the global economic landscape. However, they can cause adverse impacts on the environment and human health by mobilizing potentially toxic elements (PTEs) into soils and waters. Among the main PTEs, arsenic (As) and lead (Pb) have a high potential to cause health damage. However, determining only the pseudo-total contents of these PTEs in soils may be inadequate to predict real adverse effects, as bioavailability can be influenced by various physical and chemical properties of the soil. Thus, the objective of this study was to evaluate the environmental and human health risks in soils with abnormal levels of As in irrigated agricultural areas of Paracatu (MG), Brazil. Additionally, we evaluated the potential health risks of As and Pb in soils sampled from two contrasting areas with different origins and land uses, one in agricultural areas of Paracatu (MG), Brazil, and another in areas of an abandoned gold mine in Marmora and Lake (ON), Canada, using oral bioaccessibility tests of As and Pb developed by the Solubility Bioaccessibility Research Consortium (SBRC). In Brazil, soil and plant tissue samples were collected from ten agricultural and reference areas. In Canada, soil samples were collected from ten areas of an abandoned gold mine and its adjacent areas. In general, the pseudo-total contents of As and Pb in soils exceeded the regulatory soil quality limits of Brazil and Canada. However, the levels of As in plant tissues in the agricultural area were below the detection limit. The pseudo-total levels of As in agricultural soils did not differ between soil depths, indicating that the source of As in these soils is likely natural. Overall, the bioaccessibility of As and Pb in soils was low, with values of 5.57% for As_{IVBA} and 17.19% for Pb_{IVBA} in agricultural soils and 31.53% for As_{IVBA} and 20.58% for Pb_{IVBA} in mine soils. There was a significant positive correlation between the bioaccessible levels of As and Pb and some soil properties, mainly total and extractable iron (Fe) contents. The bioaccessible levels of As and Pb, by the SBRC method, were used in risk assessment calculations for accidental soil ingestion. For agricultural areas, in general, occupational risks are not concerning. However, for the abandoned mine areas, there was a high level of carcinogenic risk of As for adults and children. In both areas, there was no risk associated with Pb exposure. We concluded that assessment based only on the total levels of As and Pb is not sufficient to predict adverse health effects, overestimating chronic exposure to these elements. Therefore, we suggest a correction factor of 10% bioaccessibility of As for Brazilian agricultural soils with high Fe content. This study provides valuable insights for localized risk assessments and guides future research on the oral bioavailability of As and Pb.

Keywords: oral bioaccessibility; bioavailability; gold mining; irrigated agriculture.

INDICADORES DE IMPACTO

As principais atividades econômicas do município de Paracatu, Minas Gerais, Brasil, incluem a mineração de ouro e a agricultura. No entanto, a presença de anomalias geogênicas de arsênio (As) devido aos minérios de ouro representa um desafio ambiental e de saúde pública. A agricultura em Paracatu abrange mais de 40 mil hectares de áreas irrigadas, sendo um pilar econômico crucial para a região. A suspensão temporária do uso dos recursos hídricos do Córrego Rico, devido aos elevados níveis de arsênio na água - que em algumas áreas ultrapassaram em até 100 vezes os limites estabelecidos pela legislação - resultou em perdas econômicas significativas para os produtores locais que dependem dessa água para irrigação. Após uma avaliação de risco ambiental e à saúde humana, constatou-se que os teores de As nos solos eram de origem natural e que a irrigação com águas contendo As não aumentava esses níveis no solo agrícola. Os estudos realizados incluíram a avaliação dos teores de As totais e disponíveis em solos de áreas cultivadas e reservas naturais, bem como a análise da bioacessibilidade do As no solo e em partes comestíveis das plantas. Como resultado, o governo de Minas Gerais autorizou a retomada do uso da água do Córrego Rico para irrigação. Esses resultados foram essenciais para garantir a segurança alimentar e minimizar riscos à saúde humana. Além disso, a utilização de ensaios de bioacessibilidade de As contribuiu para uma avaliação de risco à saúde humana mais precisa, fornecendo uma base de dados robusta para futuras pesquisas e políticas públicas, promovendo uma agricultura mais segura. Para refinar os dados de avaliação de risco à saúde humana, foram realizados ensaios de bioacessibilidade de As e chumbo (Pb) em solos agrícolas, no Brasil, e áreas de mineração, no Canadá. Os resultados indicaram que a bioacessibilidade de As e Pb nos solos é significativamente baixa, apesar das altas concentrações totais desses elementos encontradas tanto em solos agrícolas brasileiros quanto em áreas de mineração canadense. A suposição de que 100% do As e Pb presentes no solo são biodisponíveis resulta numa superestimação do risco potencial de exposição a esses elementos, podendo levar a decisões de remediação e gestão desnecessárias e onerosas, impactando significativamente a economia local e as atividades agrícolas. Portanto, a inclusão de dados bioacessíveis nos cálculos de risco evita a superestimação do potencial de exposição, orientando decisões de gestão e remediação mais informadas e economicamente viáveis. A utilização de testes de bioacessibilidade, como o SBRC (Solubility Bioaccessibility Research Consortium), refina a compreensão da exposição humana e dos riscos associados. Com base nos resultados, este estudo sugeriu um fator de correção de 10% de bioacessibilidade de As para solos agrícolas brasileiros com altos teores de ferro. Esses insights são valiosos para avaliações de risco localizadas e orientam futuras pesquisas sobre a biodisponibilidade oral de As e Pb, contribuindo para a saúde e bem-estar das populações impactadas.

IMPACT INDICATORS

The main economic activities in the municipality of Paracatu, Minas Gerais, Brazil, include gold mining and agriculture. However, the presence of geogenic anomalies of arsenic (As) due to gold ores represents an environmental and public health challenge. Agriculture in Paracatu covers more than 40,000 hectares of irrigated areas, serving as a crucial economic pillar for the region. The temporary suspension of the use of water resources from the Córrego Rico, due to high levels of As in the water - which in some areas exceeded the legal limits by up to 100 times - resulted in significant economic losses for local producers who depend on this water for irrigation. After an environmental and human health risk assessment, it was found that the As levels in the soils were of natural origin and that irrigation with As-containing water did not increase these levels in agricultural soil. The studies conducted included the evaluation of total and available As levels in soils from cultivated areas and natural reserves, as well as the analysis of the bioaccessibility of As in soil and edible parts of plants. As a result, the government of Minas Gerais authorized the resumption of the use of water from the Córrego Rico for irrigation. These results were essential to ensure food safety and minimize risks to human health. Furthermore, the use of As bioaccessibility assays contributed to a more accurate human health risk assessment, providing a robust database for future research and public policies, promoting safer agriculture. To refine human health risk assessment data, bioaccessibility assays for As and lead (Pb) were conducted in agricultural soils in Brazil and mining areas in Canada. The results indicated that the bioaccessibility of As and Pb in soils is significantly low, despite the high total concentrations of these elements found in both Brazilian agricultural soils and Canadian mining areas. The assumption that 100% of the As and Pb present in the soil are bioavailable results in an overestimation of the potential exposure risk to these elements, potentially leading to unnecessary and costly remediation and management decisions, significantly impacting the local economy and agricultural activities. Therefore, the inclusion of bioaccessible data in risk calculations avoids the overestimation of exposure potential, guiding more informed and economically viable management and remediation decisions. The use of bioaccessibility tests, such as those from the Solubility Bioaccessibility Research

Consortium (SBRC), refines the understanding of human exposure and associated risks. Based on the results, this study suggested a 10% bioaccessibility correction factor for As in Brazilian agricultural soils with high iron content. These insights are valuable for localized risk assessments and guide future research on the oral bioavailability of As and Pb, contributing to the health and well-being of affected populations.

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FIRST PART

1 GENERAL INTRODUCTION

Agriculture and mining are activities of great importance in the global economic landscape, fostering development and sustaining communities around the world. However, while these activities are fundamental, they can have adverse consequences for the environment and human health (Bundschuh *et al.*, 2020; Billmann *et al.*, 2023). The mobilization of potentially toxic elements (PTEs) into water, soils, plants, and other environments is one of the main challenges associated with these activities (Bundschuh *et al.*, 2020). This mobilization may be related to anthropogenic activities, such as the application of irrigation water with high PTE content, the use of fertilizers and pesticides in soils and plants, and the exploration and processing of minerals, among others (Liu *et al.*, 2018). As a result, these mobilized PTEs can impact human health, as they are susceptible to entering the human food chain. The mobilization of PTEs can also occur naturally through physical and chemical weathering of rocks rich in these elements, resulting in soils with geological anomalies. While this represents a natural process, it remains equally concerning in terms of potential contamination (Ayangbenro and Babalola, 2017).

Some PTEs, such as arsenic (As) and lead (Pb), have the potential to cause undesirable impacts on human health and the environment due to their toxicity and persistence in the ecosystem (Billmann *et al.*, 2023). The intensity of these impacts, however, is directly related to the speciation and concentration of these elements in the environment (Bundschuh *et al.*, 2020). Additionally, the physicochemical properties of the soil perform a crucial role in the geochemical behavior of PTEs. Factors such as pH, redox potential, and the presence of aluminum (Al), iron (Fe), and manganese (Mn) oxyhydroxides significantly influence the interaction of these elements in the soil (El-Naggar *et al.*, 2019; El-Naggar *et al.*, 2018; Lima *et al.*, 2019; Shahid *et al.*, 2017; Yadav *et al.*, 2018). Therefore, understanding the behavior of PTEs in the soil is crucial for assessing risks to human and environmental health.

In mining, certain PTEs are often associated with the exploited ores, as seen with As found in arsenopyrite minerals in gold mining (Ciminelli *et al.*, 2018; Ng *et al.*, 2019). This element may be present in high concentrations in the soils of these areas and their surroundings. Moreover, the indiscriminate closure and abandonment of mining regions can lead to extensive contamination, increasing the risk of contact and contamination for the population, especially children, who are more vulnerable in risk assessment scenarios (USEPA, 2006; OECD, 2023). In an agricultural context, irrigating cultivated areas with river waters rich in As, for example, can result in soil and plant contamination, amplifying its impact throughout the trophic chain (Yang *et al.*, 2018; Palansooriya *et al.*, 2020). Therefore, understanding the complex interaction between natural processes and human activities is crucial for developing effective environmental management strategies and mitigating the impacts associated with these activities (Palansooriya *et al.*, 2020).

Risk assessment stands out as a crucial tool for making systematic and reliable decisions, aiming to protect health and enhance social and environmental conditions (USEPA, 1998). Many countries implement guidelines for soil quality assessment to protect the environment and human health (CCME, 1997; CONAMA, 2009; MTES, 2017). These guidelines are designed to cover both ecological receptors and humans, considering potential exposure to contaminants through various pathways associated with specific land use categories. However, current legislation relies solely on total metal concentrations in soil particles, which may lead to an overestimation of exposure and risk. In this regard, it becomes imperative to discuss legislative modifications when assessing health risks related to soil ingestion. This revision should incorporate an adjustment factor based on the oral bioavailability of PTEs to enhance the toxicity values of their total concentrations in the soil (Environment Agency, 2009; Grøn and Andersen, 2003; Health Canada, 2017; MTES, 2017; Ng *et al.*, 2015; Oomen *et al.*, 2006; USEPA, 2007). Thus, it is essential to conduct bioavailability and bioaccessibility tests for PTEs, determining the fraction of the contaminant potentially soluble in the human body.

Bioavailability and bioaccessibility assays for PTEs provide an estimate of the number of contaminants that can be released from the soil or other matrices into the digestive system and enter systemic circulation (Ng *et al.*, 2015; Kastury *et al.*, 2017; Billmann *et al.*, 2023). These analyses offer crucial information for assessing human health risks related to PTE exposure. In this context, this study investigated two geographically distinct areas, one in Brazil and the other in Canada, both exhibiting geological anomalies of As. Besides As, these areas showed elevated concentrations of other PTEs such as nickel (Ni), Pb, cobalt (Co), and copper (Cu). In Brazilian soils, covering agricultural areas and natural reserves, a high presence of As was observed, especially in soils irrigated with water containing high levels of As, originally with elevated levels of iron and manganese oxy-hydroxides and clay. On the other hand, Canadian soils, originating from an abandoned gold mining region and its surroundings, displayed high concentrations of As and other PTEs, deriving from a stony calcareous reddish-brown till parent material (Gillespie *et al.*, 1962). This research aims to understand the relationship between the physical and chemical properties of the soil and its implications for the bioaccessibility of PTEs.

The objectives of this study were: (1) To assess total As levels (at different depths) in soils from agricultural and reference areas in Paracatu, Minas Gerais, Brazil. (2) To evaluate the reactive fractions and bioaccessibility of As in the soil, as well as As levels in leaf tissues and edible parts (*i.e.*, grains), in order to estimate the actual risks of As in these agroecosystems. (3) To assess the environmental risks and the impact on human health from total As concentrations in irrigated agricultural areas in Paracatu-MG, Brazil. (4) To assess the total levels and bioaccessibility of As and Pb in two contrasting areas with different origins and land uses, one in agricultural areas in Paracatu-MG, Brazil, and the other in an abandoned gold mine in Marmora and Lake-ON, Canada, using the Solubility/Bioaccessibility Research Consortium (SBRC) assay. (5) To evaluate the relationship between soil properties and the bioaccessibility of As and Pb to identify soil factors that may attenuate the bioaccessibility of PTEs in soils. (6) To assess the carcinogenic and non-carcinogenic risk of As and Pb exposure, calculated from estimated soil intake rates for children and adults and the bioaccessibility of As and Pb.

2 LITERATURE REVIEW

2.1 Potentially Toxic Elements (PTEs) in soil

The sources of PTEs in the environment can be of natural origin, such as volcanic eruptions and geological material, as well as anthropogenic origin, such as mining, agricultural, and industrial activities, among others (Gupta *et al.*, 2019). Rock weathering and erosion have the potential to release PTE-rich minerals, influencing the formation of soils with anomalous levels of several of these elements (Ayangbenro and Babalola, 2017; FAO and UNEP, 2021). Some PTEs, such as arsenic (As) and lead (Pb), can have undesirable impacts on human health and the environment due to their toxicity and persistence in the environment; however, this depends on their speciation and concentration in the environment (Bundschuh *et al.*, 2020; Billmann *et al.*, 2023). PTEs can be mobilized and transported to soils, sediments, groundwater, and surface water resources used for human consumption and irrigation, and consequently enter the human food chain (Antoniadis *et al.*, 2017; Bundschuh *et al.*, 2020). Once they enter the trophic chain, there is a likelihood that these PTEs represent a significant risk to human health.

Mining and agriculture are important economic activities for the development of nations, but these practices can significantly contribute to increased levels of PTEs in natural soil environments (Liu *et al.*, 2018). In Brazil, in an area with a history of over 300 years of gold mining in Paracatu, Minas Gerais, As levels exceeding 2666 mg kg^{-1} were found in mine tailings (Ono *et al.*, 2016). In gold mining tailings, arsenic is usually associated with sulfide minerals such as arsenopyrite (Bidone *et al.*, 2018). In agricultural areas, PTE sources are more related to the local geology (Yang *et al.*, 2018; Palansooriya *et al.*, 2020). However, the use of irrigation water with high PTE levels, as well as the application of fertilizers and pesticides, are important PTE sources (Palansooriya *et al.*, 2020). There are few studies available on quantifying the safe limit of As in irrigation water; for example, in India, a study on two types of rice-cultivated soils, Alluvial and Red soil, with loamy clay and loamy sand textures, respectively, concluded that the safe limit for irrigation water for the studied soils is 0.75 mg L^{-1} in terms of hazard quotient (Kumari *et al.*, 2021).

The distribution of PTEs in soils can be influenced by various factors, including mineral precipitation-dissolution, ion exchange, adsorption-desorption, complexation, pH, redox conditions, mobilization, biological transformations, leaching, and plant uptake (El-Naggar *et* *al.*, 2019; El-Naggar *et al.*, 2018; Lima *et al.*, 2019; Shahid *et al.*, 2017; Yadav *et al.*, 2018). The main soil factors influencing the geochemical behavior of PTEs are pH and redox potential. pH affects the solubility of metals in the soil and consequently their availability for plant uptake. The solubility of cationic PTEs tends to decrease as soil pH increases, while the bioavailability of anionic PTEs increases due to the increase in negative charges and thus the adsorption of anions decreases as pH increases (Bradl, 2004; Sheoran *et al.*, 2016). The soil redox potential influences the mobility of PTEs from soil to plants, such as in the cultivation of rice in flooded areas, where flooding conditions favor the mobility of As (Rahman *et al.*, 2018).

The presence of aluminum (Al), iron (Fe), and manganese (Mn) oxides and hydroxides in soils influences the immobilization of certain PTEs in soils due to the formation of inner-sphere complexes under oxidation conditions, specific sorption by metal oxides, and the formation and precipitation of specific minerals (Zeng *et al.*, 2017). Brazilian soils, such as Oxisols and Ultisols, are predominantly rich in Fe and Mn oxides, thus exhibiting a higher capacity for the adsorption of various PTEs (Feitosa *et al.*, 2021). For As, the presence of Fe oxides can reduce its mobility in the soil because the positive charges on the surfaces of Fe oxides interact with the negative charges of this anionic PTE (AsO_4^{3-} and AsO_3^{3-}) (Warren and Alloway, 2003; Komárek *et al.*, 2013). Additionally, As can also be immobilized by Mn oxides due to the formation of a highly insoluble mineral at low pH, manganese-hörnesite ($Mn_3(AsO_4)_2.8H_2O$) (Porter *et al.*, 2004; Tournassat *et al.*, 2002).

Some PTEs are essential for proper plant development, such as copper (Cu), Mn, zinc (Zn), and Fe; however, they can induce phytotoxicity and inhibit plant growth if found in excessive levels in soils (Yang *et al.*, 2018). Therefore, it is necessary to determine the bioavailable levels of PTEs for plants to assess ecological risk, as only free ions in solution can cause any form of toxicity (Menzies *et al.*, 2007). Additionally, factors such as plant species, elements present in the soil solution, and soil type can influence the phytoavailability of PTEs in the soil (Salam *et al.*, 2019). However, insoluble forms of PTEs can be transformed into more bioavailable forms through biochemical interactions in the plant rhizosphere, contributing to greater efficiency in the assimilation of these elements by the plant. Thus, information on the accumulation of different PTEs in different plant species, as well as soil factors controlling the bioavailability of PTEs to plants, is important for food security.

In this context, the potential migration of these elements to groundwater, surface water, and plants, followed by their subsequent entry into the human food chain, raises significant concerns regarding environmental risks and health. Simultaneously, recognizing the essential role of some PTEs for plants, it becomes crucial to assess their bioavailability for accurate analysis of the ecological risks associated with their excess. In the pursuit of food security, information regarding the accumulation of different PTEs in various plant species and the soil factors governing their bioavailability becomes indispensable. Therefore, understanding the behavior of PTEs in the soil is crucial for evaluating environmental risks and implementing appropriate remediation measures.

2.2 Risk assessment

Risk assessment involves the identification of potential adverse effects on humans or ecological systems resulting from exposure to hazardous substances (USEPA, 1998). Risk assessment constitutes the preliminary phase of the risk analysis process, where scientific data on estimated risk are collected and compared with values derived from toxicological or ecotoxicological tests (USEPA, 1998). The purpose is to guide potential risk management and risk communication strategies, empowering regulatory authorities to make decisions aimed at preventing or controlling ecological and human health risks (Guilherme, 2005). This multifaceted process encompasses: (1) Hazard Identification, assessing whether a substance can cause harm to humans and/or ecological systems; (2) Dose-Response Assessment, determining the numerical relationship between exposure and the probability of harm; (3) Exposure Assessment, quantifying the extent of exposure; and (4) Risk Characterization, describing the nature, intensity, and uncertainty of the risk (USEPA, 1989; Bourgeois; Johnson; Harbison, 2017).

Human health and environmental risk assessments can estimate the harm to an organism from its exposure to PTEs. For regulatory purposes, risks are classified as acceptable or unacceptable (USEPA, 2007). Risk estimates use parameters that consider the toxicity of PTEs and their exposure to humans, such as the reference dose (RfD) or acceptable daily intake (ADI) values. The RfD represents the allowable amount of a specific pollutant that can be exposed to daily over an individual's lifetime, proportionally to body weight, without causing adverse effects. Meanwhile, ADI values guide the establishment of permissible levels of contaminants in food and water (EPA, 1993). If the estimated risk value is equal to or less than the specified ADI or RfD, no intervention in the environment is necessary. However, if it is higher, on-site remediation techniques should be implemented, such as the removal of contaminated soil and/or water from the contaminated site.

The American agencies, the Environmental Protection Agency (EPA), and the Agency for Toxic Substances and Disease Registry (ATSDR), classify a list of substances with potential health risks. The priority list of hazardous substances is based on frequency, toxicity, and the potential for human exposure to environmental pollution (ATSDR, 2022). Among these substances are various organic compounds, xenobiotics, and several chemical elements with the potential to cause harm. The main PTEs include arsenic, lead, mercury, and cadmium. PTEs can cause various health problems such as circulatory diseases, acute toxicity, dermatitis, skin cancer, cardiovascular diseases, neuronal damage in children, impaired cognition, anorexia, chronic nephropathy, high blood pressure, hyperactivity, insomnia, reduced fertility, kidney problems, digestive system damage, and various deleterious effects on the hematopoietic and central nervous systems (Abdul *et al.*, 2015; Assi *et al.*, 2016; Raj and Maiti, 2020; Wang *et al.*, 2023b).

Children are particularly susceptible to health risks when exposed to contaminated environments, mainly due to their lower body weight and bodily systems that are still developing. If a child is exposed to pollutants, the same amount that may pose little or no risk to an adult can cause deleterious effects in a child (OECD, 2023). One of the main routes of contamination for children is the accidental ingestion of soil, resulting from their natural habits such as crawling and putting their hands to their mouths (USEPA, 2006). For this reason, when calculating the potential risk to human health, the recommended daily intake rates of soil, dust, and sediments for children are 200 mg of soil per day, compared to the 100 mg per day established for adults (ATSDR, 2022). Therefore, it is crucial to consider these differences between children and adults when assessing health risks to ensure their adequate protection.

There are several methodologies employed in assessing risks to human health and the environment. These risks can be empirically calculated through equations estimating both non-carcinogenic and carcinogenic potentials, in both children and adults (USEPA, 2001). This mathematical model utilizes total PTE concentrations and various variables to estimate the average daily doses through the three main pathways of human exposure to a contaminant (ingestion, inhalation, and dermal contact), thus estimating the risk quotient and risk index for adults and children (USEPA, 2001). Another approach involves determining risk through specific laboratory tests, such as those assessing the bioavailability and bioaccessibility of

PTEs, which utilize animals or solutions simulating the human digestive system to determine the fraction of the contaminant that can be absorbed into the body and cause harm to human health (USEPA, 2007; 2017). Therefore, for each risk assessment study, the choice of appropriate methodology will primarily depend on the type of PTE, the matrix, and the human exposure pathway, as well as human, ethical, and financial resources.

2.3 Bioavailability and bioaccessibility of PTEs

One way to assess the true risks to human health is through tests of the bioavailability and bioaccessibility of PTEs. These tests aim to determine the available fraction of an exposed dose of contaminants that can be absorbed by the digestive system and enter systemic circulation (Koch *et al.*, 2007). *In vivo* bioavailability assays are tests conducted on animals and determine the absolute bioavailability (ABA), which is the fraction of an ingested dose of an element, such as As, that is absorbed by the gastrointestinal tract and enters the bloodstream (USEPA, 2007). Relative bioavailability (RBA) is the ratio between ABA for As present in soil and a reference form of water-soluble As, usually sodium arsenate (USEPA, 2007). However, RBA can also be predicted through *in vitro* bioaccessibility assays (IVBA) (USEPA, 2017). These *in vitro* bioaccessibility assays (IVBA) are methods that simulate human gastrointestinal conditions in the laboratory (USEPA, 2021). They provide an estimate of the amount of contaminant that can be released from soil or another matrix into the digestive system, providing crucial information for the assessment of human health risks associated with exposure to PTEs.

Exposure pathways to PTEs include inhalation, oral ingestion, or dermal absorption. The main routes involve water intake and consumption of vegetables and, particularly in the case of children, ingestion of soil or dust containing PTEs. Within the human body, PTEs can compete for the same physiological sites as essential elements due to their similarities, such as arsenate and phosphate or cadmium and calcium, leading to toxicity (Ng *et al.*, 2015). Thus, the bioavailability of PTEs can vary primarily according to the ingested matrix, contaminant solubility, soil type, presence of other dietary constituents, nutrients in the gastrointestinal tract, and size of the ingested material (Ng *et al.*, 2015). Smaller particle sizes exhibit higher bioavailability compared to larger particles of the same material. Hence, there is significant methodological variation in bioavailability and bioaccessibility tests worldwide (Kastury *et al.*, 2017).

Oral bioavailability tests can be conducted using various animal models such as monkeys, mice, rabbits, and pigs (Ng *et al.*, 2015). The choice of animal model considers factors such as the type and quantity of the biological sample, animal availability, breeding requirements, and associated costs. In the context of As RBA in soils, studies have indicated similar results among mice, pigs, and monkeys in the same soils (Bradham *et al.*, 2013, 2018; Li *et al.*, 2016). However, mouse bioassays have emerged as an economically viable alternative for this measurement (Bradham *et al.*, 2011, 2013, 2015). These studies typically analyze the levels of these elements in blood, urine, and fecal excretion, as well as evaluate affected organs such as the liver and kidneys (Ng *et al.*, 2015). *In vivo* assays are vital for validating *in vitro* assays as surrogate measures to refine human exposure and risk. However, these studies are costly and often encounter lengthy approval processes in ethics and animal care committees. For this reason, oral bioaccessibility assessment models are employed to determine the fraction of soil contaminants that can reach the bloodstream and cause toxic effects (Denys *et al.*, 2012; Kumpiene *et al.*, 2017; Li *et al.*, 2020).

Several *in vitro* tests, simulating gastric and gastrointestinal phases, are employed to replace *in vivo* assays in animals (Li *et al.*, 2021). Among them, notable ones include the Physiologically Based Extraction Test (PBET; Ruby *et al.*, 1996), the Solubility/Bioavailability Research Consortium method or Relative Bioavailability Leaching Procedure (SBRC or RBALP; Kelley *et al.*, 2002), the US EPA Method 1340 (USEPA, 2017a, USEPA, 2017b, USEPA, 2021), derived from SBRC (gastric phase only) and SBET (Single Extraction Test Bioaccessibility; Medlin, 1997), the *in vitro* gastrointestinal test (IVG; Rodriguez *et al.*, 1999) and its modified version (Basta *et al.*, 2007) without a dosing vehicle, the Deutsches Institut für Normung method (DIN 19738; Hack *et al.*, 2002), and the Unified BARGE Method (UBM; Denys *et al.*, 2012; BARGE 17924, 2019), which is derived from the Dutch National Institute for Public Health and the Environment method (RIVM; Oomen *et al.*, 2003). Additionally, a modified extraction procedure known as the California Arsenic Bioaccessibility Method (CAB; California DTSC, 2015) has been developed to enhance the ability to predict arsenic bioavailability (Whitacre *et al.*, 2017).

There are also alternative methods for *in vitro* bioaccessibility testing, as in the case of As. According to Ono *et al.* (2012a), one of the methods used to estimate bioaccessible As is the Mehlich I (Mehlich, 1953), a routine methodology in soil fertility laboratories. In this study, in an area near a gold mine, the authors found a significant positive correlation in As levels in soils and sediments between values extractable by Mehlich I and bioaccessible by *in vitro* gastrointestinal ingestion protocol (IVG). Therefore, the authors proposed that Mehlich I can be used as a quick and economical alternative to estimate gastric bioaccessibility of As. Despite the wide variety of methodologies, bioaccessibility values can vary significantly among them (Kierulf *et al.*, 2022; Li *et al.*, 2013; Li *et al.*, 2021; Zingaretti and Baciocchi, 2021), mainly due to different pH conditions applied in the acidic stage of gastric digestion simulation (Bagherifam *et al.*, 2019; Li *et al.*, 2019). As in the case of As, minerals formed in an acidic pH, such as arsenopyrite and scorodite, tend to be preferentially solubilized, while minerals formed in an alkaline pH, such as calcium arsenate, are more resistant to destabilization after exposure to acidic gastric conditions (Sowers *et al.*, 2022). Therefore, recognition of typical conditions for As mineral formation is essential to predict bioaccessibility.

In the current management of contaminated soils, only the total concentrations of PTEs are considered in risk calculations; however, to obtain a more realistic risk estimate, the use of oral bioaccessibility could be proposed as a corrective factor for total concentration (Environment Agency, 2009; Grøn and Andersen, 2003; Health Canada, 2017; MTES, 2017; Ng *et al.*, 2015; Oomen *et al.*, 2006; USEPA, 2007). Several countries implement soil quality guidelines to protect the environment and human health. These guidelines are designed for both ecological and human receptors, considering potential exposure to contaminants through various pathways associated with specific land use categories. Among PTEs, As is a priority and represents significant health risks due to its high toxicity, which can lead to cancer and various health problems, including circulatory, dermatological, neural, and cardiovascular diseases (Abdul *et al.*, 2015). In Brazil, a soil guideline value of 15 mg As kg^{-1} was established as a preliminary limit through ecological risk assessment (CONAMA, 2009). Intervention values were set at 35 mg As kg^{-1} soil for agricultural areas, 55 mg As kg^{-1} soil for residential areas, and 150 mg As kg^{-1} soil for industrial areas. In Canada, the soil quality guideline from the Canadian Council of Ministers of the Environment (CCME) is 12 mg As kg^{-1}, applicable to agricultural, residential, commercial, and industrial areas (CCME, 1997). This guideline was derived assuming a natural background concentration of As in soil of 10 mg kg^{-1}. Thus, it is important to conduct human health risk assessment tests in locations with abnormal levels of As in soil, especially in agricultural areas and areas near the local community. Additionally, a site-specific approach is crucial due to the dependence of contaminant bioaccessibility on soil type.

2.4 Case Studies in Areas with Anomalous Levels of Arsenic in Soils

Arsenic is a metalloid that occurs naturally in the environment and is considered highly toxic to human health as it is carcinogenic (USEPA, 2001; ATSDR, 2022). In soil, As is primarily associated with minerals, including arsenates, sulfides, sulfosalts, arsenites, arsenides, native elements, and metal alloys (Moreno-Jiménez *et al.*, 2012). However, anthropogenic activities such as gold mining and the use of water resources with elevated levels of arsenic for irrigation can contribute to increased concentrations of this element in both soils and water bodies (Bundschuh *et al.*, 2020). During mineral exploration, this contaminant is released into waterways, later being transported to groundwater, surface water, soils, and sediments (Bundschuh *et al.*, 2020). The use of these arsenic-rich river waters for irrigation in agricultural areas can result in soil and plant contamination, extending its impact through the food chain (Datta *et al.*, 2012; Gillispie *et al.*, 2015).

Arsenic is commonly present in soils in the inorganic form of arsenate (AsO_4^{3-}), which is less toxic than arsenite (AsO_3^{3-}) (Bundschuh *et al.*, 2020). Inorganic forms are more toxic than organic forms (Tuzen *et al.*, 2010). Human exposure to arsenic can cause various diseases, such as diabetes, cardiovascular diseases, reproductive dysfunctions, anemia, and cancer (Argos *et al.*, 2010; Cohen *et al.*, 2013; Da Silva *et al.*, 2017; Medina *et al.*, 2017). Due to the potential risks associated with arsenic exposure, it is crucial to investigate the sources of arsenic and biogeochemical controls of As. The bioavailability of As can be influenced by various physical, chemical, and biological properties of the soil, including Fe and Mn oxides, pH, cation exchange capacity, carbon content, biological activity, aggregation, and particle size (El-Naggar *et al.*, 2019; El-Naggar *et al.*, 2018; Lima *et al.*, 2019; Shahid *et al.*, 2017; Yadav *et al.*, 2018).

Of these properties, the binding of As(V/III) to Fe(III) oxyhydroxides is important when assessing biogeochemical constraints on the bioaccessibility and bioavailability of As. This occurs due to the high affinity between positively charged surfaces in soils, such as Fe(III) oxides, and oxyanions, such as As(V), which carry a negative charge in the soil in the common values of soil pH's (Fendorf *et al.*, 2010). Arsenic associated with amorphous metal oxide minerals has higher bioaccessibility, while crystalline phases generally exhibit lower bioaccessibility (Meunier *et al.*, 2010; Kim, Yoo and Baek, 2014). For example, soils from gold mining areas have higher As bioaccessibility when associated with goethite and amorphous Fe, compared to lower arsenic bioaccessibility for arsenopyrite and scorodite (Toujaguez *et al.*, 2013). However, variable biogeochemical conditions such as acidic pH, reducing conditions, and the presence of competing ions can increase As availability in soils (Deng *et al.*, 2020; Gillispie *et al.*, 2015), which can affect bioaccessibility and bioavailability measurements. However, few studies correlate As bioaccessibility with bioavailability in the presence of Fe and Mn oxides in the soil. This type of research is crucial for accurately determining bioaccessibility for soils that vary in mineralogy and composition.

In this context, the Fe content is considered the variable that influences the most the expected heterogeneity of bioaccessibility results in all assays and phases of the assay (Juhasz *et al.*, 2014, 2015, 2009; Lee *et al.*, 2015; Sowers *et al.*, 2022). Therefore, two study areas with abnormal levels of As in soils and different geological origins are presented below, one in Brazil and the other in Canada. These areas also exhibited high levels of other PTEs, such as nickel (Ni), lead (Pb), cobalt (Co), and copper (Cu). The study area in Brazil, in Paracatu-MG, is classified as Red Oxisols, with high levels of Fe and Mn and clay, and samples were collected in both agricultural and adjacent natural reserve areas. The study area in Canada, in Marmora and Lake-ON, is classified as Deloro Loam, originating from a brown-red rocky limestone, and samples were collected in a decommissioned gold mining area and its surroundings. Therefore, one of the main objectives of this study was to compare the oral bioaccessibility of As in two areas with different geological origins and land uses.

2.4.1 Arsenic Anomaly from Irrigated Areas along the Córrego Rico Watershed in Paracatu Municipality, Minas Gerais, Brazil

The main economic activities in the municipality of Paracatu, Minas Gerais, Brazil, include gold mining and agriculture. In Brazil, gold (Au) is the third most produced metallic substance, accounting for 8.9% of the mineral production value (ANM, 2020). Minas Gerais is the leading Au-producing state, accounting for 43.7% of the national production (ANM, 2020). These activities have a history of over 300 years in the municipality, currently operated by the company Kinross Brasil Mineração (KBM) (Bundschuh *et al.*, 2017). Since the 1980s, extensive and high-tech agriculture has been implemented in this region. Paracatu has over 40 thousand hectares of irrigated areas equipped with central pivot irrigation systems, producing large agricultural products such as corn, beans, soybeans, coffee, and cotton (Souza; Fernandes; Alamino, 2011). However, it is important to note that As levels in these soils are higher than those reported as average values for soils worldwide, ranging from 32 to 2980 mg kg^{-1} (ONO *et al.*, 2012a).

Paracatu is known to have areas with geogenic As anomalies originating from extensive sulfide Au ore deposits (Borba & Figueiredo, 2004), mainly scorodite ($FeAsO_4.2H_2O$) and arsenopyrite (FeAsS) (Ciminelli *et al.*, 2018). However, this element is strongly bound to crystalline iron oxide nanoparticles, resulting in As immobilization in the soil (Ciminelli *et al.*, 2018). Thus, even at high concentrations in the soil, this contaminant presents a low risk to the environment and human health due to its less bioavailable form in the soil. In Paracatu, several studies have been dedicated to the elevated levels of As in soils near gold mines (ONO *et al.*, 2012; Rezende *et al.*, 2015; Bidone *et al.*, 2018; Ng *et al.*, 2019; Bundschuh *et al.*, 2020). However, when it comes to agricultural areas, few studies address these regions recognized for their As anomalies.

One of the main water basins in Paracatu is the Córrego Rico, which crosses the entire region and flows into the Paracatu River, an important tributary of the São Francisco River (IGAM, 2020b). This stream was one of the most important points for gold exploration in the region (Santos, 2012). The waters of this stream are mainly used for irrigation of surrounding agricultural areas and, in some cases, for human and animal consumption. However, elevated levels of total and dissolved As have been identified at certain points in this water basin (IGAM, 2020b). Considering that the soils in this region are naturally enriched with As due to its geology rich in arsenopyrite (Kinross, 2019), it is likely that the high levels in soils irrigated with water from this stream are of natural origin.

In the historical data series from 2000 to 2019, the total As concentrations in the waters of a segment monitored by IGAM in Córrego Rico exceeded the limits of class 2 (0.01 mg L^{-1}) by up to 100 times, ranging from 0.011 to 1.065 mg L^{-1} (IGAM, 2020b). According to FAO, the safe limit for As in irrigation water is 0.100 mg L^{-1} (Ayers and Westcot, 1994). Consequently, an investigation was carried out on the scenario and water quality in the municipality of Paracatu, resulting in the temporary suspension of water resource use in that specific segment for five years. This action was outlined in IGAM Ordinance No. 09, dated February 7, 2020

(IGAM, 2020c). This suspension directly impacts the agricultural production of the region, which heavily relies on the waters of this river, mainly for irrigation. This scenario could result in substantial economic losses for local producers. Therefore, it is essential to conduct a risk assessment in these irrigated agricultural areas to understand the As-associated risk that may be introduced into the soil through irrigation.

According to IGAM Ordinance No. 24, dated May 20, 2020, temporary water use permits were rescinded for specific sections of the Córrego Rico water basin (IGAM, 2020d). Nevertheless, the section located at coordinates S 17°16'13.21464" W 46°51'12.77748" and S 17°20'19.32684" W 46°42'51.21648" remained restricted for the use of water resources from the water basin. Additionally, the ordinance proposed the initiation of environmental and human health risk assessment studies in these areas. The aim is to verify if the high levels of total and dissolved As in the waters of this section do not pose health risks regarding the use of water from Córrego Rico. Therefore, it is fundamental to investigate the soils of the impacted areas and assess the presence of this contaminant in grains and plants collected in agricultural areas irrigated with this water.

The potential health risks associated with the use of water with high As levels for irrigation depend on its bioavailability to plants and humans, a factor limited by environmental conditions (pH and Eh) and adsorption on colloidal particles in soils and sediments. Ciminelli *et al.* (2018), using high-resolution transmission electron microscopy, observed in mining areas in Paracatu that As is predominantly associated with crystalline iron oxide nanoparticles. Furthermore, As bound to oxides is highly resistant to weathering and consequently less soluble (Kim *et al.*, 2014). Therefore, it is believed that this contaminant is unlikely to pose a significant risk to the local population using stream water for irrigation.

Phosphate is atomically like arsenate, and therefore, they behave similarly in soils, both strongly adhering to Fe/Al/Mn oxides and hydroxides, humic substances, and clay minerals (Bauer and Blodau, 2009; Campos *et al.*, 2007, 2013; Fendorf *et al.*, 2010; Herath *et al.*, 2016; Ciminelli *et al.*, 2018; Menezes *et al.*, 2020). Because they belong to Group 15 of the periodic table, both exist in the "5+" oxidation state in well-drained environments and share the same metabolic pathway for human absorption (Pintor *et al.*, 2020; Souza Neto *et al.*, 2020). In well-drained agricultural soils in Brazil, both As and phosphorus (P) demonstrate significant adsorption capacities, reducing their immediate availability for plant uptake (Pintor *et al.*, 2020; Zhang *et al.*, 2019). Consequently, it is assumed in Brazil that only a small fraction of As is in its bioavailable form. Despite the high total concentrations in soil and water, this contaminant is considered of low risk to human health (Ono *et al.*, 2012b; Guilherme *et al.*, 2014; Silva Júnior *et al.*, 2019).

Assuming that the behavior of As and P in Brazilian soils is comparable, we can investigate whether irrigation with water containing arsenic influences the elemental content in the soil by determining As and P at different soil depths. Our hypothesis is that if As is introduced into tropical agroecosystems through irrigation, it is expected to accumulate predominantly near the soil surface due to its limited mobility in Oxisols. This behavior is like that of P when applied to native soils of the Brazilian Cerrado through phosphate fertilization. However, as these are agricultural areas, As anomalies in soils should meet the agricultural investigation values stipulated in Brazilian legislation; otherwise, these areas may be permanently prohibited for agricultural activities. There is insufficient information about the behavior of As in irrigated agricultural soils and its bioavailability. Therefore, conducting studies that can anticipate ecological and human risks in areas affected by arsenic due to irrigation is crucial (Campos *et al.*, 2013; Machado *et al.*, 2019; Ng *et al.*, 2019).

2.4.2 Arsenic Anomaly from the decommissioned Deloro Gold Mine in Marmora and Lake Municipality, Ontario, Canada

The Deloro Mine Site is renowned for its historical mining and industrial activity over 100 years, located in the municipality of Marmora and Lake, Ontario, Canada. From 1860 to 1960, a 202-hectare gold mine existed at this site, which is now inactive. In addition to Au, the site refined and produced As, silver (Ag), Ni, Co, and stellite, an alloy of Cr, Cu, and tungsten (W) (Tenkouano *et al.*, 2019). In 1885, Canada began refining As in Deloro, primarily for the manufacturing of insecticides and glass (Azcue & Nriagu, 1993). Approximately 650 thousand m^3 of waste were produced in this area and left abandoned. The waste, mainly rich in As, was deposited along the Moira River, which flows into the Bay of Quinte, Lake Ontario. Therefore, due to its significant environmental impact, Deloro is an important research area for risk assessment.

The gold ore at the Deloro Mine Site consists of arsenopyrite-quartz veins in the gabbro, which are important natural sources of As. In Deloro, arsenopyrite consisted of about 55% Fe, 25% As, and 20% sulfur (S) (Mir *et al.*, 2007). As is primarily bound to Fe oxides, and there is a predominance of As(V) in the solid phase (Mir *et al.*, 2007; Tenkouano *et al.*, 2019). Elevated levels of As in soil samples ranging from 335 to 100,000 mg kg^{-1} and in plant samples ranging from 2.3 to 241 mg kg^{-1} have been found near the abandoned mine site (Mir *et al.*, 2007). Additionally, the highest Ni levels in soil were about 10,000 mg kg^{-1} due to the proximity to the former Ni refinery (MOEE, 1995). Although mining activities at this site ceased in 1961, the area remains contaminated by various PTEs such as As, Co, Cu, Ni, low-level radioactive waste, and other materials.

Since 1979, the Ontario Ministry of the Environment (OME) has played a significant role in the remediation of the Deloro site, utilizing PTE remediation practices. The site cleanup project includes the construction of two large engineered covers, in the industrial and mine area and in the tailings area, to contain site waste and contaminated material (completed phase); construction of a disposal area to isolate and protect waste for long-term storage in the Young's Creek area (completed phase); directing rain and melted snow away from engineered covers to prevent dispersion of contaminated material (ongoing phase); operating an As treatment station to pump and treat contaminated groundwater and leachate collected throughout the site (ongoing phase) (Whiffin *et al.*, 2006). At the end of the project, as a hazardous waste facility, the site will remain closed and controlled (Whiffin *et al.*, 2006).

Ontario Ministry of the Environment (OME) conducted a soil investigation and human health risk assessment report (MOE, 1999; MOE, 2002). The results revealed high concentrations of As and metals in the soil but concluded that they did not pose significant risks to residents' health. However, they pointed out that the predicted skin cancer risks associated with As were notably higher for Deloro residents compared to typical Ontario residents. Precautionary measures were implemented, including restricting access to areas with extremely high concentrations. In Canada, the soil quality guideline from the Canadian Council of Ministers of the Environment (CCME) for As is 12 mg kg^{-1}, applicable to agricultural, residential, commercial, and industrial areas (CCME, 1997). This guideline was derived assuming a natural background concentration of As in soil of 10 mg kg^{-1}. Given this, it is crucial for regulatory purposes to anticipate the risk associated with metal mixtures in soils present in mining areas in Canada. This approach is essential for proper management and mitigation of potential environmental and human health impacts.

Therefore, our main objective was to assess the bioaccessibility of As and Pb present in high concentrations in this soil with a history of gold mining and its surroundings. Additionally, we investigated the correlation between As bioaccessibility and soil properties in two distinct soils, an agricultural area in Brazil and an area of an abandoned mine in Canada. The study area in Brazil, in Paracatu-MG, is classified as Red Oxisols, with high levels of Fe and Mn and clay. The study area in Canada, in Marmora and Lake-ON, is classified as Deloro Loam (SCWG, 1998), originating from brownish-red stony limestone. US Soil Taxonomy classifies most of these Brunisols as Inceptisols. Thus, it is expected that the soil Fe content significantly influences the results of As bioaccessibility tests in these two soils of distinct origin due to variations in precipitation-dissolution chemistry and sorption reactivity. Therefore, our hypothesis is that As found in Brazilian soils is less bioaccessible than those in Canada due to the higher Fe contents found in these soils.

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SECOND PART – PAPER(S)*

PAPER 1 ENVIRONMENTAL AND HUMAN-HEALTH RISKS OF As IN SOILS WITH ABNORMAL ARSENIC LEVELS LOCATED IN IRRIGATED AGRICULTURAL AREAS OF PARACATU (MG), BRAZIL*

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Abstract

The municipality of Paracatu (Brazil) is notorious for its large irrigated agricultural area and by abnormal arsenic (As) levels in selected soils of the region. Concerns regarding As exposure via ingestion of water and food are frequent, yet little is known about the behavior of arsenic in irrigated agricultural soils, as well as on As bioaccessibility/bioavailability in agroecosystems of this region. This work evaluated total and available As in agricultural soils cultivated under irrigation and in soils under native vegetation in Paracatu. We also assessed reactive arsenic fractions and As bioaccessibility in the soil, as well as arsenic levels in plant shoots to estimate As risks in these agroecosystems. Soil (different depths) and plant tissue samples were collected in 6 irrigated agricultural areas (CA1 to CA6) and 4 reference areas (RA1 to RA4). Total soil-

As did not differ between soil depths, reinforcing that the source of As in agricultural soils is natural. This was evident when counterpointing arsenic and phosphorus contents at different soil depths, as both accumulate on the surface of oxidic soils when added to agroecosystems by anthropogenic routes (*e.g.*, phosphate fertilization for P and irrigation for As). Available As levels in soils and plants were very small (below detection limit, <0.02). Furthermore, all soils presented very low oral As bioaccessibility. Our findings revealed that the irrigated soils are not As polluted due to the low enrichment and accumulation of arsenic, as well as the prevalence of low ecological risks. There is no carcinogenic risk for the local population, except for children in RA2. The estimated carcinogenic risk for children followed the order RA2 > CA3 > CA4 > RA3 > CA2, and for adults, RA2 > CA3. Ultimately, the strategy of comparing the behavior of P and As in the soils of this study proved to be efficient in showing that there are no major risks to humans and the environment in the investigated area. However, periodic monitoring of As bioavailability in these areas is recommended.

Keywords: Arsenic bioaccessibility; Risk assessment; Environmental pollution; Phosphorus.

1. Introduction

One of the greatest challenges facing humanity in this century is to ensure food security for all people. Irrigation plays a major role in enabling greater agriculture yields, as well as the production of high-quality food with desirable nutritional standards. However, the use of contaminated water in irrigation may represent a source of contamination of the food chain with potentially toxic elements, *e.g.*, arsenic (Bundschuh et al., 2020).

Brazil stands out in the worldwide agricultural production as an important global food producer and exporter. Agricultural lands irrigated by center pivots have shown persistent growth in recent decades in Brazil, especially in Paracatu-MG. In fact, this municipality - with 72,726 ha of installed center pivots - has the largest potentially irrigated area in the country (Embrapa, 2020).

Soils nearby Paracatu are well-known for having arsenic (As) contents higher than the world average of 6.83 mg kg^{-1} (Bundschuh et al., 2020). However, this element has a geogenic origin, due to the large occurrence of gold sulphide ores in the region (Ciminelli et al., 2018). The soils of Paracatu are predominantly Red Latosols with a clayey texture and a high capacity to adsorb phosphate and, owing to their resemblance, arsenate – $As_{(V)}$ (Silva Júnior et al., 2019, Wang et al., 2018). Indeed, due to the similarity of the elements, adopting a risk assessment strategy in which the chemical behavior between P and As is compared in tropical soils is appropriate to trace their source of contamination. If confirmed, this approach could be replicated in other areas of oxidic soils from Brazil and conceivably other tropical regions.

The municipality of Paracatu, located in the heart of the Cerrado region of Brazil, in addition to standing out in the agricultural sector, has had gold mining as one of its main economic activities for over 300 years (Ng et al., 2019). There is a recurrent concern that mineral exploration will release As to watercourses and that it may be transported to ground and surface water, soils, and sediments (Bundschuh et al., 2020, Teixeira et al., 2020).

River waters of the Paracatu region are used primarily for human consumption and for irrigation of agricultural areas (Ng et al., 2019) and high total As contents (ranging from 0.011 to 1.065 mg L^{-1}) were recently found in the watercourses of the Córrego Rico - part of the Paracatu river (IGAM, 2020). Such waters might represent a potential source of As contamination of soils and plants, yet there is little information about the behavior of As in irrigated agricultural soils of this region, as well as on soil-As bioaccessibility, which speaks for the need of studies that can predict the ecological and human risks in areas eventually contaminated with As by irrigation (Ng et al., 2019).

One of the means to address arsenic risks is to assess As content in the main routes of human exposure, *i.e.*, water and food intake (Rezaei et al., 2019), although ingestion of soil is also relevant in the case of children. Due to its high toxicity, the regulatory limit established by WHO (World Health Organization) for As in drinking water is 10 µg L^{-1}. Indeed, arsenic is bioaccumulative and, if it reaches toxic levels in the organism, it can cause adverse effects on human health, such as genetic mutations, cancers and abnormalities in embryonic or fetal development (Sun et al., 2018). Therefore, it is necessary to perform As bioavailability and oral bioaccessibility tests in these areas. *In vitro* gastrointestinal (IVG) ingestion protocols are the most conventional methods for As (Kumpiene et al., 2017), but an alternative method also exists (Ono et al., 2012a, Ono et al., 2012b). This consists of estimating the bioaccessible As by Mehlich I (Ono et al., 2012a), due to a strong significant and positive correlation between the methodologies (IVG and Mehlich I protocols).

Assuming that the behavior of As and P in Brazilian soils are similar, it its possible to verify whether the effect of irrigation with waters containing As causes an increase in the contents of this element in the soil by determining As and P at different soil depths. We hypothesized that, similarly to what occurs for P when applied in native Cerrado soils of Brazil (via phosphate fertilization), if arsenic is added to tropical agroecosystems by irrigation, one can expected that As will remain mostly on the soil surface, due to its low mobility in oxidic soils. Moreover, under such circumstances, arsenic from irrigation water is not expected to increase As to toxic levels in oxidic soils having abnormal As contents in Paracatu (Brazil), since soil-As in several agricultural areas of the region is expected to be of lithogenic/pedogenic origin and, as such, has low bioavailability and low risk (Ng et al., 2019).

Thus, with the aim of assessing environmental and human-health risks of As, this work evaluated total and available As contents (at different depths) in soils from cultivated areas and in natural reserves (*i.e.*, reference areas) in the region of Paracatu-MG, Brazil. Additional analyses were performed to evaluate reactive fractions and As bioaccessibility in the soil, as well as arsenic levels in leaf tissues and edible parts (*i.e.*, grains) in order to estimate the real risks of As in these agroecosystems.

2. Material and methods

2.1. Study area

The study area is located in the Córrego Rico basin and its contribution basin (17°16' 13.21464" S 46°51'12.77748" W and 17°20'19.32684" S 46°42'51.21648" W), Paracatu municipality, northwest of the State of Minas Gerais, southeastern Brazil (Fig. 1 and Table 1S). The municipality has an area of 8229.6 km^2 and more than 93 thousand inhabitants (IBGE, 2019). The climate of the municipality is humid tropical, Aw type, according to the Köppen classification, with dry winter and rainy summer. The annual average of precipitation is of 1400 to 1500 mm and the temperature of 21-23°C. The relief is smooth to smooth-wavy and the biome is Cerrado.

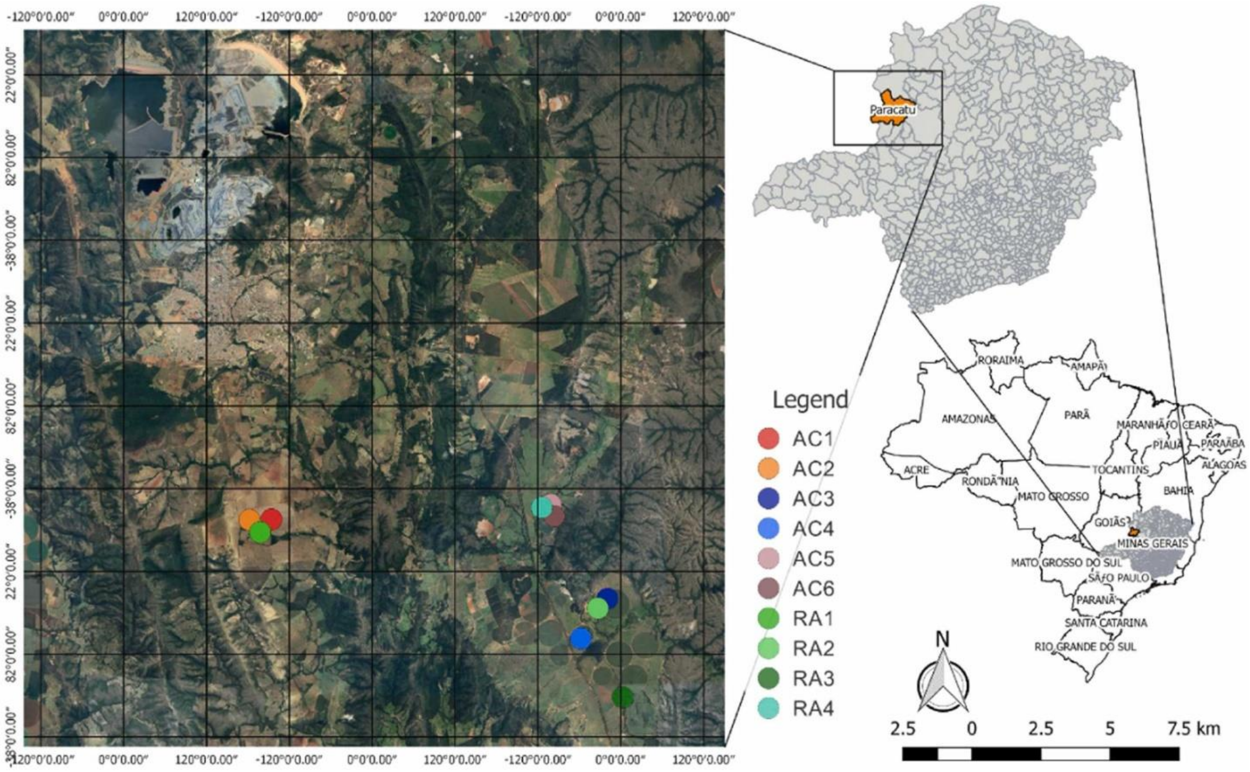


Figure 1 Location map of sampling points in the studied areas, in the city of Paracatu, Minas Gerais, Brazil. Where: CA1 = Cultivated Area 1; CA2 = Cultivated Area 2, CA3 = Cultivated Area 3, CA4 = Cultivated Area 4, CA5 = Cultivated Area 5, and CA6 = Cultivated Area 6, RA1 = Reference Area 1, RA2 = Reference Area 2, RA3 = Reference Area 3, and RA4 = Reference Area 4.

2.2. Soil and plant sampling

The sampling was performed in June 2020, in Red Oxisols, the predominant soils in the region. Samples of soil and plant tissue (grains and leaves) were collected in six agricultural areas irrigated with water from the Córrego Rico basin and in four reference areas, with native vegetation and without anthropic action, such as legal or permanent reserves. The areas were identified as Cultivated Areas (CA1, CA2, CA3, CA4, CA5, and CA6) and Reference Areas (RA1, RA2, RA3, and RA4). The CAs were divided into two types of soil management: conventionally cultivated areas, with soil tillage (CA1, CA2, and CA6) and no-till areas, without soil tillage (CA3, CA4, and CA5). CA4, CA5, and CA6 were irrigated by a center pivot. In the CAs, grains were collected, except for CA5, which was a site with forage (brachiaria grass). In the RAs, grasses were collected. In each area, five subsamples were collected, with four points distributed radially around a central point, in order to form a composite sample, with three replicates, totaling 120 soil samples and 30 samples of plant tissue.

The soil samples were collected with a stainless-steel helical drill to avoid contamination. The subsamples were placed in polyethylene bags and homogenized. The collection site was previously cleaned, with the excess of vegetation in the surface layer, leaves, crop residues, and litter eventually being removed. The collection was divided into two periods. The first, for a preliminary assessment of the spatial distribution of As and the identification of anomalous points (hot spots). In this condition, in a large portion of the area of interest, soil samples from the 0–20 cm layer and remaining grains and plants in the area were collected and analyzed for total As. The second collection - a more detailed one - was performed to verify the vertical distribution of As in the soil profile and its possible origin. In this case, soil samples were collected at four different depths (0–5, 5–10, 10–20, and 20–40 cm), by opening mini trenches (40-cm deep) at three selected points in each area of interest. After preparation of the soil surface, five mini trenches were opened at each selected point, four of which were distributed radially around a central point previously defined according to the total As levels obtained in the tests of the previous step (Fig. 1S). Stainless steel spatulas were used to collect the samples to preserve the limits of each layer of interest. The composite samples were air dried, sieved through a 2-mm sieve, and stored for physical and chemical characterization.

In each area, samples of plant tissue were also collected. The collections were performed according to the same criteria defined for soil sampling, that is, five samples collected radially around a central point, forming a composite sample. Samples of grains from plants of recent harvest and samples of leaves of crops and grasses were collected, the latter especially in the areas of the legal and permanent reserve (native areas). After collection, the samples were transferred to previously identified paper bags and sent directly to the laboratory, where they were prepared, homogenized, dried, and ground for further analysis.

2.3. Physical and chemical characterization of soil

For chemical and granulometric analyzes, the protocols described by EMBRAPA (2017) were used. The granulometric analysis was performed using the densimeter method. The clay fraction was separated by sedimentation, the sand was sieved and the silt was calculated by difference. The sample pH was measured in a suspension at a soil-water ratio of 1: 2.5 and $CaCl_2$ at 0.01 mol L^{-1}. The extraction of exchangeable levels of calcium (Ca^{2+}), magnesium

(Mg^{2+}), and aluminum (Al^{3+}) was by KCl 1 mol L^{-1}, while for phosphorus (P), potassium (K^+), iron (Fe), and manganese (Mn) by Mehlich I (HCl 0.05 mol L^{-1} and H_2SO_4 0.0125 mol L^{-1}). The extracts were analyzed by inductively coupled plasma optical emission spectrometry - ICP OES (equipment brands Spectro model Ciros Vision and Agilent model 5800). The determination of soil organic carbon was based on the $K_2Cr_2O_7$ - H_2SO_4 oxidation method. Data were used to calculate the chemical index of alteration (CIA), according to Nesbitt and Young (1982): CIA = $[Al_2O_3 / (Al_2O_3 + Na_2O + CaO + K_2O)] \times 100$.

The extraction of total arsenic from soil samples was performed using the EPA 3051 A method (USEPA, 2007). A mass of 0.5 g of sample was digested in an acid solution in a Microwave Oven (CEM Model MARS 6) with a temperature of 175 ºC for 10 min. After digestion, the digested extract was quantitatively transferred to a 50 mL volumetric flask filled with reagent grade water and filtered. Then, it was determined by ICP OES (Agilent 5100) coupled with a hydride generator (CETAC HGX 200). The calibration curves were constructed using Certified Reference Material - Standards with ISO GUIDE 34, as well as all other analytical procedures that were performed by the requirements of ISO/IEC 17025. The recovery for As was 105.3 ± 3.8%.

Soluble arsenic was also extracted using a Mehlich I solution, as previously described. This extraction solution is used in laboratory routines to extract phosphorus, potassium, sodium, and micronutrients from the soil and is based on the solubilization of these elements by the pH effect, between 2 and 3, with the role of SO_4^{-2} and Cl^- being to restrict the process of reabsorption of the newly extracted nutrients. In addition to being able to be used to determine phytoavailable levels of As in soils, studies have shown the existence of a close correlation between the values obtained in the analysis of As extracted by the Mehlich I solution and the fraction absorbed in the gastric phase by humans, enabling the methodology to be used as a suitable alternative to estimate the bioaccessibility of the element, replacing complex *in vivo* and *in vitro* methods (Ono et al., 2012a, Ono et al., 2012b). Thus, considering that the accidental ingestion of soil is one of the main routes of exposure to arsenic, especially for children, soil samples were also evaluated by this method for considerations on aspects related to human-health risks. For these analyzes, the same procedures described for the extraction of nutrients P, K, and micronutrients mentioned above were used, differing as to the technique used to quantify the element, the latter being performed by Hydride Generation ICP OES.

2.4. Chemical characterization of plants

Plant tissue samples (leaves and grains) were prepared according to the protocol described by Malavolta et al. (1997). The leaf and grain samples were carefully washed in deionized water and left to dry at 65 °C in an oven with forced air circulation until constant weight. Subsequently, the material was ground in a Willey mill and stored in polyethylene bottles. Nitrogen analyzes were performed using the Kjeldahl digestion method (Bremner and Mulvaney, 1982). Determination of P, K, Ca, Mg, S, Cu, Fe, Mn, and Zn were performed from the nitric digestion of a mass 0.5 g of the sample in a digesting block, and then swelled to 50 mL. The extracts were analyzed by ICP OES (Spectro brand, Ciros Vision model).

The digestion of plant tissue samples for As determination were performed using nitric acid with a high degree of purity, according to USEPA 3051 A method (USEPA, 2007). A mass of 0.5 g of sample was previously digested in a CEM Microwave Oven (Model MARS 6) with a temperature of 175 ºC for 10 min. After digestion, the digested extract was transferred quantitatively to a 50 mL volumetric flask, swollen with reagent grade water, and then determined by ICP OES (Agilent 5100) coupled to a hydride generator (CETAC HGX 200).

The equipment's calibration curves were all constructed using Certified Reference Materials that meet the requirements of ISO GUIDE 34, as well as all other analytical procedures, which were performed by the requirements of ISO / IEC 17025: 2009. All tests are performed using QA/QC controls that include method blank, equipment blank, fortified standards, and standard samples. All analyzes were conducted in the Soil, Vegetable, and Environmental Analysis laboratories at the CAMPO Agricultural and Environmental Technology Center in Paracatu-MG.

2.5. Chemical fractionation of As

Chemical fractionation of As was performed only in CA3, CA4, RA2, and RA3, which presented the levels of As higher than the soil prevention values adopted in Brazil (> 15 mg kg^{-1}). The sequential extraction of As followed the methodology proposed by Wenzel et al. (2001). The methodology consists of adding 25 mL of the extractant to 1 g of soil (<150 μm) sequentially to extract the easily-exchangeable As (F1) and the specifically-sorbed As (F2) fractions. The F1 fraction was obtained with 0.05 mol L^{-1} $(NH_4)_2SO_4$ in 4 h of agitation (0.04 % m/v, 20 °C) and the F2 fraction was obtained with 0.05 mol L^{-1} $NH_4H_2PO_4$ in 16 h of agitation of the extractant with the residual soil (0.04 % m/v, 20 °C). Between steps, the tube containing the soil and extractant were centrifuged for 15 min at 1700 × g. All extractions were performed in duplicate and filtered through 0.45 µm cellulose acetate filter paper. Arsenic concentrations were determined via graphite-furnace atomic absorption spectrometry (GFAAS) (Perkin Elmer AAnalyst800).

2.6. Pollution indices

Soil pollution can be measured by assessing the enrichment factor (EF) and the geoaccumulation index (I_{geo}). These are geochemical parameters that use the background value of element's concentration in the calculation. For that, it is recommended to use the local reference values for better accuracy because the regions have high geological variability. For example, in Brazil, in Oxisols, the average concentration of As is 5.2 mg kg^{-1} (Campos et al., 2007), however, the levels of As in reference soils in the country can vary from 0.14 to 41.1 mg kg^{-1} (Menezes et al., 2020). The conservative element used was Fe due to its geochemical behavior similar to that of several potentially toxic elements (Souza Neto et al., 2020). With that, the EF equation is written as follows:

$$EF = (C_{As}/C_{Fe})/(B_{As}/B_{Fe}) \ (1)$$

where C_{As} is the concentration of As (mg kg^{-1}) in the cultivated area, C_{Fe} is the measured concentration of Fe (mg kg^{-1}) in the same sample, B_{As} is the concentration of As (mg kg^{-1}) in the reference area and B_{Fe} is the concentration of Fe (mg kg^{-1}) in the reference (native vegetation reserve). According to the classification of Lin et al. (2019), soils can have minimal enrichment (EF<2), moderate enrichment (2 <EF<5), significant enrichment (5 <EF<20), very high enrichment (20 <EF<40), and extremely high enrichment (EF>40).

To assess the level of contamination in soils, the geoaccumulation index (I_{geo}) was calculated using the equation below:

$$Igeo = \log 2(C_{As}/(1.5 \times B_{As})) \ (2)$$

where C_{As} is the measured concentration of As (mg kg^{-1}) in the cultivated area, B_{As} is the concentration of As (mg kg^{-1}) in the reference area and 1.5 is a constant used to correct possible variations in the background values caused by small anthropic actions (Souza et al., 2017). According to Müller (1986), samples can be classified into non-contaminated soil ($I_{geo}<0$), uncontaminated to moderately contaminated soil ($0 <I_{geo}<1$), moderately contaminated soil ($1 <I_{geo}<2$), moderately to very contaminated ($2 <I_{geo}<3$), highly contaminated soil ($3 <I_{geo}<4$), extremely contaminated soil ($4 <I_{geo}<5$), and extremely contaminated soil ($I_{geo}>5$).

2.7. Assessment of environmental and human-health risks

To assess the environmental risk of As in agricultural soils, the potential ecological risk index (PERI) was calculated (Hakanson, 1980), using the equation below:

$$PERI = T_{As} \times (C_{As} / B_{As}) \quad (3)$$

where T_{As} is the toxic response factor for the potentially toxic element, which for As is equal to 10 (Hakanson, 1980), CAs is the measured concentration of As (mg kg^{-1}) in the cultivated area, and B_{As} is the concentration of As (mg kg^{-1}) in the reference area. According to Hakanson (1980), PERI values can be classified as: low ecological risk ($PERI<40$), moderate ecological risk ($40 <PERI<80$), considerable ecological risk ($80 <PERI<160$), high ecological risk ($160 <PERI<320$) and very high ecological risk ($PERI>320$).

To assess the risk to human health, the potential non-carcinogenic (HI) and carcinogenic (RISK) risk were calculated (USEPA, 2001). First, the average daily doses (ADD) of the three main human exposure routes for As were estimated - ingestion (ADD ing), inhalation (ADD inh), and dermal contact (ADD der) (USEPA, 2001). Detailed version can be found in the Supplementary material.

2.8. Statistical analysis

Descriptive statistics were calculated for concentrations of total As and P ($P < 0.05$). The map was made using the ArcGIS program. Pearson (r) correlation was carried out between the chemical parameters evaluated among themselves and with the texture of the soils of the studied areas, in the latter case, only at a depth of 0–20 cm. For a correct proportion, a weighted average was made, assigning weight 25% to the values found for depth 0–5 cm and for depth 5–10 cm and weight 50% for soil values at depth 10–20 cm. Boxplot graphics were made in the R program (version 3.4.3) and those of multiple linear distributions in SigmaPlot (version 11). All statistical analyzes were performed using R (version 3.4.3) (R Core Team, 2017).

3. Results and discussion

3.1. Characterization of irrigated agricultural soils and reference areas

Soil pH varied between irrigated agricultural areas and reference (natural vegetation reserve) areas (Table 1). In cultivated soils, the pH was more alkaline in the first layers and more acidic in the last, possibly due to the correction of soil acidity and high base saturation. In agricultural soils, the pH values varied from 5.2 to 6.5 in the 0–5 and 5–10 cm layers and from 3.8 to 5.3 in the 10–20 and 20–40 cm layers. In general, in the reference soils, the pH was more acidic and was constant throughout the profile, with values varying from 4 to 5. The parent material of Paracatu is mainly composed of gold sulfide ores and high levels of arsenopyrite (FeAsS) (Bidone et al., 2018). Usually, tropical soils are known for their acidity, due to the high leaching of exchangeable bases (Lopes and Guilherme, 2016).

In cultivated soils and reference areas, soil organic carbon (SOC) was higher in the first layers, decreasing with soil depth (Table 1). In cultivated areas, the levels were higher in the 0–5 cm layer, varying from 1.33% to 2.20%. CA5 had the highest SOC levels among the agricultural areas, while CA2 had the lowest. This is mainly due to the management system of the areas, *i.e.*, CA5 is a no-tillage area, whereas CA2 is a conventional cultivation area. In the deeper layers, the values ranged from 0.33% to 1.70%. In reference areas, the first two layers (0–5 and 5–10 cm) presented the highest values, between 1.50% and 2.33%. RA3 had the lowest levels. In tropical soils, organic matter decomposes faster due to the hot and humid climate of the tropics (Gmach et al., 2018).

The cation exchange capacity (CEC) also showed the highest values in the first layers, reducing with soil depth. The highest values were in reference areas compared with agricultural areas. Since the cultivated soils were possibly amended with lime, the contents of exchangeable

Al in these soils were below the detection limit in the first layers. Agricultural areas presented smaller CEC values when compared with reference areas, which might be related to the higher SOC values found in native areas (Souza et al., 2015).

High rates of K and P, especially in irrigated agricultural areas, are applied to the soil surface using fertilization. Therefore, in these soils, decreasing concentrations of K and P occur in the soil layers (Table 1). In forests, high levels of K are also found on the soil surface, because vegetation cover contributes for reducing K losses (Chen et al., 2017). In tropical soils, P is strongly adsorbed onto Fe and Al oxides in the clay fraction, being an element of low mobility in the soil profile. In the Brazilian Cerrado, soils have naturally low levels of phosphorus, with an average value of < 2 mg kg^{-1} of P (Lopes and Guilherme, 2016).

All soils studied are clayey, due to the predominance of Red Oxisols with high clay contents (Table 1 and Fig. 2S). In general, agricultural soils have higher clay contents than reference soils, except for RA3, which presented very high clay contents (between 67.7% and 70.3%). In cultivated soils, all clay contents were above 60%, with a maximum value in CA6 of 75%. Clay soils have a higher P adsorption capacity compared with sandy soils, due to their greater specific surface area (Lopes and Guilherme, 2016). Among agricultural soils, CA3 was the one with the highest sand content, greater than 24%. In RA2 and RA4, the silt contents are very similar to those of clay.

Table 1 Descriptive statistical analysis (means followed by standard deviation, n = 3) of physical and chemical attributes of soil samples stratified at four depths (0–5, 5–10, 10–20, and 20–40 cm) collected in six cultivated areas (CA1, CA2, CA3, CA4, CA5, and CA6) and four reference areas (RA1, RA2, RA3, and RA4) in Paracatu-MG.

Area	Depth	pH		SOC	P	K	Ca	Mg	Al^{3+}	H+Al	CEC^{a}	V^{b}	m^{c}	CIA
	(cm)	H_2O	$CaCl_2$	%	-- mg kg^{-1} --		----------- cmolc dm^{-3} -----------					----- % -----		
CA1	0-5	7.15^{d} ± 0.24^{e}	6.51 ± 0.19	1.40 ± 0.10	7.38 ± 4.88	235.56 ± 102.13	7.00 ± 0.48	1.43 ± 0.34	<0.1	0.91 ± 0.00	9.47 ± 0.29	95.33 ± 4.62	0.00 ± 0.00	-
	5-10	6.19 ± 0.36	5.72 ± 0.41	0.87 ± 0.15	9.35 ± 11.70	164.08 ± 107.27	3.58 ± 0.60	1.29 ± 0.51	<0.1	1.95 ± 0.82	7.27 ± 0.38	72.33 ± 11.72	0.00 ± 0.00	-
	10-20	5.20 ± 0.14	4.71 ± 0.26	0.63 ± 0.06	7.32 ± 4.91	104.36 ± 54.15	1.70 ± 0.65	0.73 ± 0.53	0.36 ± 0.25	2.97 ± 0.76	5.70 ± 1.21	46.67 ± 12.01	9.33 ± 10.07	-
	20-40	5.07 ± 0.27	4.43 ± 0.29	0.33 ± 0.25	<0.3	64.45 ± 13.62	0.82 ± 0.15	0.40 ± 0.16	0.65 ± 0.49	3.08 ± 1.04	4.47 ± 1.31	31.67 ± 4.04	28.33 ± 14.19	-
CA2	0-5	6.78 ± 0.53	6.42 ± 0.60	1.33 ± 0.06	8.61 ± 3.50	130.42 ± 52.52	6.44 ± 0.19	1.17 ± 0.08	<0.1	1.73 ± 0.00	8.63 ± 0.85	92.67 ± 9.24	0.00 ± 0.00	-
	5-10	6.19 ± 0.15	5.67 ± 0.20	0.93 ± 0.15	26.54 ± 29.26	124.09 ± 65.22	4.35 ± 1.35	1.22 ± 0.42	<0.1	2.12 ± 1.04	8.00 ± 1.56	72.67 ± 14.74	0.00 ± 0.00	-
	10-20	5.53 ± 0.54	5.07 ± 0.55	0.67 ± 0.12	11.93 ± 6.63	75.36 ± 43.75	2.21 ± 1.11	0.79 ± 0.44	0.27 ± 0.00	2.84 ± 0.92	6.03 ± 1.21	51.67 ± 18.34	4.33 ± 7.51	-
	20-40	5.08 ± 0.20	4.62 ± 0.22	0.33 ± 0.06	0.13 ± 0.00	35.17 ± 13.05	1.03 ± 0.26	0.44 ± 0.15	0.25 ± 0.08	2.72 ± 0.66	4.30 ± 0.96	36.67 ± 5.51	9.67 ± 10.02	-
CA3	0-5	6.38 ± 0.17	5.95 ± 0.16	1.37 ± 0.15	43.21 ± 13.27	233.08 ± 34.68	3.98 ± 0.83	1.75 ± 0.20	<0.1	1.71 ± 0.76	7.97 ± 0.65	79.00 ± 9.64	0.00 ± 0,00	92.2 ± 5.31
	5-10	6.06 ± 0.27	5.60 ± 0.36	0.93 ± 0.25	42.49 ± 7.14	193.98 ± 29.53	3.05 ± 0.54	1.11 ± 0.04	<0.1	2.29 ± 0.64	6.93 ± 0.40	67.00 ± 8.66	0.00 ± 0,00	95.4 ± 0.94
	10-20	5.67 ± 0.30	5.29 ± 0.35	0.80 ± 0.10	14.36 ± 3.64	143.97 ± 31.13	1.92 ± 0.26	0.68 ± 0.06	<0.1	2.50 ± 0.83	5.47 ± 0.55	55.00 ± 10.54	0.00 ± 0,00	93.7 ± 4.58
	20-40	5.15 ± 0.46	4.72 ± 0.46	0.37 ± 0.12	0.15 ± 0.00	88.88 ± 12.98	1.01 ± 0.21	0.44 ± 0.08	<0.1	2.00 ± 0.44	3.67 ± 0.15	46.00 ± 9.85	0.00 ± 0,00	96.4 ± 0.68
CA4	0-5	6.15 ± 0.09	5.77 ± 0.08	1.80 ± 0.87	38.45 ± 8.08	240.16 ± 35.91	4.27 ± 0.48	2.29 ± 0.20	<0.1	1.54 ± 0.21	8.73 ± 0.68	82.33 ± 2.89	0.00 ± 0,00	87.4 ± 0.46
	5-10	5.88 ± 0.12	5.49 ± 0.16	1.57 ± 0.12	43.78 ± 7.14	191.15 ± 37.08	3.48 ± 0.32	1.55 ± 0.08	<0.1	2.04 ± 0.63	7.60 ± 0.44	73.00 ± 6.93	0.00 ± 0,00	86.9 ± 1.20

	10-20	5.67 ± 0.17	5.22 ± 0.11	0.67 ± 0.35	21.69 ± 11.13	146.71 ± 36.58	2.68 ± 0.29	1.27 ± 0.09	<0.1	2.12 ± 0.33	6.43 ± 0.80	67.33 ± 1.15	0.00 ± 0,00	87.6 ± 0.50
	20-40	5.58 ± 0.27	5.26 ± 0.27	0.37 ± 0.12	2.00 ± 0.23	78.95 ± 18.57	1.44 ± 0.24	0.83 ± 0.09	<0.1	1.71 ± 0.25	4.20 ± 0.53	59.67 ± 3.51	0.00 ± 0,00	88.0 ± 2.84
CA5	0-5	5.73 ± 0.16	5.13 ± 0.33	2.20 ± 0.50	18.55 ± 6.17	300.17 ± 33.96	5.57 ± 0.80	1.99 ± 0.47	<0.1	3.25 ± 0.61	11.57 ± 0.67	71.67 ± 6.43	0.00 ± 0.00	-
	5-10	5.66 ± 0.35	5.15 ± 0.43	2.03 ± 0.78	18.25 ± 9.76	276.10 ± 103.31	4.95 ± 1.3	1.65 ± 0.27	0.29 ± 0.00	3.63 ± 1.45	10.93 ± 1.46	67.00 ± 11.27	1.67 ± 2.89	-
	10-20	4.98 ± 0.51	4.51 ± 0.49	1.70 ± 0.46	3.75 ± 3.01	129.79 ± 31.17	3.06 ± 1.38	0.95 ± 0.40	0.59 ± 0.62	4.70 ± 0.95	9.07 ± 1.17	47.00 ± 16.82	11.67 ± 17.67	-
	20-40	4.84 ± 0.49	4.26 ± 0.45	0.90 ± 0.10	<0.3	64.19 ± 40.28	1.89 ± 0.71	0.57 ± 0.19	0.69 ± 0.75	4.10 ± 0.94	6.73 ± 0.49	39.33 ± 15.01	22.00 ± 24.58	-
CA6	0-5	6.16 ± 0.14	5.74 ± 0.27	1.60 ± 0.10	8.51 ± 14.15	419.83 ± 9.77	4.50 ± 0.24	2.34 ± 0.12	<0.1	1.93 ± 0.38	9.87 ± 0.68	80.67 ± 2.89	0.00 ± 0.00	-
	5-10	5.73 ± 0.28	5.28 ± 0.31	1.27 ± 0.12	11.91 ± 5.46	297.06 ± 40.28	4.03 ± 0.88	2.22 ± 0.49	0.12 ± 0.00	2.72 ± 0.46	9.73 ± 0.91	71.33 ± 7.37	0.67 ± 1.15	-
	10-20	4.88 ± 0.15	4.39 ± 0.12	0.80 ± 0.17	5.72 ± 7.31	174.88 ± 12.15	1.79 ± 0.65	1.15 ± 0.40	0.88 ± 0.59	4.10 ± 0.21	7.50 ± 0.87	44.67 ± 8.74	21.67 ± 16.80	-
	20-40	4.54 ± 0.24	3.84 ± 0.11	0.57 ± 0.12	<0.3	114.38 ± 38.48	0.75 ± 0.09	0.61 ± 0.09	2.20 ± 0.14	4.73 ± 0.10	6.37 ± 0.12	26.33 ± 1.15	57.33 ± 0.58	-
RA1	0-5	5.53 ± 0.34	4.97 ± 0.35	2.33 ± 0.59	1.62 ± 3.38	311.63 ± 65.09	3.13 ± 1.86	1.91 ± 0.95	1.22 ± 0.00	6.02 ± 0.29	11.87 ± 3.18	46.33 ± 15.04	11.33 ± 19.63	-
	5-10	5.33 ± 0.17	4.56 ± 0.18	1.60 ± 0.44	1.10 ± 0.90	269.20 ± 76.33	3.39 ± 1.67	2.01 ± 0.57	0.28 ± 0.16	6.47 ± 0.62	12.57 ± 2.65	47.67 ± 5.51	4.67 ± 3.21	-
	10-20	5.13 ± 0.03	4.29 ± 0.20	1.30 ± 0.56	0.94 ± 0.51	247.77 ± 79.34	2.38 ± 1.47	1.53 ± 0.59	0.72 ± 0.36	5.80 ± 1.57	10.37 ± 3.24	43.33 ± 9.87	16.00 ± 11.53	-
	20-40	4.97 ± 0.13	4.24 ± 0.09	0.80 ± 0.35	<0.3	162.37 ± 61.51	1.43 ± 0.80	1.02 ± 0.34	1.15 ± 0.18	6.38 ± 2.19	9.23 ± 3.25	30.67 ± 1.53	30.00 ± 9.54	-
RA2	0-5	4.84 ± 0.81	4.43 ± 0.78	1.93 ± 0.15	1.05 ± 0.21	102.39 ± 28.12	1.93 ± 1.29	1.18 ± 0.68	0.44 ± 0.00	6.52 ± 3.67	9.90 ± 1.83	37.00 ± 25.87	4.33 ± 7.51	80.6 ± 2.56
	5-10	4.89 ± 0.74	4.33 ± 0.82	1.50 ± 0.17	<0.3	63.05 ± 22.30	1.12 ± 1.07	0.63 ± 0.52	1.52 ± 0.00	6.63 ± 3.74	8.57 ± 2.19	27.33 ± 28.45	18.00 ± 31.18	78.2 ± 3.53
	10-20	4.66 ± 0.58	4.04 ± 0.57	0.87 ± 0.25	<0.3	45.45 ± 21.77	0.75 ± 0.93	0.31 ± 0.35	<0.1	6.35 ± 3.22	7.57 ± 1.97	20.33 ± 25.70	0.00 ± 0.00	78.2 ± 4.52

	20-40	4.49 ± 0.49	4.05 ± 0.38	0.63 ± 0.12	<0.3	31.22 ± 13.84	0.62 ± 0.85	0.42 ± 0.00	<0.1	5.83 ± 2.55	6.70 ± 1.56	16.67 ± 21,08	0.00 ± 0.00	82.0 ± 0.30
RA3	0-5	5.09 ± 0.24	4.50 ± 0.34	1.20 ± 0.35	1.60 ± 0.34	188.96 ± 89.75	1.68 ± 0.42	1.54 ± 0.38	0.32 ± 0.30	4.87 ± 1.30	8.60 ± 0.75	43.67 ± 10.69	6.00 ± 7.94	85.2 ± 1.78
	5-10	4.83 ± 0.29	4.37 ± 0.34	0.93 ± 0.21	1.48 ± 0.28	116.11 ± 48.87	1.06 ± 0.69	0.92 ± 0.43	0.57 ± 0.38	5.14 ± 0.91	7.40 ± 0.98	30.33 ± 12.06	23.00 ± 17.06	84.2 ± 2.92
	10-20	4.72 ± 0.37	4.10 ± 0.23	0.57 ± 0.06	1.14 ± 0.07	69.99 ± 38.95	0.74 ± 0.52	0.58 ± 0.29	0.94 ± 0.39	5.58 ± 0.34	7.07 ± 0.45	20.67 ± 9.61	41.00 ± 22.27	87.0 ± 4.74
	20-40	4.60 ± 0.33	4.01 ± 0.19	0.37 ± 0.15	0.98 ± 0.10	47.43 ± 15.99	0.50 ± 0.44	0.36 ± 0.19	0.77 ± 0.37	4.59 ± 0.62	5.57 ± 0.06	17.67 ± 10.69	45.67 ± 22.48	85.1 ± 3.67
RA4	0-5	5.30 ± 0.30	4.74 ± 0.57	2.13 ± 0.21	1.23 ± 5.39	210.81 ± 76.56	3.91 ± 1.29	1.69 ± 0.40	0.80 ± 0.00	4.73 ± 1.70	10.83 ± 0.25	56.33 ± 16.07	5.33 ± 9.24	-
	5-10	5.09 ± 0.36	4.42 ± 0.46	1.70 ± 0.20	0.44 ± 0.49	202.15 ± 91.91	2.86 ± 0.77	1.44 ± 0.43	0.58 ± 0.32	5.06 ± 1.50	9.87 ± 0.91	49.00 ± 13.00	7.67 ± 7.51	-
	10-20	5.04 ± 0.51	4.14 ± 0.42	1.30 ± 0.17	<0.3	152.75 ± 73.49	2.25 ± 0.44	1.12 ± 0.27	1.18 ± 0.40	4.90 ± 1.01	8.70 ± 0.26	43.33 ± 10.41	17.00 ± 15.72	-
	20-40	4.98 ± 0.33	4.21 ± 0.21	0.90 ± 0.26	<0.3	105.76 ± 82.08	1.93 ± 0.17	0.82 ± 0.26	0.93 ± 0.67	4.46 ± 0.99	7.53 ± 0.42	40.67 ± 10.60	23.33 ± 16.04	-

Where: CA1 = Cultivated Area 1; CA2 = Cultivated Area 2, CA3 = Cultivated Area 3, CA4 = Cultivated Area 4, CA5 = Cultivated Area 5, and CA6 = Cultivated Area 6, RA1 = Reference Area 1, RA2 = Reference Area 2, RA3 = Reference Area 3, and RA4 = Reference Area 4.

a Effective cation exchange capacity.

b Base saturation.

c Aluminum saturation.

d Mean.

e Standard deviation.

3.2. Total As and available P concentration

The total As levels in all agricultural areas irrigated with waters from the Córrego Rico basin and in soils of the reference (natural reserve) areas did not differ between soil layers (Table 2S). This is probably associated with the parent material of the region, rich in arsenopyrite, which under oxidized conditions released As homogeneously in the soil profile (Ciminelli et al., 2018, Veloso et al., 2019). Abnormally high concentrations of As, with values ranging from 240 to 380 mg kg^{-1} (this last value refers to a replicate of RA2), were found in the soils of one reference area (RA2), which is 30–48 times greater than the reference values of As set for the State of Minas Gerais (Table 2S; COPAM, 2011). Paracatu soils are mainly composed of gold sulfides, with high As contents that can vary from 32 to 2980 mg kg^{-1} (Ono et al., 2012b). According to Ciminelli et al. (2018), in Paracatu, As is retained preferentially by inner-sphere complexation/co-precipitation with iron (hydr)oxides nanoparticles. This reinforces that, under the abovementioned circumstances, even with high concentrations in the soil, arsenic poses a low risk to the environment and to human health, since it is very stable in the soil.

Soil-As levels varied significantly among the cultivated areas. The total As concentrations were higher in CA3 (25.67–28.33 mg kg^{-1}) at all depths, followed by CA4 (17.33–18.67 mg kg^{-1}) and CA2 (9.03–14.33 mg kg^{-1}) (Table 2S and Fig. 2A). Besides, As did not differ between areas CA1 (5.9–7.67 mg kg^{-1}) and CA6 (2.93–4.50 mg kg^{-1}) (Table 2S). These low concentrations of As in CA1 and CA6 are within the range of values reported for native Brazilian Oxisols by Campos et al. (2007).

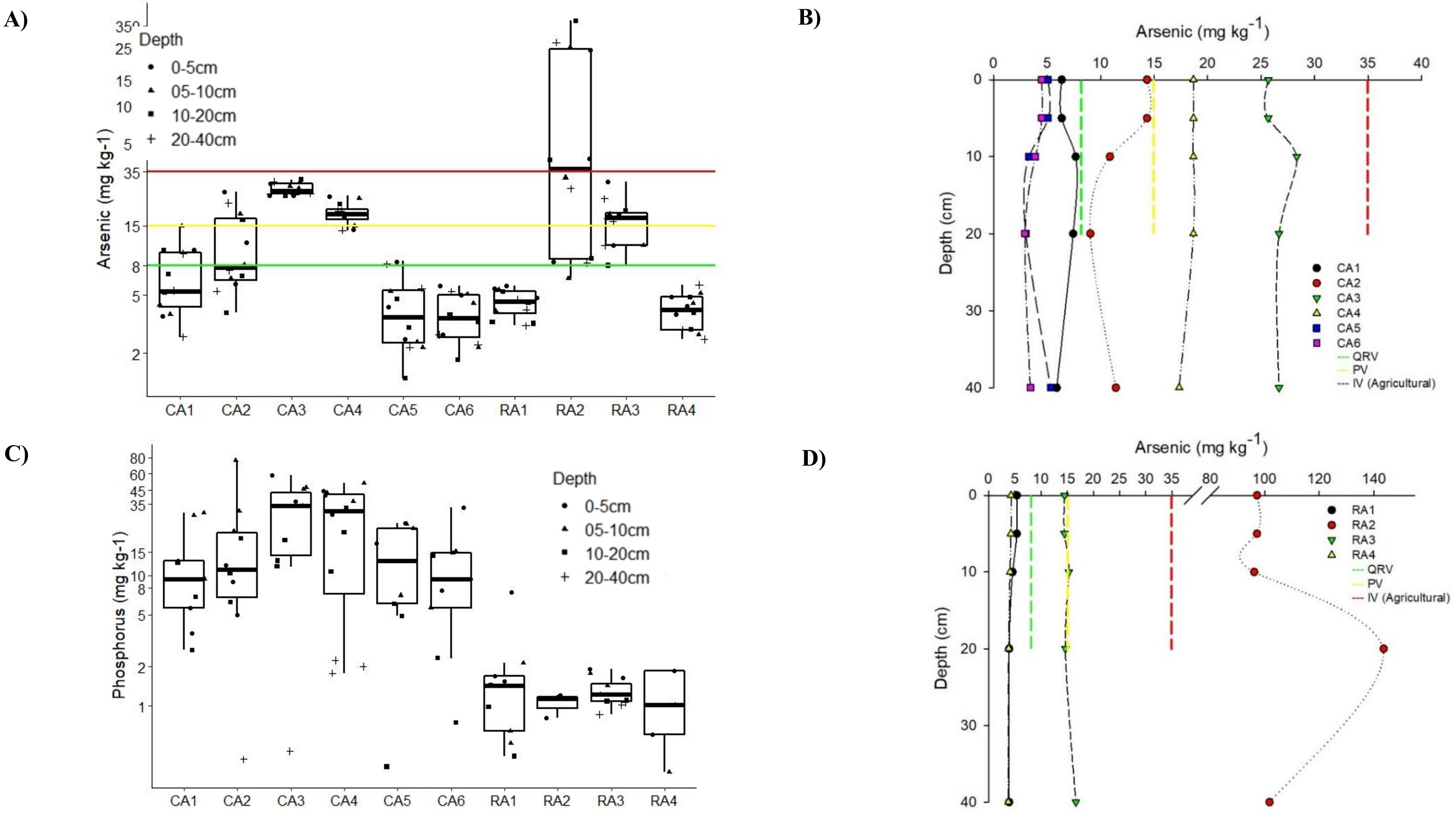


Figure 2 Box-Plots of total arsenic **(A)** and phosphorus **(C)** data in four soil depths (0-5, 5-10, 10-20, and 20-40 cm deep) collected in the ten areas, Paracatu-MG. **B)** Behavior in the soil profile of the total arsenic content in depth in the cultivated areas studied; **D)** Behavior in the soil profile of the total arsenic content in depth in the nature reserves studied in Paracatu-MG. Lines in green color - QRV, yellow for prevention (PV) and red for investigation (IV) agricultural.

In all cultivated areas, it is noteworthy that the total As contents were lower than the investigation values (VI) proposed for agricultural areas in Brazil, which is 35 mg kg^{-1}, and only CA3 and CA4 presented values above the prevention value (VP) for As, *i.e.*, 15 mg kg^{-1} (COPAM, 2011) (Fig. 2B). This confirms that cultivated areas do not present a potential risk to human health, yet in CA3 and CA4, the current Brazilian legislation recommends environmental monitoring. Ng et al. (2019) studied different As exposure pathways in Paracatu and observed that human exposure to soil and particulate matter with high As contents poses a relatively lower risk than ingestion of contaminated food. However, the levels of As available in the soil and the harvested products were below the detection limit. Thus, we suggest periodic monitoring of these areas, due to the lack of evidence of unacceptable risks to human health and the environment derived from the use of water resources in the Córrego Rico for irrigation purposes.

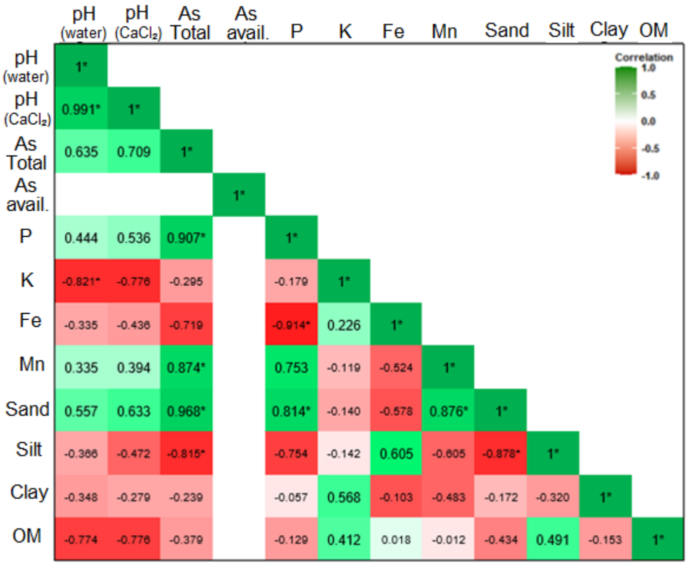
The levels of P in all cultivated areas, at a depth of 20–40 cm, were below the detection limit or lower than the concentrations in the other layers (Table 2S and Fig. 2C). CA3, CA4, and CA5 showed decreasing P concentrations in the layers, while for CA1 and CA6 there was no difference in P concentration in the layers within the initial 20 cm of soil depth (Table 2S). For CA2, the depth of 5–10 cm showed a higher concentration of P. Considering soil management, in areas of conventional cultivation (conventional tillage), the concentrations of P were higher in the 0–20 cm layers (CA1, CA2, and CA6), whereas in no-till areas (CA3, CA4, and CA5), high concentrations of P were restricted to the superficial layers (0–10 cm) (Table 2S).

Unlike As, for P there is a clear heterogeneity in the distribution of this element in the different soil layers, and the depths of 0–5 cm and 5–10 cm presented the samples with the highest levels of available P, whereas in the layer 20–40 cm of soil, when detectable, the levels of available P were much lower than those previously mentioned. In Brazil, several studies have also found high P adsorption capacity in soils with high clay contents, especially in the Brazilian Cerrado (Lopes and Guilherme, 2016).

In the reference areas (RAs), the levels of P were significantly lower than those observed in the cultivated areas (CAs), which was expected, since these reserves of native vegetation do not receive any intentional phosphate fertilization. In these RAs, P levels are typically similar to those found in native soils of the Cerrado region (Lopes and Guilherme, 2016), with the highest value found being equal to 1.62 mg kg^{-1} (Table 2S). In RA2, it was only possible to determine the concentration of P at a depth of 0–5 cm of soil, while in RA4 it was not possible to determine the levels of available P at a depth below 10 cm, *i.e.*, the values were below the detection limit (Table 2S).

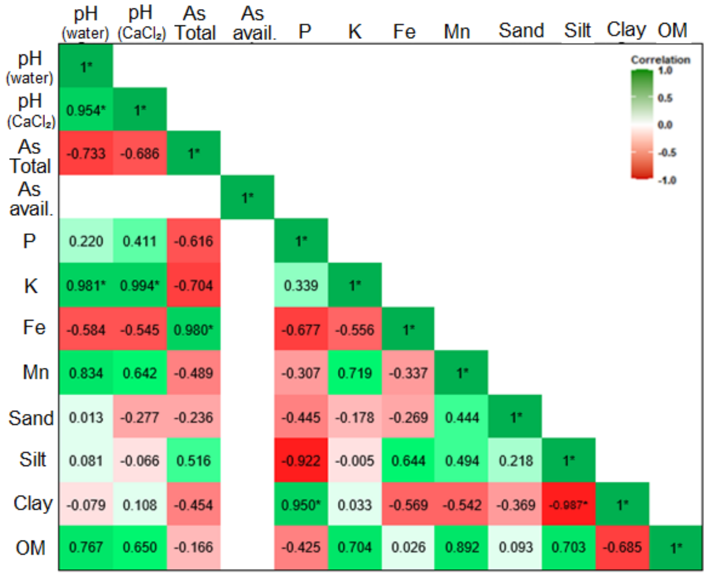
The total levels of As and P showed a significant positive correlation of 0.907 (Fig. 3A). This proves the similarity of As with P, in areas with fertilization management, since they share the same chemical properties. Thus, if As was added to the medium by irrigation, its effect would be analogous to that of P and its available concentrations would be higher in the more superficial layers of the soil due to the low mobility in the profile of the soil, differently from what was observed.

A)



	pH (water)	pH ($CaCl_2$)	As Total	As avail.	P	K	Fe	Mn	Sand	Silt	Clay	OM
pH (water)	1*											
pH ($CaCl_2$)	0.991*	1*										
As Total	0.635	0.709	1*									
As avail.				1*								
P	0.444	0.536	0.907*		1*							
K	-0.821*	-0.776	-0.295		-0.179	1*						
Fe	-0.335	-0.436	-0.719		-0.914*	0.226	1*					
Mn	0.335	0.394	0.874*		0.753	-0.119	-0.524	1*				
Sand	0.557	0.633	0.968*		0.814*	-0.140	-0.578	0.876*	1*			
Silt	-0.366	-0.472	-0.815*		-0.754	-0.142	0.605	-0.605	-0.878*	1*		
Clay	-0.348	-0.279	-0.239		-0.057	0.568	-0.103	-0.483	-0.172	-0.320	1*	
OM	-0.774	-0.776	-0.379		-0.129	0.412	0.018	-0.012	-0.434	0.491	-0.153	1*

B)



	pH (water)	pH ($CaCl_2$)	As Total	As avail.	P	K	Fe	Mn	Sand	Silt	Clay	OM
pH (water)	1*											
pH ($CaCl_2$)	0.954*	1*										
As Total	-0.733	-0.686	1*									
As avail.				1*								
P	0.220	0.411	-0.616		1*							
K	0.981*	0.994*	-0.704		0.339	1*						
Fe	-0.584	-0.545	0.980*		-0.677	-0.556	1*					
Mn	0.834	0.642	-0.489		-0.307	0.719	-0.337	1*				
Sand	0.013	-0.277	-0.236		-0.445	-0.178	-0.269	0.444	1*			
Silt	0.081	-0.066	0.516		-0.922	-0.005	0.644	0.494	0.218	1*		
Clay	-0.079	0.108	-0.454		0.950*	0.033	-0.569	-0.542	-0.369	-0.987*	1*	
OM	0.767	0.650	-0.166		-0.425	0.704	0.026	0.892	0.093	0.703	-0.685	1*

Figure 3 A) Pearson's correlation of soil samples (0-20 cm) collected in the six cultivated areas, Paracatu-MG, **B)** Pearson's correlation of soil samples (0-20 cm) collected in the four nature reserves, Paracatu-MG, The weighted averages of the main chemical analyzes of the soil samples stratified at three depths (0-5 cm - weight 25%; 5-10 cm - weight 25% and 10-20 cm - weight 50%) were correlated with each other and with the texture of the soil

The total levels of As were also positively correlated with Mn (0.874). This is probably related to the fact that arsenic is also adsorbed by Mn oxides found in many oxidic soils, which explains the correlation between the elements (Silva Júnior et al., 2019). The significant negative correlation between total contents of As and silt (−0.815) and the positive correlation with sand (0.968) suggests that As is linked to coarser fractions in these cultivated soils, possibly associated with stable Mn minerals, which also showed a positive correlation with sand.

In the reference areas, the average levels of total As varied between 3.77 and 143.63 mg kg^{-1} (Table 2S). The average values of total As in area RA2 (96.17–143.63 mg kg^{-1}) were higher when compared with other reserves in all soil depths, followed by RA3 (14.5–16.67 mg kg^{-1}). RA1 (3.93–5.40 mg kg^{-1}) and RA4 (3.77–4.27 mg kg^{-1}) did not differ between them. RA2 showed values above the VI (35 mg kg^{-1}) for As (Fig. 2D). However, when the levels of As available in the soil were evaluated, all levels were below the detection limit. This reinforces that, although in some RAs very high values of As were found in the soil, this element is present in its unavailable form, possibly associated with iron oxides (Fe) (Ciminelli et al., 2018). These results are also supported by studies carried out by Bidone et al. (2018) who found, in the Paracatu River, a reduction of As in the dissolved fraction of the water column from 110 to 31 µg L^{-1}, when Fe increased in the sediment (3–9%), suggesting greater retention by Fe oxides.

In reference areas, concerning total As, there was a significant positive correlation only with Fe (0.980), probably due to the high selectivity of Fe oxides for As (Ciminelli et al., 2018). Differently from what was found in CAs, the correlation between total As and P was negative (−0.616), due to the low levels of P found in native Cerrado soils (Lopes and Guilherme, 2016), *i.e.*, natural values around 1 mg kg^{-1} in the superficial layer of soil (Fig. 3B).

The reserve soils are predominantly clayey, so the P present had a significant positive correlation with clay (0.950). In tropical soils, the interaction of As and P with Fe oxides and clay surfaces influences the environmental fate of these elements, as they are generally adsorbed to the soil by a formation of inner-sphere complexes, *i.e.*, via specific adsorption (Wang et al., 2018). Ciminelli et al. (2018) observed by transmission electron microscopy that, in Paracatu, As is mainly associated with crystalline Fe oxides and hydroxides nanoparticles.

3.3. As concentrations in plant tissues

The results of the chemical characterization of plant tissues are shown in table 3S. All plant tissues (grains, forages, and grasses) collected in the evaluated areas (CAs and RAs) presented As levels below the detection limit (<0.05 mg kg^{-1}). Such results were expected since it was not possible to quantify available As in the soil, because its concentrations were also below the detection limit. Finally, the low As contents in leaf tissues presumes that the grains are safe with respect to this element, since in the literature, As has low accumulation in grains compared with leaves and stems (Bundschuh et al., 2020). This reinforces the food safety aspect for potential consumer markets of these agricultural products and ensures also that grain producers in the region of Paracatu, who used the water from Córrego Rico for irrigation of these soils, are not going to harvest unsafe products. In this context, it is noteworthy that studies by Monteiro et al. (2020), in fourteen rice varieties in six microclimate regions in southern Brazil, revealed that all varieties in all cities had safe levels of As in the grains, *i.e.*, all samples contained As at levels that agreed with the limits of the i-As Commission of the Codex

Alimentarius (<350 µg kg^{-1}) for husked rice, a limit that is also adopted by Brazilian regulations (CODEX, 2016). Such results reinforce that As in grains produced in agricultural areas of Brazil is unlikely to represent an eventual risk to human health, a fact that is also supported by results of a survey made by Guilherme et al. (2019) with additional agricultural products harvested in Brazil.

3.4. Oral bioaccessibility of As by Mehlich I

In all evaluated areas (CAs and RAs) and their depths, the estimated bioaccessible levels of As using the Mehlich I extractant as a surrogate for the gastric phase (Ono et al., 2012a, Ono et al., 2012b), were below the detection limit (Table 2S). According to Juhasz et al. (2014), it is in the gastric phase (pH 1.5) that the highest bioaccessible As contents occur, due to the greater solubilization of As linked to Fe oxides in these extremely acidic pH conditions. Therefore, there is no risk to human health through the ingestion of soil and edible agricultural products. Ciminelli et al. (2018) evaluated the oral bioaccessibility of As in Paracatu and also found a low risk to human health due to the ingestion of soils, with the average bioaccessibility varying between 0.44 mg kg^{-1} (2.7%) and 7.53 mg kg^{-1} (1.4%). Thus, although some abnormal high levels of total As might occur in selected soils, it is necessary to study the available fraction of As, as this is what can effectively cause damage and affect food safety in agricultural areas at risk. A similar behavior was reported by Ono et al. (2012b) in soils from mining areas in the Paracatu region. Further studies using synchrotron radiation developed by these authors were able to prove that although very high values of As were detected in selected soils of mining areas, only a very small fraction (<4.4%) was bioaccessible, due to the formation of low crystalline iron arsenates (Ono et al., 2016).

3.5. Chemical fractionation of As

In order to compare the four soil profiles (CA3, CA4, RA2, and RA3) having the highest contents of As (*i.e.*, soils with As levels higher than the prevention value set by the Brazilian legislation - 15 mg kg^{-1}), at different depths, the weighted average was adopted with 0–5 cm -

weight 12.5%; 5–10 cm - weight 12.5%, 10–20 cm - weight 25%, and 20–40 cm - weight 50%. In the studied areas, the soils showed low percentages of As in the more mobile fraction (F1), with and average As adsorbed non-specifically varying between 0.38% and 10.11% of the pseudo total As (Fig. 4). These low percentage values represent 0.09 (CA3), 1.70 (CA4), 3.14 (RA2), and 0.68 mg of As kg^{-1} (RA3) (Table 4S), which are As contents smaller than those set as background values (*i.e.*, quality reference value - QRV) for soils in the State of Minas Gerais (8 mg kg^{-1} for total As). This fraction is the most available one for absorption by plants, being considered the most toxic to the environment (Mensah et al., 2020). Irrespectively of that, we observed that the plants studied did not translocate As to the shoots, proving that this fraction is not considered an environmental risk for agricultural crops cultivated in the region (Table 3S).

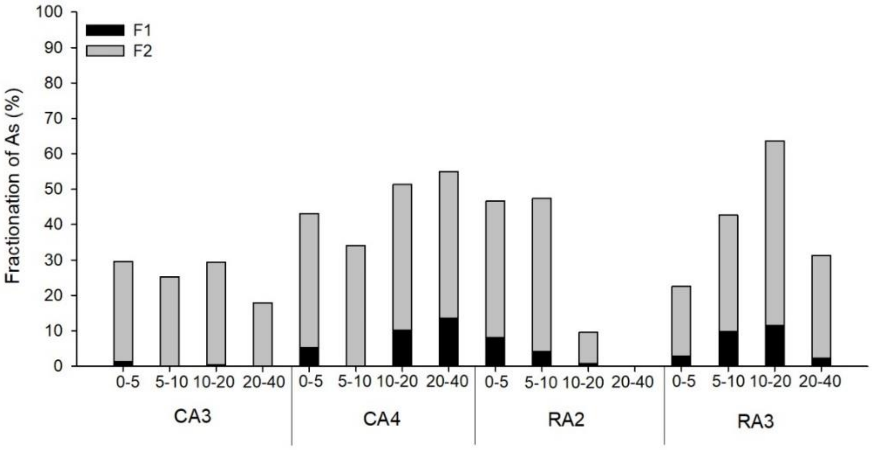


Figure 4 Chemical fractionation of the easily-exchangeable As fraction (fraction 1 - F1) and the specifically-sorbed As fraction (fraction 2 - F2), Soil samples stratified at four depths (0-5 cm, 5-10 cm, 10-20 cm, and 20-40 cm). Where: CA3 = Cultivated Area 3, CA4 = Cultivated Area 4, RA2 = Reference Area 2, and RA3 = Reference Area 3.

In the F2 fraction, *i.e.*, arsenic adsorbed specifically as an inner-sphere complex, the average fractionation percentages were 22.74 (CA3), 39.88 (CA4), 13.69 (RA2), and 33.96% (RA3) of pseudo total of As (Fig. 4), with average contents of 6.01, 7.15, 26.46 and 5.39 mg kg^{-1} (Table 4S), respectively. In general, the As levels of this fraction were also below the QRV values, except for RA2, indicating that arsenic in these areas is likely to not cause environmental or human-health risks. This can be reinforced by the results of the Mehlich I extractant, which confirmed the low bioavailability/bioaccessibility of As in these soils (see values below the detection limit - Table 2S). Results from these two fractions - F1 and F2 - are very important for a better understanding of the real risks posed by As in the soil, as these two fractions are widely used as indicative of environmental toxicity, especially in tropical regions (Ono et al., 2016).

Veloso et al. (2019) carried out a seasonal study on sediments in Paracatu and also found high As values in the specifically-sorbed fraction. In the dry season, the fractionation percentage in this fraction was 48% of the total As (2345 mg kg^{-1}), while in the same location, in the rainy season, it represented 16% (101 mg kg^{-1}). This was due to the greater trapping of As in organic matter in the dry period. Thus, they concluded that the adsorbed As fraction was one of the main As fractions that controlled seasonal mobility. In our study, samples were collected in the dry period and soils have similar OM contents to those reported by Veloso et al. (2019), which may explain these high contents of As extracted in F2. Furthermore, these soils are highly weathered, as shown in the CIA values greater than 80% (Table 1), this can probably explain these high values extracted in the second fraction (Souza Neto et al., 2020). Therefore, preventive monitoring of As in soils in this region - especially the bioavailable fraction - is necessary to guarantee low environmental and human-health risks.

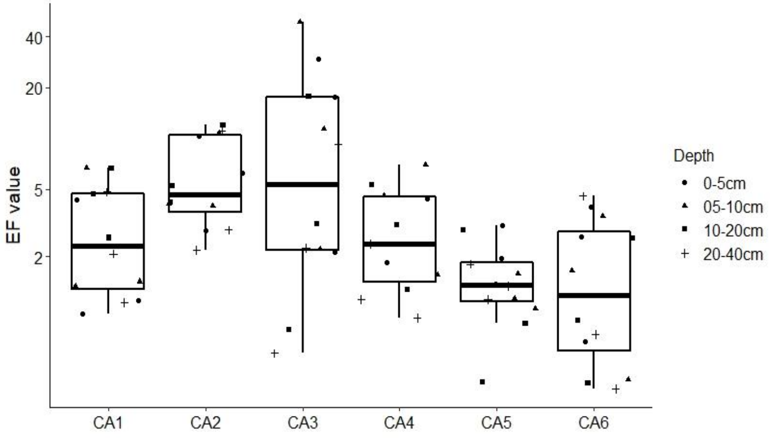
3.6. Pollution indices and environmental risk assessment

The pollution indexes indicate that the CAs did not have significant processes of enrichment by anthropic sources and accumulation of As, except for CA2 (Fig. 5A and B). The enrichment factors showed that there is a moderate enrichment mainly in the first two layers of the soil (for CA3, CA4, CA5, and CA6) and a low enrichment in the deeper layers of the soil. The Igeo did not indicate geoaccumulation of As in all CAs, except for soils in CA2, which, based on this indicator, are considered moderately polluted. The area CA1 is unpolluted in the first layer and moderately polluted in the deeper layers.

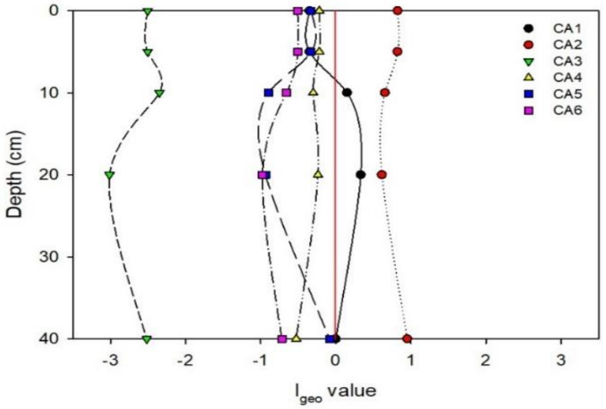
Paracatu's gold mining areas are recognized for having high concentrations of As in the soils, due to their parent material being mainly arsenopyrite (Veloso et al., 2019), which explains the enrichment and environmental contamination by this contaminant. It is true that the use of water with high As levels in agricultural irrigation can contaminate soils and plants (Bundschuh et al., 2020). Nonetheless, the results found in our study show that these soils are naturally enriched by As and do not constitute environmental and human-health risks due to contamination of As. In gold mining areas in the Amazon, EF estimates indicated high enrichment and Igeo suggested that the areas were highly polluted, concluding for high environmental risks (Souza Neto et al., 2020).

In agricultural areas, PERI is widely used to assess potential ecological risks from PTEs (Tapia-Gatica et al., 2020, Souza Neto et al., 2020). In this study, PERI values ranged from 0.66 to 69.35 (Fig. 5C). According to Hakanson (1980), the areas presented a low ecological risk, except for CA2 and CA3, in which PERI was moderate in the first layers. Ciminelli et al. (2018) found in selected soils of Paracatu total As levels between 211 and 4304 mg kg^{-1}. Also, in Pará, at a gold mining area, the total levels of As in the tailings were extremely high, ranging from 1560 to 10,000 mg kg^{-1}, and with a high ecological risk (Souza Neto et al., 2020).

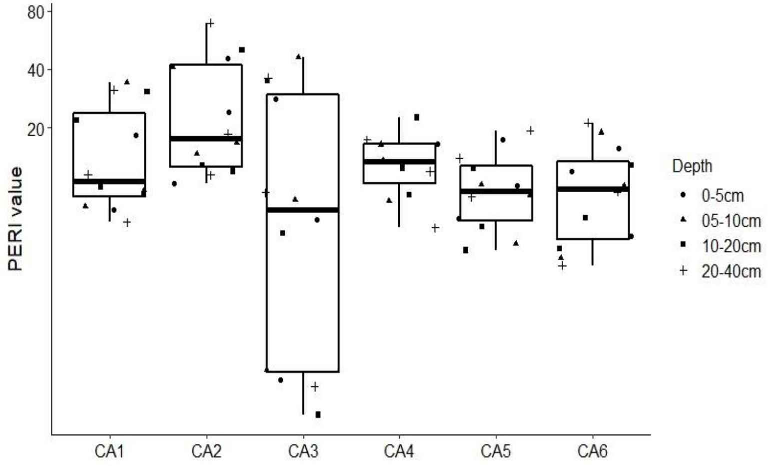
A)


40
20
5
2
EF value
CA1
CA2
CA3
CA4
CA5
CA6
Depth
0-5cm
05-10cm
10-20cm
20-40cm

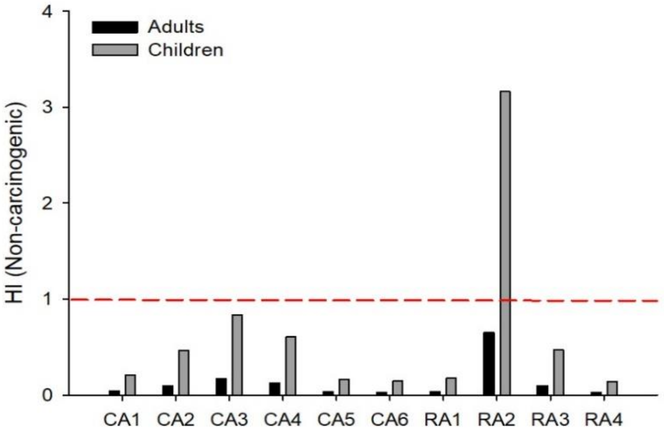
B)


0
10
20
30
40
Depth (cm)
-3
-2
-1
0
1
2
3
I_{geo} value
CA1
CA2
CA3
CA4
CA5
CA6

C)


80
40
20
PERI value
CA1
CA2
CA3
CA4
CA5
CA6
Depth
0-5cm
05-10cm
10-20cm
20-40cm

D)


4
3
2
1
0
HI (Non-carcinogenic)
Adults
Children
CA1
CA2
CA3
CA4
CA5
CA6
RA1
RA2
RA3
RA4

E)

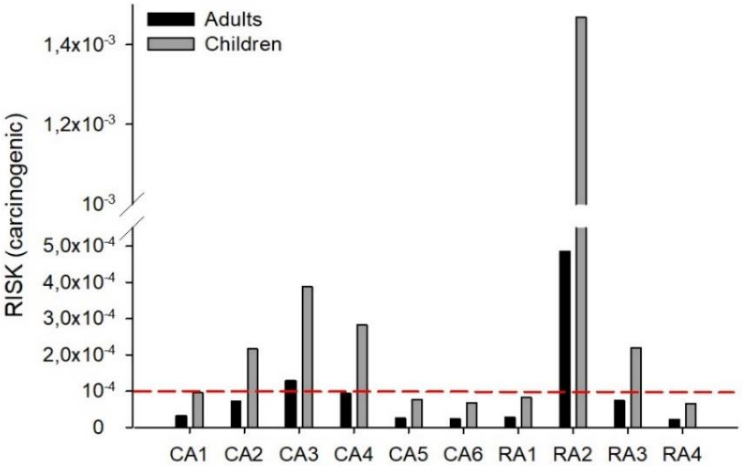


Figure 5 (A) Enrichment factor (EF); **(B)** Geoaccumulation index (Igeo); **(C)** Potential ecological risk index (PERI) of the six areas irrigated with water from the Córrego Rico basin, Paracatu-MG; **(D)** Non-carcinogenic and **(E)** carcinogenic hazard indices for adults and children in six cultivated areas (CA1, CA2, CA3, CA4, CA5, and CA6) and four reference areas (RA1, RA2, RA3, and RA4), at a depth of 0-5 cm, in Paracatu-MG. Where: CA1 = Cultivated Area 1; CA2 = Cultivated Area 2, CA3 = Cultivated Area 3, CA4 = Cultivated Area 4, CA5 = Cultivated Area 5, and CA6 = Cultivated Area 6, RA1 = Reference Area 1, RA2 = Reference Area 2, RA3 = Reference Area 3, and RA4 = Reference Area 4.

3.7. Human health risk assessment

All areas had HI values less than 1, indicating a low carcinogenic risk for children and adults (Souza et al., 2017), except for RA2, which had a value of 3.1 in the superficial layer (0–5 cm). This was because this reference area (natural reserve) had the highest total As contents (Table 2S). The values of HI for adults and children ranged from 0.03 to 0.65 and 0.14–3.1, respectively (Fig. 5D), indicating low contamination by As. In this study, since the only area with high-risk for human health was that of a natural reserve, *i.e.*, a reference area with no anthropic activity, it is concluded that the studied region presents no risks. However, as one of the main routes of exposure to As is the accidental ingestion of soil by children, this RA2 has a potential risk to children's health. Also, we can observe with this study that selected soils of those areas - which are located close to areas of gold mining activities - are naturally rich in As.

Carcinogenic risk values for As above 10^{-4} can cause cancer in humans (Liu et al., 2013). In all areas (CAs and RAs), children were more sensitive to risk, due to their lower body weight and greater intake of soil by the hand-to-mouth pathway. Areas CA1, CA5, CA6, RA1, and RA4 are safe, with no carcinogenic risk for children and adults. Areas RA2 (0.0015)>CA3 (0.0004)>CA4 (0.0003)>RA3 (0.0002)>CA2 (0.0002) presented values above the acceptable limit for children, suggesting that there is a carcinogenic risk for children in these areas (Fig. 5E). Areas RA2 (0.0005) and CA3 (0.0001) also showed higher values for adults. This is because these two areas have the highest total As contents among the areas, as can also be seen in gold mining areas in Pará (Souza Neto et al., 2020). The higher the total As contents, the greater is the human exposure to the contaminant and, consequently, the higher is the potential damage to the health of the local population and the ecosystem.

4. Conclusion

Agricultural soils irrigated with waters from the Córrego Rico, in Paracatu, Brazil, are not polluted with As. Actually, our results have shown low enrichment/accumulation of arsenic in agricultural soils, as well as the prevalence of low ecological risks. The strategy of counterpointing P and As behavior at different soil depths in this study has proved to be efficient, since it was able to demonstrate that the source of As in the soils is natural. In this study, As presented very low oral bioaccessibility estimated for the gastric phase. The distribution profile of total As in the soil is homogeneous, which allows us to infer that the As levels found do not come from irrigation waters containing arsenic. Total As concentrations found in soil, except for RA2, are below Brazilian regulatory levels for agricultural use, which are based on environmental and human-health risks. Although in areas CA3, CA4, RA2, and RA3 the specifically-sorbed As fraction may indicate high mobility, there is no potential risk regarding food safety, since As was not detected (below detection limit) in plant tissues. Concerning health risks for children and adults, they were not evidenced by non-cancer risk indices, except for children in RA2. Finally, with respect to carcinogenic risks for children, there were unacceptable risks in areas RA2 > CA3 > CA4 > RA3 > CA2 and, for adults, in RA2 > CA3. Our findings address relevant aspects of risk assessment for human health and the environment and bring evidence that there are no major risks regarding the use of water from the Córrego Rico for irrigation purposes in Paracatu. However, periodic monitoring of As bioavailability in these areas is recommended.

6. Data statement

All data generated during this study are included in this paper and its supplementary files.

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Appendix A. Supplementary material

Supplementary Material

2. Materials and methods

2.7. Assessment of environmental and human-health risks

To assess the risk to human health, the potential non-carcinogenic (HI) and carcinogenic (RISK) risks were calculated. First, the average daily doses (ADD) of the three main human exposure routes for As were estimated - ingestion (ADD ing), inhalation (ADD inh), and dermal contact (ADD der) -, as shown in the equations below:

$$ADD\ ing = C \times \left((ingR \times EF \times ED)/(BW \times AT) \right) \times CF \text{ (I-S)}$$

$$ADD\ inh = C \times (ingR \times EF \times ED)/(PEF \times BW \times AT) \text{ (II-S)}$$

$$ADD\ der = C \times ((SL \times SA \times ABS \times EF \times ED)/(BW \times AT))\ CF \text{ (III-S)}$$

Then, the risk quotient (HQ) and the risk index (HI) for adults and children were estimated for the potential non-cancerous risk (USEPA, 2001; Souza Neto et al., 2020), as shown in the equations below:

$$HQ\ ing = ADD\ ing\ /\ Rfd\ (As) \text{(IV-S)}$$

$$HQ\ inh = ADD\ inh\ /Rfd\ (As)\ \text{(V-S)}$$

$$HQ\ der = ADD\ der\ /Rfd\ (As)\ \text{(VI-S)}$$

$$HI\ (non - carcinogenic) = HQing + HQ\ inh + HQ\ der\ \text{(VII-S)}$$

where, ADD (mg kg d^{-1}) is the average daily dose; C (mg kg^{-1}) is the concentration of As in the studied areas; ingR (mg d^{-1}) is the soil intake rate, 100 mg d^{-1} for adults and 200 mg d^{-1} for children (USEPA, 2001); InhR (m^3 day^{-1}) is the inhalation rate, 20 m^3 day^{-1} for adults and 7.6 m^3 day^{-1} for children (Lu et al., 2014; USEPA, 2001); PEF (m^3 kg^{-1}) is the particle emission factor, 1.36 10^9 m^3 kg^{-1} (USEPA, 2001); SL (cm^2 day^{-1}) is the skin adherence factor, for adults 0.875 cm^2 day^{-1} and 0.2 mg cm^2 day^{-1} for children (USEPA, 2001); SA (cm^2) is the exposed skin area, for adults 3202 cm^2 and 732 cm^2 for children (USEPA, 2001); ABS is the dermal absorption factor, 0.03 (Lu et al., 2014); EF (d y^{-1}) is the frequency of exposure, 279 days (Moreira et al., 2018); ED (y) is the duration of the exposure, 24 h for adults and 4 h for children (Moreira et al., 2018); BW (kg) is the body weight, 70 kg for adults and 16 kg for children (Moreira et al., 2018); TA is the meantime, without carcinogenic effects (ED x 365 d); CF is the conversion factor of 10^{-6} kg mg^{-1} (USEPA, 2001); Rfd is the reference dose, 0.0003 for As (mg kg d^{-1}) (USEPA, 2001). According to USEPA (2001), for the potential non-cancerous risk, if HI is less than 1, there is possibly no significant risk, and if HI is greater than 1, adverse effects that tend to increase as HI increases may occur.

For carcinogenic risk, the dose (ADD) is multiplied by the corresponding slope factor (SF) to produce a level of cancer risk (Ferreira-Baptista and De Miguel, 2005). For cancer risk, the risk is acceptable or tolerable if it is below 10^{-4} (Ferreira-Baptista and De Miguel, 2005). As the equations below show:

$$Risk\ ing = ADD\ ing \times 1.5\ (As - cancer)$$ (VIII-S)

$$Risk\ inh = ADD\ inh\ \times 15.1\ (As - cancer)$$ (IX-S)

$$Risk\ der = ADD\ der \times 3.66\ (As - cancer)$$ (X-S)

$$RISK\ (carcinogenic) = Risk\ ing + Risk\ inh + Risk\ der$$ (XI-S)

Table S 1 Geographic location of the three replicates (n = 3) in the six agricultural areas irrigated with water from the Córrego Rico basin and in the four reference areas, Paracatu-MG

Area	Replicates	Geographic Coordinates
CA1	1	17°17'38.50"S; 46°51'34.10"W
	2	17°17'28.90"S; 46°51'15.40"W
	3	17°17'46.70"S; 46°51'13.80"W
CA2	1	17°17'38.90"S; 46°52'1.50"W
	2	17°17'29.40"S; 46°51'53.70"W
	3	17°17'44.70"S; 46°51'46.00"W
CA3	1	17°19'15.92"S; 46°44'43.63"W
	2	17°19'18.47"S; 46°44'36.19"W
	3	17°19'23.23"S; 46°44'33.81"W
CA4	1	17°20'2.53"S; 46°45'16.20"W
	2	17°19'56.27"S;46°45'18.11"W
	3	17°19'49.42"S; 46°45'9.83"W
CA5	1	17°17'23.70"S; 46°45'51.50"W
	2	17°17'29.30"S; 46°45'53.70"W
	3	17°17'34.20"S; 46°45'55.70"W
CA6	1	17°17'37.60"S; 46°45'47.80"W
	2	17°17'32.10"S; 46°45'44.30"W
	3	17°17'26.10"S; 46°45'42.10"W
RA1	1	17°17'53.51"S; 46°51'48.27"W
	2	17°17'55.16"S; 46°51'39.89"W
	3	17°17'57.22"S; 46°51'32.31"W
RA2	1	17°19'54.61"S; 46°44'52.33"W
	2	17°19'42.57"S; 46°44'55.10"W
	3	17°19'26.79"S; 46°44'55.16"W
RA3	1	17°21'12.06"S; 46°44'25.61"W
	2	17°21'7.56"S; 46°44'27.79"W
	3	17°21'4.72"S; 46°44'29.71"W
RA4	1	17°17'27.30"S; 46°46'2.70"W
	2	17°17'17.90"S; 46°45'53.36"W
	3	17°17'9.90"S; 46°45'40.06"W

Where: CA1 = Cultivated Area 1; CA2 = Cultivated Area 2, CA3 = Cultivated Area 3, CA4 = Cultivated Area 4, CA5 = Cultivated Area 5, and CA6 = Cultivated Area 6, RA1 = Reference Area 1, RA2 = Reference Area 2, RA3 = Reference Area 3, and RA4 = Reference Area 4.

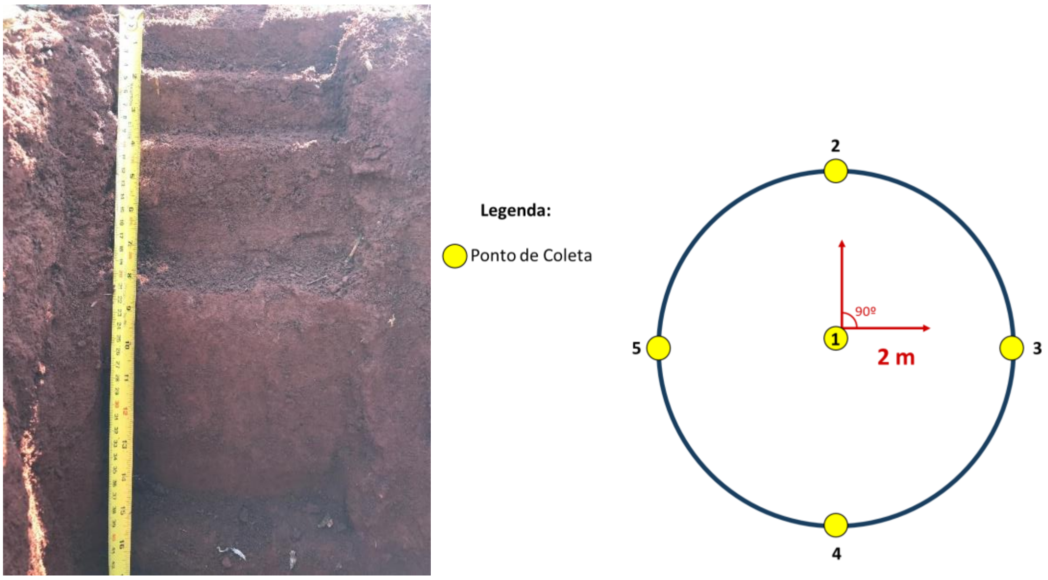

Figure S 1 Trench with sampling profiles at four different depths (0-5, 5-10, 10-20, and 20-40 cm) in the six agricultural areas irrigated with water from the Córrego Rico basin and in the four reference areas, Paracatu-MG, and sketch illustrating the position of the sampling points.

3. Results and Discussion

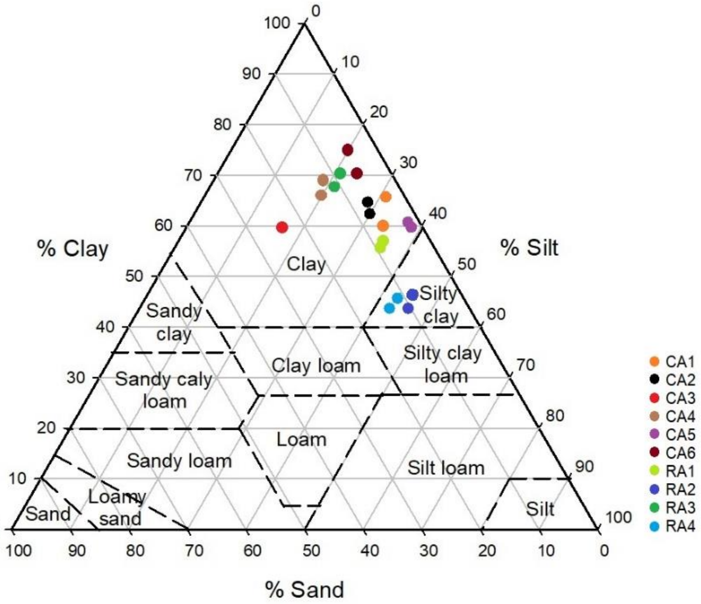

Figure S 2 Textural triangle of soil from soil samples stratified at two depths (0-10 and 10-20 cm) collected in six cultivated areas (CA1, CA2, CA3, CA4, CA5, and CA6) and four reference areas (RA1, RA2, RA3, and RA4) in Paracatu-MG. Where: CA1 = Cultivated Area 1; CA2 = Cultivated Area 2, CA3 = Cultivated Area 3, CA4 = Cultivated Area 4, CA5 = Cultivated Area 5, and CA6 = Cultivated Area 6, RA1 = Reference Area 1, RA2 = Reference Area 2, RA3 = Reference Area 3, and RA4 = Reference Area 4.

Table S 2 Descriptive statistical analysis (means followed by standard deviation, n = 3) of the main chemical analyzes of soil samples stratified in four depths (0-5, 5-10, 10-20, and 20-40 cm) collected in six cultivated areas (CA1, CA2, CA3, CA4, CA5, and CA6) and four reference areas (RA1, RA2, RA3, and RA4) in Paracatu-MG.

Area	**Depth** (cm)	**Total As**	**Available As (Mehlich I)**	**P**
		----------------------- mg kg^{-1} -----------------------		
CA1	0-5	6.37 ± 3.43 aC	<0.02	7.38 ± 4.88 a
	5-10	7.67 ± 6.36 aC	<0.02	9.35 ± 0.00 a
	10-20	7.43 ± 2.48 aC	<0.02	7.32 ± 4.91 a
	20-40	5.90 ± 3.58 aC	<0.02	<0.3
CA2	0-5	14.33 ± 10.05 aBC	<0.02	8.61 ± 3.50 b
	5-10	10.87 ± 6.23 aC	<0.02	26.54 ± 6.83 a
	10-20	9.03 ± 6.64 aC	<0.02	11.93 ± 6.63 b
	20-40	11.42 ± 8.79 aBC	<0.02	0.13 ± 0.23 c
CA3	0-5	25.67 ± 2.89 aA	<0.02	43.21 ± 13.27 a
	5-10	28.33 ± 1.53 aA	<0.02	42.49 ± 7.14 a
	10-20	26.67 ± 3.79 aA	<0.02	14.36 ± 3.64 b
	20-40	26.67 ± 2.89 aA	<0.02	0.15 ± 0.26 c
CA4	0-5	18.67 ± 5.03 aAB	<0.02	38.45 ± 8.08 ab
	5-10	18.67 ± 4.04 aB	<0.02	43.78 ± 7.14 a
	10-20	18.67 ± 2.08 aB	<0.02	21.69 ± 11.13 b
	20-40	17.33 ± 2.89 aB	<0.02	2.00 ± 0.23 c
CA5	0-5	5.08 ± 3.12 aC	<0.02	18.55 ± 6.17 a
	5-10	3.30 ± 1.73 aC	<0.02	18.25 ± 9.76 a
	10-20	3.02 ± 1.68 aC	<0.02	3.75 ± 3.01 b
	20-40	5.33 ± 3.01 aC	<0.02	<0.3
CA6	0-5	4.50 ± 1.61 aC	<0.02	8.51 ± 1.25 a
	5-10	3.90 ± 1.51 aC	<0.02	11.91 ± 5.46 a
	10-20	2.93 ± 1.00 aC	<0.02	5.72 ± 7.31 a
	20-40	3.43 ± 1.63 aC	<0.02	<0.3
RA1	0-5	5.40 ± 0.53 aC	<0.02	1.62 ± 0.11 a
	5-10	4.60 ± 0.82 aC	<0.02	1.10 ± 0.90 ab
	10-20	3.93 ± 1.18 aC	<0.02	0.94 ± 0.51 b
	20-40	3.93 ± 0.80 aC	<0.02	<0.3
RA2	0-5	97.17 ± 124.89 aA	<0.02	1.05 ± 0.21 a
	5-10	96.17 ± 133.83 aA	<0.02	<0.3
	10-20	143.63 ± 205.37 aA	<0.02	<0.3
	20-40	101.77 ± 145.99 aA	<0.02	<0.3
RA3	0-5	14.50 ± 9.61 aB	<0.02	1.60 ± 0.34 a
	5-10	15.33 ± 3.79 aB	<0.02	1.48 ± 0.28 ab
	10-20	14.67 ± 5.86 aBC	<0.02	1.14 ± 0.07 bc
	20-40	16.67 ± 6.03 aB	<0.02	0.98 ± 0.10 c
RA4	0-5	4.27 ± 0.60 aC	<0.02	1.23 ± 0.88 a
	5-10	4.10 ± 1.28 aC	<0.02	0.44 ± 0.52 a
	10-20	3.85 ± 0.98 aC	<0.02	<0.3

20-40	3.77 ± 1.86 aC	<0.02	<0.3

Data evaluated by analysis of variance and Tukey's test ($P < 0.05$). Different lower-case letters represent statistically significant differences ($P < 0.05$) for the concentrations of the element between depths within the same cultivated area. Different capital letters represent statistically significant differences ($P < 0.05$) for the concentrations of the element at the same depth in all cultivated areas. Where: CA1 = Cultivated Area 1; CA2 = Cultivated Area 2, CA3 = Cultivated Area 3, CA4 = Cultivated Area 4, CA5 = Cultivated Area 5, CA6 = Cultivated Area 6, RA1 = Reference Area 1, RA2 = Reference Area 2, RA3 = Reference Area 3, and RA4 = Reference Area 4.

Table S 3 Chemical analysis of vegetable tissue samples (n = 3) collected in six cultivated areas (CA1, CA2, CA3, CA4, CA5, and CA6) and four reference areas (RA1, RA2, RA3, and RA4) in Paracatu-MG

Area	Tissue	As	N	P	K	Ca	Mg	S	B	Zn	Fe	Mn	Cu
		mg kg^{-1}	------------------ g kg^{-1} ------------------						------------- mg kg^{-1} -------------				
		<0.05	17.46	4.01	4.5	0.3	1.49	0.69	<0.05	17.46	4.01	4.5	0.3
CA1	Grains	<0.05	14.88	4.05	4.5	0.44	1.48	0.78	<0.05	14.88	4.05	4.5	0.44
		<0.05	16.82	3.88	3.98	0.37	1.3	0.68	<0.05	16.82	3.88	3.98	0.37
		<0.05	14.88	3.2	2.56	<0.2	0.9	0.57	<0.05	14.88	3.2	2.56	<0.2
CA2	Grains	<0.05	13.58	3.02	2.3	<0.2	0.83	0.61	<0.05	13.58	3.02	2.3	<0.2
		<0.05	12.94	3.26	2.89	<0.2	0.88	0.57	<0.05	12.94	3.26	2.89	<0.2
		<0.05	9.06	1.21	1.91	<0.2	0.52	0.84	<0.05	9.06	1.21	1.91	<0.2
CA3	Grains	<0.05	14.88	2.7	3.14	<0.2	1.19	1.09	<0.05	14.88	2.7	3.14	<0.2
		<0.05	15.52	2.42	3.01	<0.2	1.08	0.94	<0.05	15.52	2.42	3.01	<0.2
		<0.05	18.76	1.96	2.44	<0.2	0.88	0.9	<0.05	18.76	1.96	2.44	<0.2
CA4	Grains	<0.05	21.34	1.63	2.12	<0.2	0.72	0.84	<0.05	21.34	1.63	2.12	<0.2
		<0.05	18.11	2.58	4.02	<0.2	1.18	1.1	<0.05	18.11	2.58	4.02	<0.2
		<0.05	21.99	2.37	26.62	2.56	2.97	1.37	<0.05	21.99	2.37	26.62	2.56
CA5	Grasses	<0.05	21.34	2.72	26.59	2.04	3.11	1.27	<0.05	21.34	2.72	26.59	2.04
		<0.05	27.17	3.25	28.79	3.1	3.3	1.59	<0.05	27.17	3.25	28.79	3.1
		<0.05	15.52	2.03	3.3	<0.2	0.83	1.18	<0.05	15.52	2.03	3.3	<0.2
CA6	Grains	<0.05	16.17	2.34	3.86	<0.2	0.9	0.98	<0.05	16.17	2.34	3.86	<0.2
		<0.05	12.94	2.52	4.03	<0.2	0.95	1.06	<0.05	12.94	2.52	4.03	<0.2
		<0.05	11	1.81	19.87	6.7	3.34	0.95	5.6	21	138	123	3
RA1	Grasses	<0.05	11.64	2.11	16.36	6.85	3.75	0.93	15.2	20	130	110	3
		<0.05	8.41	1.94	16.64	2.98	2.19	0.57	6.8	14	81	120	1
		<0.05	16.17	1.02	12.69	2.74	3.75	0.84	1.39	25.7	362.9	102.8	6.9
RA2	Grasses	<0.05	10.35	0.98	13.03	1.98	3	0.7	1.17	51.1	103.8	193.8	3.1
		<0.05	14.88	0.85	12.5	1.59	2.34	0.98	27.83	45.4	157.5	134.2	5.5
		<0.05	10.35	0.74	21.75	1.33	1.71	0.71	1.76	49.9	231.2	160.1	7
RA3	Grasses	<0.05	12.94	0.86	14.73	2.9	3.62	0.58	2.27	29.5	53.9	108.2	2.6
		<0.05	12.94	0.91	15.4	1.96	2.64	0.61	1.5	38.9	54.4	228.1	2.9
		<0.05	13.58	1.4	20.71	3.26	2.61	0.82	2.11	44.9	522.3	121.4	4.7
RA4	Grasses	<0.05	11.64	1.09	21.03	3.43	2.41	1.17	2.31	32.2	155.7	140.3	3.7
		<0.05	10.35	0.63	19.6	2.57	2.13	0.77	<1	79.8	204.1	410.4	6.7

Where: CA1 = Cultivated Area 1; CA2 = Cultivated Area 2, CA3 = Cultivated Area 3, CA4 = Cultivated Area 4, CA5 = Cultivated Area 5, CA6 = Cultivated Area 6, RA1 = Reference Area 1, RA2 = Reference Area 2, RA3 = Reference Area 3, and RA4 = Reference Area 4.

Table S 4 Descriptive statistical analysis (means followed by standard deviation, n = 3) of the chemical fractionation of the easily exchangeable As fraction (fraction 1 - F1) and the specifically-sorbed As fraction (fraction 2 - F2)

Area	**Depth**	**As Total**	**F1**	**F2**	**F1+F2**	**F1**	**F2**	**F1+F2**
	(cm)	--------------- mg kg^{-1} ---------------				--------- % ---------		
CA3	0-5	25.67 ± 2.89	0.32 ± 0.56	7.09 ± 2.76	7.41 ± 3.31	1.34 ± 2.32	28.19 ± 12.73	29.53 ± 15.04
	5-10	28.33 ± 1.53	<LD	7.11 ± 1.46	7.11 ± 1.46	<LD	25.26 ± 6.01	25.26 ± 6.01
	10-20	26.67 ± 3.79	0.15 ± 0.25	7.49 ± 2.40	7.63 ± 2.30	0.61 ± 1.05	28.76 ± 11.15	29.37 ± 10.98
	20-40	26.67 ± 2.89	0.03 ± 0.05	4.73 ± 0.60	4.76 ± 0.59	0.12 ± 0.20	17.74 ± 0.79	17.85 ± 0.95
	weighted average	**26.75**	**0.09**	**6.01**	**6.10**	**0.38**	**22.74**	**23.12**
CA4	0-5	21.00 ± 4.24	1.31 ± 1.86	7.68 ± 0.71	8.99 ± 1.15	5.48 ± 7.75	37.68 ± 11.00	43.15 ± 3.26
	5-10	18.67 ± 4.04	<LD	6.40 ± 1.62	6.40 ± 1.62	<LD	34.14 ± 1.94	34.14 ± 1.94
	10-20	18.67 ± 2.08	1.92 ± 1.71	7.57 ± 0.04	9.49 ± 1.67	10.39 ± 9.72	40.87 ± 4.46	51.26 ± 11.12
	20-40	17.33 ± 2.89	2.11 ± 2.05	7.00 ± 0.23	9.11 ± 2.27	13.66 ± 14.70	41.38 ± 8.82	55.03 ± 23.22
	weighted average	**18.29**	**1.70**	**7.15**	**8.85**	**10.11**	**39.88**	**49.99**
RA2	0-5	97.17 ± 124.89	11.43 ± 15.19	67.21 ± 101.43	78.64 ± 116.56	8.34 ± 7.24	39.29 ± 38.35	47.63 ± 44.66
	5-10	96.17 ± 133.83	6.54 ± 9.66	54.22 ± 84.57	60.76 ± 94.21	4.42 ± 3.85	42.91 ± 17.78	47.33 ± 18,62
	10-20	143.63 ± 205.37	3.58 ± 6.20	45.13 ± 75.99	48.71 ± 82.19	0.94 ± 1.63	13.66 ± 18.70	14.60 ± 20.31
	20-40	17.65 ± 13.22	<LD	<LD	<LD	<LD	<LD	<LD
	weighted average	**68.90**	**3.14**	**26.46**	**29.60**	**1.83**	**13.69**	**15.52**
RA3	0-5	19.67 ± 6.61	0.34 ± 0.59	2.60 ± 2.11	2.94 ± 2.69	3.10 ± 5.37	19.55 ± 22.57	22.65 ± 27.89
	5-10	15.33 ± 3.79	1.09 ± 1.88	4.24 ± 2.91	5.33 ± 4.79	9.89 ± 17.13	32.82 ± 31.41	42.71 ± 48.53
	10-20	14.67 ± 5.86	1.22 ± 1.08	6.25 ± 4.13	7.47 ± 3.71	11.71 ± 12.93	51.95 ± 44.01	63.65 ± 53.41
	20-40	19.50 ± 4.95	0.39 ± 0.55	5.95 ± 4.00	6.34 ± 3.44	2.45 ± 3.47	28.85 ± 13.19	31.30 ± 9.71
	weighted average	**17.79**	**0.68**	**5.39**	**6.07**	**5.78**	**33.96**	**39.74**

The weighted average was adopted with 0-5 cm - weight 12.5%; 5-10 cm - weight 12.5%. 10-20 cm - weight 25%, and 20-40 cm - weight 50%. <LD = below the detection limit (0.02 mg kg^{-1}). Where: CA3 = Cultivated Area 3, CA4 = Cultivated Area 4, RA2 = Reference Area 2, and RA3 = Reference Area 3.

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MANUSCRIPT 2 - ORAL BIOACCESSIBILITY OF As AND Pb IN SOILS OF CONTRASTING ORIGINS AND LAND USES

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Abstract

The mobility of potentially toxic elements (PTEs) in soil, such as arsenic (As) and lead (Pb), is related to soil properties and anthropogenic activities such as agriculture and mining. Protecting communities potentially exposed to these PTEs requires a thorough health risk assessment. Oral bioaccessibility is a key parameter for accurately assessing health risks. This study aimed to evaluate the potential health risks of As and Pb through oral bioaccessibility of soils from contrasting areas with different land origins and uses (agricultural areas in Paracatu-MG-Brazil, and abandoned gold mine areas in Marmora and Lake-ON-Canada). Maximum total concentrations were 387.81 mg As kg^{-1} and 517.52 mg Pb kg^{-1} for Brazilian agricultural areas, and 334.87 mg As kg^{-1} and 132.68 mg Pb kg^{-1} for mine areas in Canada, considered higher than regulatory soil quality limits in Brazil and Canada. Bioaccessibility levels were low, with maximum values of 5.57% As_{IVBA} and 17.19% Pb_{IVBA} for Brazilian agricultural soils and 31.53% As_{IVBA} to 20.58% Pb_{IVBA} for soils from the abandoned mine in Canada. Gastric phase bioaccessibility of As correlated positively with total As levels and negatively with extractable

Fe and total Fe levels in agricultural areas and in abandoned mine areas. The gastric phase bioaccessibility of Pb showed strong positive correlations with total Pb levels in both Brazilian agricultural areas and Canadian mine areas. In mine areas, positive correlations were also found with organic carbon and clay. For agricultural and reference areas, the carcinogenic risk level associated with As exposure ($< 8.1\text{x}10^{-6}$), except for RA2 ($1.80 \text{ x } 10^{-5}$), and the non-carcinogenic hazard index (< 0.04) were within regulatory limits, indicating no concerning occupational risks. However, for abandoned mine areas, there was a high carcinogenic risk level of As for adults ($5.1 \text{ x}10^{-5}$) and children ($< 4.5\text{x}10^{-4}$) in most areas, but the non-carcinogenic hazard index (< 1.00) was within regulatory limits; nevertheless, there is no reason for concern as it is a restricted access area. Notably, there was no carcinogenic risk associated with Pb exposure in either land use. The use of total As and Pb levels inadequately predict adverse effects on human health and overestimate chronic exposure risks.

Keywords: human health risk assessment, environmental pollution, gold mining, irrigated agricultural.

1. Introduction

Mining and agriculture are essential activities for the economic and social development of nations. However, it is important to recognize that these activities have the potential to cause undesirable impacts on the environment and human health. Ore mining and the use of agricultural inputs such as fertilizers and pesticides can elevate levels of potentially toxic elements (PTEs) in the soil, often surpassing regulatory soil quality limits (Liu *et al.*, 2018; Gupta *et al.*, 2019). Additionally, these elements can be transported to other environments and, consequently, enter the human food chain (Bundschuh *et al.*, 2020; Billmann *et al.*, 2023).

In mining areas, anomalous levels of various PTEs, such as arsenic (As) and lead (Pb), can often be present in association with ores (Bundschuh *et al.*, 2020). Meanwhile, in agricultural areas, PTE sources are more related to local geology (Yang *et al.*, 2018; Palansooriya *et al.*, 2020), but they can also be associated with management practices (Menezes *et al.*, 2020). These anomalous levels of PTEs only pose health risks if the population comes into direct or indirect contact with soils that are potentially contaminated or have high geological background. However, the actual toxic effects on human health are related to the amount of PTEs that can be assimilated and reach the bloodstream and organs (USEPA, 2007; Ng *et al.*, 2015; Kumpiene *et al.*, 2017; Li *et al.*, 2020). Therefore, it is crucial to determine the bioaccessible levels of PTEs in the soil, especially in mining and agricultural areas, to mitigate risks to the local population.

The main route of exposure to As and Pb involves the accidental ingestion of soil, especially by children due to their natural habits such as crawling and putting their hands in their mouths (Zingaretti & Baciocchi, 2021). Soil ingestion introduces contaminants into the digestive system, where compartments influence the dissolution and absorption of contaminants from the soil matrix (ISO 17924, 2019). Therefore, assessing the total concentration of PTEs in soils may be inadequate for predicting actual adverse effects on the environment and human health (Juhasz *et al.*, 2007; Lu *et al.*, 2011; Ono *et al.*, 2012; Dodd *et al.*, 2017; Fernández-Landero *et al.*, 2021). However, current regulations are based solely on total metal concentrations in soil particles, potentially overestimating exposure, and risk (CONAMA, 2009; Environment Agency, 2009; Grøn and Andersen, 2003; Health Canada, 2017; MTES, 2017; Ng *et al.*, 2015; Oomen *et al.*, 2006; USEPA, 2007). Thus, it is crucial to advocate for legislative changes to assess health risks associated with soil ingestion. This amendment should incorporate an adjustment factor based on the oral bioavailability of PTEs to refine the toxicity values of total metal concentrations in soils.

The physical and chemical properties of soil play a crucial role in the geochemical behavior of PTEs (Lima *et al.*, 2022). Factors such as pH, redox potential, cation exchange capacity, total inorganic carbon, organic carbon, particle size, and the presence of aluminum (Al), iron (Fe), and manganese (Mn) oxyhydroxides significantly influence the interaction of these elements in the soil (El-Naggar *et al.*, 2019; El-Naggar *et al.*, 2018; Lima *et al.*, 2019; Shahid *et al.*, 2017; Yadav *et al.*, 2018). Among these factors, soil Fe is an important variable, as iron oxides are capable of sequestering As in the soil (Fischel *et al.*, 2015). However, the effects of this sequestration process on bioaccessibility and bioavailability are still poorly understood (Sowers *et al.*, 2022).

Therefore, understanding the relationship between bioaccessibility and soil properties is crucial for assessing human health risks. In this context, our study investigated two geographically distinct areas: an agricultural area in Brazil and an area of an abandoned mine in Canada. The study area in Brazil, in Paracatu-MG, is classified as Red Oxisols (Soil Survey Staff, 1999), with high levels of Fe and Mn and clay, and samples were collected from agricultural areas and adjacent natural reserves. The study area in Canada, in Marmora and Lake-ON, is classified as Deloro Loam of the order Brunisols (Gillespie, Wicklund and Richards, 1962; SCWG, 1998), originating from brownish-red stony limestone, and samples were collected from a deactivated gold mining area and its surroundings. This research aims to deepen the understanding of the variability of these environmental conditions and their implications on the bioaccessibility of As and Pb.

With this study, it is expected that soil properties, particularly the Fe levels, will influence the bioaccessibility of As and Pb in soils of different origins and land uses. The purpose of this study was (1) To assess the total levels and bioaccessibility of As and Pb in two contrasting areas with different origins and land uses, one in agricultural areas in Brazil and the other in an abandoned gold mine in Canada, using the Solubility/Bioaccessibility Research Consortium (SBRC) assay. (2) To evaluate the relationship between soil properties and the bioaccessibility of As and Pb to identify soil properties that may attenuate the bioaccessibility of PTEs in soils. (3) To assess the carcinogenic and non-carcinogenic risk of As and Pb exposure, calculated from estimated soil intake rates for children and adults and the bioaccessibility of As and Pb.

2. Materials and Methods

2.1. Study areas

The soils were collected in two distinct study areas with abnormal As levels, one located in Brazil and the other in Canada (Tables 1 and 2). The study area for the Brazilian soil comprises 120 agricultural and reference soils (Table 1). These samples were collected in 2020 from a region known for high natural levels of As in the soil in Paracatu Municipality, Minas Gerais, Brazil (17° 16’ 13" S, 46° 51’12" W). Soil samples were collected from different locations with potential risk to human health due to the history of high natural As levels in these soils and included six irrigated agriculture areas (Agricultural area) and four natural reserve areas adjacent to these agricultural areas but could also have high natural levels of As (Reference), at four different depths (0–5, 5–10, 10–20, and 20–40 cm), and three replicates (Table 1). Further details of soil collection are described in Feitosa *et al.* (2021). The areas were identified as Cultivated Areas (from CA1 to CA6) and Reference Areas (from RA1 to RA4). The soils in this site are classified as Red Oxisols with high clay levels (Feitosa *et al.*, 2021).

The climate in this municipality is characterized as tropical wet and dry or savanna (Aw), according to the Koppen classification, with dry winter and rainy summer. The annual average of precipitation is from 1400 to 1500 mm and the temperature is from 21 to 23ºC. The topography is predominantly smooth to smooth-wavy, and the predominant biome is Cerrado.

The study area for the Canadian soil comprises 10 field-contaminated and background soils (Table 2). These samples were collected in 2006 from the decommissioned Deloro Gold Mine in Marmora and Lake Municipality, Ontario, Canada (44° 30' 43" N, 77° 37' 12" W). Soil samples were collected from different locations close to the decommissioned mine and included eight mine areas directly at the mine (Mine Site), and two adjacent areas to the mine site (Background Area) (Table 2). The areas were identified as Mine Sites (#1, #2, #3, #4, #5, #10, #11, and #23), and Background Areas (#21 and #28), but the geographic locations of each sample were not specified, and there are no field replicates. Further details of soil collection are described in Arora (2019). The soils at this site are classified as Deloro Loam of the order Brunisols, originating from a stony calcareous reddish-brown till parent material (Gillespie *et al.*, 1962). US Soil Taxonomy classifies most of these Brunisols as Inceptisols (Soil Survey Staff, 1999). Mining activities at the location resulted in high levels of As, cobalt (Co), copper (Cu), and nickel (Ni) in the soil (CH2M HILL, 2004). The climate in this municipality is characterized as humid continental mild summer, wet all year (Dfb), according to the Koppen classification. The annual average of precipitation is 997 mm, and it is equally distributed across the year. The average temperature is 7.2ºC.

2.2. Soil characterization

The sample pH was measured in a suspension at a soil-water ratio of 1:2.5. The extraction of exchangeable levels of iron (Fe) and manganese (Mn) was performed by Mehlich I (HCl 0.05 mol L^{-1} and H_2SO_4 0.0125 mol L^{-1}). The extracts were analyzed by inductively coupled plasma optical emission spectrometry - ICP OES (equipment brands Spectro model Ciros Vision and Agilent model 5800). The determination of soil organic carbon was based on the $K_2Cr_2O_7$ - H_2SO_4 oxidation method (Walkley and Black, 1934).

These soils were previously identified as As-rich soils (Feitosa *et al.*, 2021; Arora, 2019). Furthermore, their origin, processing, and physical and chemical characterization have been reported in previous publications (Feitosa *et al.*, 2021; Arora, 2019). All samples were air-dried, sieved to 2 mm, homogenized, and subsequently further sieved to a final size of < 250 µm. The concentration of pseudo-total metals in the soil was determined using a modified methodology based on the United States Environmental Protection Agency (US-EPA) Method 3051a (USEPA, 2007). The adaptations made included employing an oven instead of a microwave. A mass of 0.5 g of each sample was pre-digested overnight in a solution containing 9.0 mL of HNO_3 and 3.0 mL of HCl (both reagent grade, Sigma Aldrich Canada Co., Oakville, ON). Subsequently, the samples were heated in an oven at 110 °C for approximately 8 h for digestion. The digested soils were then filtered through Whatman 42 filter paper and diluted to 25 mL with ultrapure water. The concentrations of As and Pb were determined using ICP OES (Inductively Coupled Plasma - Optical Emission Spectrometry/Varian Vista Pro ICP-OES 15 with axial viewed plasma). Standard reference materials (SRMs), SRM 2711 and SRM 2710a (National Institute of Standards and Technology), and a laboratory blank (no soil added) were also evaluated in all batches. Furthermore, soil samples from Canada were evaluated in five laboratory replicates while those from Brazil, as there were already three field replicates, were carried out in duplicates. The recovery for As and Pb were 77.9 ± 4.2% and 82.8 ± 4.6% (SRM 2711) and 74.3 ± 6.7% and 80.2 ± 4.1% (SRM 2710a), respectively.

Table 1. Chemical attributes of Brazilian soils based on three field replicates (n = 3), Paracatu-MG, Brazil

Brazilian soil	Depth cm	Land use	pH	OC	Fe	Mn	As	Pb	Soil Texture
				%	mg kg^{-1}				
CA1	0-5	Agricultural	7.15 ± 0.24	1.40 ± 0.10	59.50 ± 22.48	53.40 ± 14.66	8.63 ± 2.41	137.15 ± 23.68	Clayey
	5-10		6.19 ± 0.36	0.87 ± 0.15	63.48 ± 20.90	29.51 ± 3.77	8.47 ± 2.74	139.86 ± 29.49	Clayey
	10-20		5.20 ± 0.14	0.63 ± 0.06	73.64 ± 21.03	15.15 ± 6.84	8.95 ± 2.64	143.21 ± 28.79	Clayey
	20-40		5.07 ± 0.27	0.33 ± 0.25	69.59 ± 4.28	9.31 ± 4.82	9.08 ± 3.44	146.83 ± 28.92	Clayey
CA2	0-5	Agricultural	6.78 ± 0.53	1.33 ± 0.06	34.27 ± 6.62	46.94 ± 2.98	12.33 ± 4.90	160.50 ± 35.96	Clayey
	5-10		6.19 ± 0.15	0.93 ± 0.15	41.22 ± 10.41	40.04 ± 12.76	12.41 ± 5.08	161.24 ± 38.28	Clayey
	10-20		5.53 ± 0.54	0.67 ± 0.12	50.65 ± 5.31	17.30 ± 7.77	12.12 ± 5.52	159.59 ± 26.38	Clayey
	20-40		5.08 ± 0.20	0.33 ± 0.06	68.84 ± 5.12	6.98 ± 2.64	9.11 ± 1.44	149.02 ± 32.68	Clayey
CA3	0-5	Agricultural	6.38 ± 0.17	1.37 ± 0.15	31.12 ± 4.22	121.92 ± 19.31	29.39 ± 3.03	422.96 ± 59.40	Clayey
	5-10		6.06 ± 0.27	0.93 ± 0.25	32.04 ± 3.76	92.97 ± 12.88	29.64 ± 2.88	410.78 ± 45.72	Clayey
	10-20		5.67 ± 0.30	0.80 ± 0.10	49.58 ± 4.97	46.66 ± 4.55	28.22 ± 2.13	418.18 ± 53.33	Clayey
	20-40		5.15 ± 0.46	0.37 ± 0.12	66.51 ± 9.11	29.69 ± 7.46	28.15 ± 1.89	447.56 ± 65.03	Clayey
CA4	0-5	Agricultural	6.15 ± 0.09	1.80 ± 0.87	24.96 ± 4.60	66.07 ± 8.29	21.86 ± 1.32	176.67 ± 15.62	Clayey
	5-10		5.88 ± 0.12	1.57 ± 0.12	22.85 ± 1.54	49.20 ± 13.73	20.94 ± 1.69	174.19 ± 11.61	Clayey
	10-20		5.67 ± 0.17	0.67 ± 0.35	28.11 ± 0.98	29.12 ± 2.74	20.82 ± 2.02	168.27 ± 14.16	Clayey
	20-40		5.58 ± 0.27	0.37 ± 0.12	45.90 ± 7.83	13.75 ± 3.47	19.59 ± 2.89	164.55 ± 21.45	Clayey
CA5	0-5	Agricultural	5.73 ± 0.16	2.20 ± 0.50	60.71 ± 25.16	59.17 ± 18.12	5.29 ± 3.52	56.81 ± 15.61	Clayey
	5-10		5.66 ± 0.35	2.03 ± 0.78	58.59 ± 20.81	59.65 ± 28.48	4.78 ± 2.86	56.41 ± 15.81	Clayey
	10-20		4.98 ± 0.51	1.70 ± 0.46	77.77 ± 48.15	19.31 ± 2.84	5.35 ± 3.54	58.36 ± 17.78	Clayey
	20-40		4.84 ± 0.49	0.90 ± 0.10	62.4 ± 13.53	8.79 ± 6.25	5.52 ± 3.74	65.01 ± 16.33	Clayey
CA6	0-5	Agricultural	6.16 ± 0.14	1.60 ± 0.10	59.54 ± 3.76	34.58 ± 0.25	9.58 ± 2.11	90.73 ± 13.74	Clayey
	5-10		5.73 ± 0.28	1.27 ± 0.12	65.03 ± 14.58	27.93 ± 3.57	8.98 ± 2.33	90.83 ± 14.94	Clayey
	10-20		4.88 ± 0.15	0.80 ± 0.17	75.91 ± 27.83	9.90 ± 1.84	9.26 ± 2.08	92.26 ± 14.07	Clayey
	20-40		4.54 ± 0.24	0.57 ± 0.12	58.80 ± 11.98	4.04 ± 0.41	8.71 ± 1.65	90.31 ± 13.40	Clayey
RA1	0-5	Reference	5.53 ± 0.34	2.33 ± 0.59	86.19 ± 13.35	152.98 ± 52	7.06 ± 0.73	91.61 ± 9.68	Clayey
	5-10		5.33 ± 0.17	1.60 ± 0.44	106.77 ± 27.78	90.71 ± 22.92	7.38 ± 0.83	91.00 ± 10.63	Clayey

	10-20		5.13 ± 0.03	1.30 ± 0.56	171.46 ± 59.12	72.88 ± 15	6.68 ± 1.19	86.10 ± 12.54	Clayey
	20-40		4.97 ± 0.13	0.80 ± 0.35	116.19 ± 16.49	37.11 ± 17.46	6.95 ± 1.59	77.19 ± 9.44	Clayey
RA2	0-5	Reference	4.84 ± 0.81	1.93 ± 0.15	576.41 ± 177.56	96.98 ± 11.87	144.20 ± 182.03	99.30 ± 34.29	Silty clayey
	5-10		4.89 ± 0.74	1.50 ± 0.17	461.53 ± 118.33	50.42 ± 3.54	143.02 ± 190.14	97.78 ± 37.59	Silty clayey
	10-20		4.66 ± 0.58	0.87 ± 0.25	350.64 ± 137.32	31.40 ± 3.54	132.84 ± 182.01	98.24 ± 37.84	Silty clayey
	20-40		4.49 ± 0.49	0.63 ± 0.12	226.48 ± 83.94	22.13 ± 4.12	11.30 ± 1.14	84.25 ± 13.41	Silty clayey
RA3	0-5	Reference	5.09 ± 0.24	1.20 ± 0.35	77.28 ± 43.26	64.31 ± 7.55	18.11 ± 2.67	156.36 ± 33.93	Clayey
	5-10		4.83 ± 0.29	0.93 ± 0.21	84.81 ± 55.60	40.17 ± 0.68	20.77 ± 9.16	168.83 ± 50.42	Clayey
	10-20		4.72 ± 0.37	0.57 ± 0.06	63.26 ± 31.91	25.67 ± 7.24	20.30 ± 10.94	164.17 ± 55.23	Clayey
	20-40		4.60 ± 0.33	0.37 ± 0.15	57.55 ± 18.62	16.66 ± 8.20	19.89 ± 4.34	162.15 ± 38.32	Clayey
RA4	0-5	Reference	5.30 ± 0.30	2.13 ± 0.21	115.19 ± 43.47	202.16 ± 72.18	6.43 ± 1.97	69.36 ± 13.72	Silty clayey
	5-10		5.09 ± 0.36	1.70 ± 0.20	89.98 ± 19.05	112.27 ± 20.28	6.78 ± 2.01	75.10 ± 13.07	Silty clayey
	10-20		5.04 ± 0.51	1.30 ± 0.17	91.35 ± 22.74	67.69 ± 11.03	6.76 ± 1.55	72.05 ± 11.59	Silty clayey
	20-40		4.98 ± 0.33	0.90 ± 0.26	68.79 ± 33.03	36.01 ± 11.52	6.44 ± 1.38	69.52 ± 7.55	Silty clayey

Table 2. Chemical attributes of Canadian soils based on five replicates (n = 5) from the decommissioned Deloro Gold Mine in Marmora and Lake Municipality, Ontario, Canada

Canadian soil	Land use	pH	OC	Fe	Mn	As	Pb	Soil Texture
		H_2O	%			mg kg^{-1}		
#1	Mining	4.97 ± 0.02	2.2 ± 0.59	72500	2310	131.63 ± 6.73	89.90 ± 11.40	Loam
#2	Mining	4.92 ± 0.03	1.84 ± 0.32	54600	1070	142.60 ± 9.62	86.25 ± 4.93	Loam
#3	Mining	5.05 ± 0.08	2.75 ± 0.61	49900	917	187.20 ± 10.35	94.28 ± 13.35	Loam
#4	Mining	-	-	-	-	101.94 ± 9.15	40.03 ± 5.78	
#5	Mining	5.45 ± 0.03	2.84 ± 0.54	59100	1240	218.91 ± 16.40	99.60 ± 9.34	Loam
#10	Mining	4.79 ± 0.04	2.39 ± 0.59	51000	887	134.04 ± 12.58	92.76 ± 8.31	Loam
#11	Mining	4.86 ± 0.02	2.96 ± 0,26	47800	1100	197.65 ± 9.75	118.81 ± 9.87	Loam
#21	Background	4.66 ± 0.09	1.62 ± 0.28	23500	330	165.63 ± 10.87	26.71 ± 7.45	Sandy Loam
#23	Mining	5.04 ± 0.03	3.09 ± 0.53	42000	939	321.01 ± 9.84	88.21 ± 8.08	Loam
#28	Background	5.53 ± 0.08	1.92 ± 0.05	33500	443	160.25 ± 21.94	51.44 ± 14.19	Silt Loam

2.3. Bioaccessibility assay: determination of $[As]_{IVBA}$ and $[Pb]_{IVBA}$ in soils

The bioaccessible fractions of As and Pb were determined using the standard procedure endorsed by the United States Environmental Protection Agency (USEPA, 2017) and developed by the Solubility/Bioaccessibility Research Consortium (SBRC). Due to its strong correlation with the swine bioassay (Drexler and Brattin, 2007), the SBRC assay has been accepted by the USEPA for assessing the bioaccessibility of Pb in contaminated soils, specifically outlined in Method 1340 of the USEPA (USEPA, 2013). This method involves an extraction using a fluid of 0.4 mol L^{-1} glycine adjusted to pH 1.5 with the addition of hydrochloric acid and warmed to 37°C in a water bath to simulate the gastric phase. A mass of 1.0 g of each soil sample was sieved to <150 μm to 100 mL of the designated extraction fluid in a 125 mL high-density polyethylene bottle. Subsequently, the bottles were positioned into a water bath incubator at 37± 2°C and rotated at a speed of 30 ± 2 rpm for 1 h. Subsequently, a 15 mL portion of the extracts was filtered through a 0.45 μm cellulose acetate membrane and stored at 4 ± 2°C. The concentrations of As and Pb were determined using inductively coupled plasma mass spectrometry (ICP-MS). All samples were extracted in duplicate or quintuplicate for the Brazilian and Canadian soils, respectively. Each batch of extraction experiments contained three blanks with a glycine solution at pH 1.5, and a reference soil material (NIST 2710a and 2711).

The bioaccessibility of As and Pb was determined using the equation below, where As_{IVBA} and Pb_{IVBA} represent the amount of As and Pb (mg kg^{-1}) extracted from the soil after gastric phase extraction, and As_T and Pb_T represent the pseudototal concentrations (mg kg^{-1}) of As and Pb in contaminated soil before in vitro evaluation.

$$\%\text{AsIVBA and }\%\text{PbIVBA} = \frac{(\text{[As and Pb]IVBA}, \frac{mg}{kg})}{(\text{[As and Pb]T}, \frac{mg}{kg})} \times 100\%$$

2.4. Exposure to As and health risk

The assessment of exposure risk to PTEs in soils can be based on bioaccessibility tests (Rodriguez *et al.*, 1999; Schroder *et al.*, 2004; Lu *et al.*, 2011), using the gastric bioaccessibility protocol from SBRC. The chronic daily intake (CDI) of As and Pb, which represents the hazards related to accidental oral ingestion of contaminated soil, was determined by the equation below (USEPA, 1989).

$$CDI = \frac{AsBA \ or \ PbBA \ x \ IR \ x \ CF \ x \ FI \ x \ EF \ x \ ED}{BW \ x \ AT}$$

where CDI is the chronic daily intake of As and Pb (mg day^{-1} kg^{-1}), AsBA and PbBA the bioaccessible concentration of As and Pb in gastric extraction (mg kg^{-1}), IR is the soil ingestion rate of 100 mg day^{-1} for adult and 200 mg day^{-1} for children (USEPA, 2002), CF is a conversion factor (10^{-6} kg mg^{-1}), FI is the fraction of soil ingested (= 1) (USEPA, 2002), EF is the frequency of exposure (300 days $year^{-1}$) (Mikutta *et al.*, 2014), ED is the duration of exposure (25 years) (USEPA, 2002), BW is the body weight of 70 kg for adults and 16 kg for children (Mikutta *et al.*, 2014) and AT the average time (25,550 days = 70 years).

For As, the CDI value multiplied by the cancer slope factor (1.5 mg $kg^{-1}day^{-1}$) (USEPA, 2015) determines the heightened risk of cancer incidence throughout an average lifespan (cancer risk, CR) (USEPA, 1989). Furthermore, the hazard quotient was assessed to gauge the potential risk of non-cancerous effects (USEPA, 1989):

$$HQ = \frac{CDI}{RfD}$$

The CDI is based on an AT value of 365 × ED, and RfD refers to the oral reference doses for As (0.0003 mg kg^{-1} day^{-1}) and for Pb (0.025 mg kg^{-1} day^{-1}) (Fernández-Landero *et al.*, 2021; USEPA, 2013, 2015).

2.5. Data Analyses

All analyses of variance, Tukey's test, and regression used the RStudio (version 3.4.3) (R Core Team, 2017) and SigmaPlot (version 15). The critical p-values for all comparisons and effects considered were < 0.05 and < 0.01. Values expressed after "±" are the standard deviation. The effects of soil properties on bioaccessibility were explored using scatterplots and Pearson correlation coefficients using metal bioaccessibility as the dependent variable and soil properties including total metal concentrations, major element concentrations (*e.g.*, Fe, Mn), pH, OC, and clay as independent variables. The parameters with the strongest linear relationship and $p < 0.05$ were used in a regression analysis to determine the factors that best explained the data.

3. Results and Discussion

3.1. Pseudototal concentration of As and Pb in soils

The average pseudototal As levels in agricultural and reference soils in Brazil ranged from 4.78 to 144.20 mg kg^{-1} (Tables 1 and 3). For all areas, the total As contents did not differ significantly ($p<0.05$) among the four depths collected within the same area, except for RA2, which exhibited the highest pseudototal As levels in the top layers of the soil (0-5, 5-10, and 10-20 cm) (Table 3). This homogeneity is indicative that the As in these areas is likely of geogenic origin (Feitosa *et al.*, 2021). In agricultural areas, PTE sources are more related to the local geology (Yang *et al.*, 2018; Palansooriya *et al.*, 2020). According to Brazilian soil quality guidelines, CA3 (28.85 mg kg^{-1}), CA4 (20.80 mg kg^{-1}), and RA3 (19.77 mg kg^{-1}) showed total As contents above the prevention values of 15 mg As kg^{-1} of soil (CONAMA, 2009). RA2 is a reference area (natural reserve) adjacent to agricultural areas and showed average contents four times above the investigation values for agricultural areas of 35 mg As kg^{-1}, with an average value among the top layers of the soil of 140 mg kg^{-1}.

The average pseudototal Pb levels in soil samples from Brazil ranged from 56.41 to 447.56 mg kg^{-1} Pb (Table 1 and 3). In all areas of Paracatu-MG, except for CA5 (59.15 mg kg^{-1}), the pseudototal Pb levels were above the soil prevention values of 72 mg Pb kg^{-1}. CA3 showed average contents 2.5 times above the investigation values for agricultural areas of 180 mg Pb kg^{-1}, with an average value of 424.87 mg kg^{-1} (CONAMA, 2009). For all areas, the pseudototal Pb levels did not differ significantly among the four depths collected within the same area (Table 3). Pb is typically adsorbed in the top layers of the soil due to its low mobility in the soil (Rieuwerts, 2007); this occurs because of Pb's high affinity with organic matter primarily present in the soil surface (CCME, 1999). Therefore, since the analyzed soils were homogeneous across depths within each area, we can suggest that it is of geological origin. However, there was a significant difference ($p<0.05$) among the average pseudototal Pb levels concerning the same depth in all areas, following the decreasing order: CA3 (424.87 mg kg^{-1}) > CA4 (170.92 mg kg^{-1}) ≥ RA3 (162.88 mg kg^{-1}) ≥ CA2 (157.59 mg kg^{-1}) ≥ CA1 (141.76 mg kg^{-1}) ≥ RA2 (94.89 mg kg^{-1}) ≥ CA6 (91.03 mg kg^{-1}) ≥ RA1 (86.47 mg kg^{-1}) ≥ RA4 (71.51 mg kg^{-1}) > CA5 (59.15 mg kg^{-1}).

The average pseudototal As levels in soil samples from an abandoned gold mine in Canada ranged from 101.94 to 321.01 mg kg^{-1} of As (Tables 2 and 4). Among all areas, there was a significant difference ($p<0.05$) in the average pseudototal As levels, following the decreasing order: #23 (321.01 mg kg^{-1}) > #5 (218.91 mg kg^{-1}) > #11 (197.65 mg kg^{-1}) ≥ #3 (187.20 mg kg^{-1}) > #21 (165.63 mg kg^{-1}) > #28 (160.25 mg kg^{-1}) ≥ #2 (142.60 mg kg^{-1}) ≥ #10 (134.04 mg kg^{-1}) > #1 (131.63 mg kg^{-1}) > #4 (101.94 mg kg^{-1}). All areas showed As contents above the Canadian soil quality guidelines (12 mg As kg^{-1}). Due to the constant disturbance of the mined soils (Ono *et al.*, 2012), it was expected to observe such heterogeneity among areas and elevated As levels, as these are soil samples from a mine area and nearby regions. It is known that the

Deloro Mine area had intensive mineral extraction activity for nearly a century (CH2M HILL, 2004). Besides gold mining and extraction, mineral refining occurred at the site, producing gold (Au), As, silver (Ag), nickel (Ni), cobalt (Co), and stellite, an alloy of chromium, copper, and tungsten used in ammunition during the First and Second World Wars (Golder Associates Ltd., 2012). Tenkouano *et al.* (2019) conducted mineralogy studies on soil samples from this region using Scanning Electron Microscopy - Mineral Liberation Analysis (SEM-MLA), and their data showed that 98% of As was in iron oxides, while only 2% was associated with arsenic-containing pyrite.

The average pseudototal Pb levels in soil samples from Canada ranged from 26.71 to 118.81 mg Pb kg^{-1} (Table 2 and 4). All mine areas showed contents above the Canadian soil quality values of 70 mg Pb kg^{-1}; however, the background areas (#21 and #28) and mine area #4 are within the allowed limit. There was a significant difference ($p<0.05$) in the pseudototal Pb contents among all areas, following the decreasing order: #11 (118.81 mg kg^{-1}) > #5 (99.60 mg kg^{-1}) > #1 (89.90 mg kg^{-1}) = #2 (86.25 mg kg^{-1}) = #3 (94.28 mg kg^{-1}) = #10 (92.76 mg kg^{-1}) = #23 (88.21 mg kg^{-1}) > #28 (51.44 mg kg^{-1}) > #4 (40.03 mg kg^{-1}) > #21 (26.71 mg kg^{-1}).

Table 3. Total and bioaccessible levels of As and Pb of Brazilian soils based on three field replicates (n = 3), Paracatu-MG, Brazil

Brazilian soil	**Depth**	**$[As]_T$**	**$[As]_{IVBA}$**	**$\%As_{IVBA}$**	**$[Pb]_T$**	**$[Pb]_{IVBA}$**	**$\%Pb_{IVBA}$**
		mg kg^{-1}		%	mg kg^{-1}		%
CA1	0-5 cm	8.63 ± 2.41 Aa	0.24 ± 0.04 Ab	2.96 ± 0.76 Aa	137.15 ± 23.68 Abcd	7.00 ± 1.62 Ab	5.15 ± 1.10 Ac
	5-10 cm	8.47 ± 2.74 Aa	0.25 ± 0.04 Aa	3.27 ± 1.34 Aa	139.86 ± 29.49 Abcd	6.35 ± 1.44 Ab	4.57 ± 0.75 Ab
	10-20 cm	8.95 ± 2.64 Aa	0.26 ± 0.03 Aa	3.02 ± 0.75 Aab	143.21 ± 28.79 Abcd	5.15 ± 1.45 Ab	3.59 ± 0.71 Acd
	20-40 cm	9.08 ± 3.44 Aa	0.26 ± 0.05 Aa	3.20 ± 1.07 Aab	146.83 ± 28.92 Abcd	4.14 ± 1.02 Ab	2.83 ± 0.49 Ac
CA2	0-5 cm	12.33 ± 4.90 Aa	0.30 ± 0.07 Ab	2.75 ± 1.23 Aa	160.50 ± 35.96 Abc	7.06 ± 1.42 Ab	4.47 ± 0.79 Ac
	5-10 cm	12.41 ± 5.08 Aa	0.33 ± 0.06 Aa	2.98 ± 1.16 Aa	161.24 ± 38.28 Abc	6.89 ± 1.13 Ab	4.39 ± 0.86 Aa
	10-20 cm	12.12 ± 5.52 Aa	0.32 ± 0.06 Aa	3.04 ± 1.35 Aab	159.59 ± 26.38 Abc	5.20 ± 0.39 Ab	3.33 ± 0.59 Acd
	20-40 cm	9.11 ± 1.44 Aa	0.31 ± 0.06 Aa	3.47 ± 1.10 Aab	149.02 ± 32.68 Abc	3.96 ± 0.30 Ab	2.75 ± 0.58 Ac
CA3	0-5 cm	29.39 ± 3.03 Aa	0.52 ± 0.09 Aab	1.81 ± 0.41 Aa	422.96 ± 59.40 Aa	63.82 ± 15.59 Aa	15.01 ± 2.22 Aa
	5-10 cm	29.64 ± 2.88 Aa	0.41 ± 0.07 Aa	1.41 ± 0.34 Aa	410.78 ± 45.72 Aa	56.00 ± 13.04 Aa	13.60 ± 2.41 Aab
	10-20 cm	28.22 ± 2.13 Aa	0.33 ± 0.06 Aa	1.18 ± 0.25 Ab	418.18 ± 53.33 Aa	58.69 ± 16.03 Aa	13.86 ± 2.15 Aa
	20-40 cm	28.15 ± 1.89 Aa	0.30 ± 0.06 Aa	1.08 ± 0.23 Ab	447.56 ± 65.03 Aa	57.23 ± 12.46 Aa	12.74 ± 1.46 Aa
CA4	0-5 cm	21.86 ± 1.32 Aa	0.39 ± 0.07 Ab	1.78 ± 0.43 Aa	176.67 ± 15.62 Ab	18.45 ± 7.78 Ab	10.70 ± 5.07 Aab
	5-10 cm	20.94 ± 1.69 Aa	0.41 ± 0.09 Aa	1.97 ± 0.49 Aa	174.19 ± 11.61 Ab	16.44 ± 7.84 Ab	9.60 ± 4.89 Aab
	10-20 cm	20.82 ± 2.02 Aa	0.38 ± 0.07 Aa	1.83 ± 0.41 Aab	168.27 ± 14.16 Ab	13.95 ± 6.09 Ab	8.47 ± 4.13 ABbcd
	20-40 cm	19.59 ± 2.89 Aa	0.34 ± 0.08 Aa	1.78 ± 0.57 Ab	164.55 ± 21.45 Ab	8.26 ± 2.27 Ab	5.15 ± 1.77 Bbc
CA5	0-5 cm	5.29 ± 3.52 Aa	0.21 ± 0.06 Ab	3.13 ± 2.73 Aa	56.81 ± 15.61 Ae	4.48 ± 1.08 Ab	8.53 ± 3.41 Abc
	5-10 cm	4.78 ± 2.86 Aa	0.21 ± 0.06 Aa	3.22 ± 2.56 Aa	56.41 ± 15.81 Ae	4.89 ± 1.11 Ab	9.10 ± 2.63 Aab
	10-20 cm	5.35 ± 3.54 Aa	0.18 ± 0.05 Aa	2.37 ± 1.68 Aab	58.36 ± 17.78 Ae	4.88 ± 0.98 Ab	8.84 ± 2.53 Aab
	20-40 cm	5.52 ± 3.74 Aa	0.18 ± 0.04 Aa	2.48 ± 1.85 Ab	65.01 ± 16.33 Ae	4.52 ± 0.54 Ab	7.40 ± 2.27 Abc
CA6	0-5 cm	9.58 ± 2.11 Aa	0.26 ± 0.06 Ab	2.90 ± 1.07 Aa	90.73 ± 13.74 Acde	7.40 ± 1.58 Ab	8.22 ± 1.66 Abc
	5-10 cm	8.98 ± 2.33 Aa	0.21 ± 0.05 Aa	2.54 ± 1.02 Aa	90.83 ± 14.94 Acde	7.67 ± 1.53 Ab	8.67 ± 2.30 Aab
	10-20 cm	9.26 ± 2.08 Aa	0.19 ± 0.04 Aa	2.19 ± 0.80 Aab	92.26 ± 14.07 Acde	5.91 ± 1.07 Ab	6.48 ± 1.26 Abcd
	20-40 cm	8.71 ± 1.65 Aa	0.18 ± 0.03 Aa	2.19 ± 0.72 Ab	90.31 ± 13.40 Abcde	4.91 ± 1.28 Ab	5.47 ± 1.29 Abc
RA1	0-5 cm	7.06 ± 0.73 Aa	0.25 ± 0.09 Ab	3.63 ± 1.54 Aa	91.61 ± 9.68 Acde	4.44 ± 1.03 Ab	4.88 ± 1.15 Ac
	5-10 cm	7.38 ± 0.83 Aa	0.31 ± 0.12 Aa	4.24 ± 1.87 Aa	91.00 ± 10.63 Acde	4.52 ± 1.15 Ab	5.09 ± 1.64 Ab

	10-20 cm	6.68 ± 1.19 Aa	0.31 ± 0.12 Aa	4.94 ± 2.32 Aa	86.10 ± 12.54 Acde	4.82 ± 0.96 Ab	5.78 ± 1.79 Abcd
	20-40 cm	6.95 ± 1.59 Aa	0.37 ± 0.16 Aa	5.95 ± 3.67 Aa	77.19 ± 9.44 Acde	5.25 ± 1.10 Ab	6.94 ± 2.02 Abc
RA2	0-5 cm	144.20 ± 182.03 Aa	1.17 ± 1.23 Aa	1.37 ± 0.75 Aa	99.30 ± 34.29 Acde	5.59 ± 1.39 Ab	5.81 ± 1.02 Abc
	5-10 cm	143.02 ± 190.14 Aa	0.68 ± 0.60 ABa	1.34 ± 1.07 Aa	97.78 ± 37.59 Acde	5.57 ± 1.96 Ab	5.82 ± 1.05 Ab
	10-20 cm	132.84 ± 182.01 Aa	0.53 ± 0.41 Ba	1.41 ± 1.13 Ab	98.24 ± 37.84 Abcde	4.63 ± 1.24 Ab	4.90 ± 0.85 Abcd
	20-40 cm	11.30 ± 1.14 Ba	0.22 ± 0.03 Ba	1.94 ± 0.39 Ab	84.25 ± 13.41 Acde	3.49 ± 0.18 Ab	4.24 ± 0.76 Abc
RA3	0-5 cm	18.11 ± 2.67 Aa	0.35 ± 0.06 Aa	1.98 ± 0.56 Aa	156.36 ± 33.93 Abc	15.64 ± 1.49 Ab	10.45 ± 2.68 Aab
	5-10 cm	20.77 ± 9.16 Aa	0.34 ± 0.06 Aa	1.88 ± 0.83 Aa	168.83 ± 50.42 Ab	14.45 ± 1.85 Ab	8.97 ± 1.94 Aab
	10-20 cm	20.30 ± 10.94 Aa	0.34 ± 0.07 Aa	1.97 ± 0.83 Aab	164.17 ± 55.23 Ab	13.62 ± 2.16 Ab	8.79 ± 2.19 Aabc
	20-40 cm	19.89 ± 4.34 Aa	0.36 ± 0.07 Aa	1.94 ± 0.75 Ab	162.15 ± 38.32 Ab	12.67 ± 2.82 Ab	8.19 ± 2.43 Aab
RA4	0-5 cm	6.43 ± 1.97 Aa	0.16 ± 0.06 Aa	2.97 ± 1.88 Aa	69.36 ± 13.72 Ade	4.82 ± 0.78 Ab	7.31 ± 2.37 Abc
	5-10 cm	6.78 ± 2.01 Aa	0.16 ± 0.04 Aa	2.54 ± 1.08 Aa	75.10 ± 13.07 Ade	4.51 ± 0.42 Ab	6.18 ± 1.40 Ab
	10-20 cm	6.76 ± 1.55 Aa	0.17 ± 0.06 Aa	2.82 ± 1.48 Aab	72.05 ± 11.59 Ade	4.44 ± 0.76 Ab	6.38 ± 1.89 Abcd
	20-40 cm	6.44 ± 1.38 Aa	0.18 ± 0.06 Aa	2.99 ± 1.67 Aab	69.52 ± 7.55 Ade	4.14 ± 0.62 Ab	6.04 ± 1.33 Abc

Data evaluated by analysis of variance and Tukey's test (P <0.05). Different capital letters represent statistically significant differences (P <0.05) for PTE concentrations between depths within the same cultivated area. Different lower-case letters represent statistically significant differences (P <0.05) for PTE concentrations at the same depth in all cultivated areas. Where: CA1 = Cultivated Area 1; CA2 = Cultivated Area 2, CA3 = Cultivated Area 3, CA4 = Cultivated Area 4, CA5 = Cultivated Area 5, CA6 = Cultivated Area 6, RA1 = Reference Area 1, RA2 = Reference Area 2, RA3 = Reference Area 3, and RA4 = Reference Area 4.

Table 4. Total and bioaccessible levels of As and Pb in Canadian soil samples, from the decommissioned Deloro Gold Mine in Marmora and Lake Municipality, Ontario, Canada.

Canadian soil	**$[As]_T$**	**$[As]_{IVBA}$**	**$\%As_{IVBA}$**	**$[Pb]_T$**	**$[Pb]_{IVBA}$**	**$\%Pb_{IVBA}$**
	mg kg		**%**	**mg kg**		**%**
#1	131.63 ± 6.73 G	4.58 ± 0.49 D	3.49 ± 0.46 C	89.90 ± 11.40 B	6.92 ± 0.42 BCD	7.78 ± 0.98 B
#2	142.60 ± 9.62 EFG	4.80 ± 0.25 D	3.38 ± 0.33 C	86.25 ± 4.93 B	6.68 ± 0.30 BCD	7.75 ± 0.39 B
#3	187.20 ± 10.35 CD	7.96 ± 0.76 CD	4.25 ± 0.30 C	94.28 ± 13.35 B	9.27 ± 1.05 A	10.03 ± 1.98 AB
#4	101.94 ± 9.15 H	29.19 ± 4.14 A	28.72 ± 3.97 A	40.03 ± 5.78 CD	4.02 ± 0.55 FG	10.33 ± 2.70 AB
#5	218.91 ± 16.40 B	10.95 ± 1.06 C	5.05 ± 0.83 C	99.60 ± 9.34 AB	9.43 ± 0.46 A	9.54 ± 1.06 AB
#10	134.04 ± 12.58 FG	4.74 ± 0.67 D	3.59 ± 0.83 C	92.76 ± 8.31 B	5.78 ± 0.69 DE	6.32 ± 1.28 B
#11	197.65 ± 9.75 BC	7.16 ± 0.58 CD	3.63 ± 0.39 C	118.81 ± 9.87 A	8.06 ± 0.46 B	6.82 ± 0.72 B
#21	165.63 ± 10.87 DE	20.39 ± 4.39 B	12.35 ± 2.70 B	26.71 ± 7.45 D	3.12 ± 0.29 H	12.62 ± 4.69 A
#23	321.01 ± 9.84 A	19.99 ± 2.23 B	6.24 ± 0.76 C	88.21 ± 8.08 B	7.42 ± 0.54 BC	8.46 ± 0.97 AB
#28	160.25 ± 21.94 EF	7.68 ± 1.41 CD	4.80 ± 0.70 C	51.44 ± 14.19 C	4.84 ± 0.49 EF	10.00 ± 3.10 AB

Data evaluated by analysis of variance and Tukey's test ($P < 0.05$). Different capital letters represent statistically significant differences ($P < 0.05$) for PTE concentrations between areas.

3.2.Bioaccessible As and Pb in Soils

In agricultural and reference soil samples from Paracatu-MG, the average bioaccessible As levels ranged from 0.16 to 1.17 mg kg^{-1} in gastric extraction (SBRC) (Table 3). Bioaccessibility levels estimate the amount of contaminant that can be released from soil into the digestive system, providing crucial information for assessing health risks associated with exposure to PTEs (Denys *et al.*, 2012; Kumpiene *et al.*, 2017; Li *et al.*, 2020). Thus, despite some agricultural and reference soils having pseudototal As levels above Brazilian agricultural soil quality values (35 mg kg^{-1}), these soils exhibit very low As levels that can actually pose risks to human health due to their less bioavailable form in the soil. This can be explained by As being strongly bound to crystalline iron oxide nanoparticles, resulting in As immobilization in the soil (Fendorf *et al.*, 2010; Ciminelli *et al.*, 2018). Although As is mainly associated with Fe and Al (hydr)oxides, Veloso *et al.* (2019) found two of the most mobile As fractions, the adsorbed and poorly crystalline fractions, in sediments near mining areas. This may indicate that the Paracatu region has a strong seasonal dependence on As mobilization during the rainy season. Therefore, there is a concern in the study of our irrigated agricultural areas in Paracatu that are more susceptible to changes in soil moisture.

For bioaccessible As levels in Brazilian soils, there was no significant difference among all depths within the same area, except for RA2, which showed higher As_{IVBA} levels in the surface layer (0-5 cm). These soils also have a silty texture, which may have influenced the increase in As bioaccessibility in these soils. Meunier *et al.* (2011) found the highest bioaccessible concentrations of As in soil particles <45 µm in size due to higher total As concentrations. However, RA2 is a natural reserve area, and access by the local population to this area is possibly limited. Ng *et al.* (2019) also found low bioaccessible As levels of 4.1 ± 3.7 mg kg^{-1} with an average bioaccessibility of 3.4 ± 2.0% in superficial soil dust in Paracatu.

The average bioaccessible Pb levels ranged from 3.49 to 63.82 mg kg^{-1} in gastric extraction (SBRC) (Table 3). Although these values are within the Brazilian soil quality reference limits, below 72 mg kg^{-1}, there was no statistical difference between depths within the same area; however, when compared at the same depth across all areas, CA3 showed the highest Pb_{IVBA} levels ($p<0.05$) (Table 3). Therefore, being an agricultural area, this area is of concern regarding human health risk.

In abandoned gold mine soil samples, the average bioaccessible As_{IVBA} levels ranged from 4.58 to 29.19 mg kg^{-1} in gastric extraction (SBRC) (Table 6). There was a significant difference between the average bioaccessible As_{IVBA} levels and soils collected at the Deloro Site, following the decreasing order: #4 (29.19 mg kg^{-1}) > #21 (20.39 mg kg^{-1}) = #23 (19.99 mg kg^{-1}) > #5 (10.95 mg kg^{-1}) > #28 (7.68 mg kg^{-1}) = #3 (7.96 mg kg^{-1}) = #11 (7.16 mg kg^{-1}) > #1 (4.58 mg kg^{-1}) = #2 (4.80 mg kg^{-1}) = #10 (4.74 mg kg^{-1}). As_{IVBA} in the gastric phase for soils in mining areas was markedly higher than in agricultural areas (Tables 3 and 4). However, it was observed that soils with the highest pseudototal As levels also showed the lowest percentages of As bioaccessibility. Meanwhile, the average bioaccessible Pb_{IVBA} levels ranged from 3.12 to 9.27 mg kg^{-1} in gastric extraction (SBRC) (Table 6). There was a significant difference between the average bioaccessible PbIVBA levels and soils collected at the Deloro Site, following the decreasing order: #3 (9.27 mg kg^{-1}) = #5 (9.43 mg kg^{-1}) > #11 (8.06 mg kg^{-1}) ≥ #23 (7.42 mg kg^{-1}) ≥ #1 (6.92 mg kg^{-1}) ≥ #2 (6.68 mg kg^{-1}) ≥ #10 (5.78 mg kg^{-1}) ≥ #28 (4.84 mg kg^{-1}) ≥ #4 (4.02 mg kg^{-1}) > #21 (3.12 mg kg^{-1}).

3.3. Bioaccessibility of As and Pb

The average (%) bioaccessibility of As in all Brazilian soil samples was very low, ranging from 1.08 to 5.95% in gastric extraction (SBRC) (Table 3). There was no significant difference between depths within the same area. However, when comparing the same depth across all areas, RA1 exhibited the highest As bioaccessibility in the two last soil layers. It is noteworthy that areas with lower total As contents showed higher As bioaccessibility, such as RA1, which presented the highest average As bioaccessibility values (4.69%) with the lowest average total As contents (7.02 mg kg^{-1}). In contrast, RA2 exhibited the lowest As bioaccessibility values (1.52%) with the highest average total As contents (107.84 mg kg^{-1}). This low As bioaccessibility in Brazilian soils can be explained by the predominance of Fe and Mn oxides in these soils, which can strongly adsorb this PTE in the soil. Our results were similar to those of Ono *et al.* (2012b), who assessed As bioaccessibility in a gold mining area in Paracatu-MG and found an As bioaccessibility of 4.6%. In Brazilian agricultural soils, there was a significant negative correlation between $\%As_{IVBA}$ and As_T ($R = -0.30$, $P<0.01$) and extractable Fe ($R = -0.15$, $P<0.01$) (Table 5). This demonstrates that higher pseudototal As levels in these soils correspond to lower levels of bioaccessibility in these agricultural soils. This reinforces that total As levels do not adequately address the health risk to the local population.

Meanwhile, the average (%) bioaccessibility of Pb in agricultural soils ranged from 2.7 to 15% in gastric extraction (SBRC) (Table 5). There was no significant difference between depths across all areas, except for CA4, which exhibited higher bioaccessibility in the first soil layers (0-5 and 5-10 cm). CA3 showed the highest Pb bioaccessibility (Table 5). Ruby *et al.* (1996) reported that Pb bioaccessible extracted in the acidic gastric phase is strongly dependent on pH, leading to increased Pb dissolution in this phase. There was a significant negative correlation between $\%Pb_{IVBA}$ and extractable Fe ($R = -0.20$, $p<0.05$), and a positive correlation between $\%Pb_{IVBA}$ and PbT ($R = 0.55$, $p<0.01$) and Pb_{IVBA} ($R = 0.77$, $p<0.01$). Soil physical and chemical properties and Pb mineralogy can influence Pb bioaccessibility in gastric extraction (Cao *et al.*, 2020; Xia *et al.*, 2016). This is because Pb is potentially more bioavailable to animals and/or humans when ingested in the form of Pb carbonates and Fe and Mn oxides than in other mineral forms, such as PbS or Pb phosphates (Ruby *et al.*, 1999; Schroder *et al.*, 2004; Marschner *et al.*, 2006; Giráldez *et al.*, 2020).

Thus, due to the influence of soil chemical properties on As and Pb bioaccessibility, soil quality guidelines could utilize oral bioaccessibility as a corrective factor for total concentration. In Australia's current management of contaminated soils, for instance, for soil ingestion, the selected value for risk assessment is 25% bioavailability of As (Ludlow, 2010). The bioaccessibility method has a high correlation with the bioavailability index to assess the potential bioavailability of As and Pb in soil (Ruby *et al.*, 1996, 1999; Rodriguez *et al.*, 1999; Juhasz *et al.*, 2007). Our study suggests a value of 10% bioaccessibility of As for Brazilian agricultural soils with high Fe oxide contents.

In the samples from the abandoned gold mine, the average bioaccessibility of As ranged from 3.38 to 28.72% in the gastric extraction (SBRC) (Table 4). These results were similar to those found in Juhasz *et al.* (2007), with As bioaccessibility ranging from 5 to 36% in mine soils. In mining areas, there is usually low bioaccessibility of As in soils with high total As concentrations (Ono *et al.*, 2012; Palumbo-Roe and Klinck, 2007). The area with the highest level of bioaccessibility was #4, followed by #21 and the other areas, which showed no statistical differences between them. This result is interesting because area 4 had the lowest total As soil concentrations and obtained the highest levels of As bioaccessibility. There was a significant positive correlation between $\%As_{IVBA}$ and As_{IVBA} ($R = 0.84$, $P<0.05$) and a significant negative correlation between $\%As_{IVBA}$ and FeT ($R = -0.73$, $P<0.05$). This suggests that the mineralogical properties of the soils in mining sites may play an important role in As bioaccessibility (Ruby *et al.*, 1999). This study area has origins from brown-red stony limestone, and As bound to calcium in the mineral is highly soluble under acidic gastric conditions, which may have contributed to the higher bioaccessibility of As in these areas (Meunier *et al.*, 2010; Whitacre *et al.*, 2017); whereas in Brazilian agricultural soils, they may have exhibited lower bioaccessibility because As is more associated with sulfides, such as arsenopyrite (Karna *et al.*, 2017; Kim, Yoo and Baek, 2014; Whitacre *et al.*, 2017).

Meanwhile, the average bioaccessibility of Pb in mine soils from Canada ranged from 6.3 to 12.6% in the gastric extraction (SBRC) (Table 4). There was a significant difference between the areas, with the highest Pb bioaccessibility in the background area near the mine #21 (12.6%), followed by areas #3, #4, #5, #23, and #28 statistically similar, and areas #1, #2, #10, and #11 with the lowest Pb bioaccessibility. There was a significant positive correlation between $\%Pb_{IVBA}$ and $\%As_{IVBA}$ ($R = 0.81$, $P<0.01$) and a significant negative correlation between $\%Pb_{IVBA}$ and PbT ($R = -0.73$, $P<0.05$). In some studies, a significant correlation has been found between Pb bioaccessibility and soil properties such as pH, total Pb content, clay content, and organic matter (OM) (Appleton *et al.*, 2012; Caboche *et al.*, 2010; Karadas and Kara, 2011; Poggio *et al.*, 2009).

According to the mean IVBA values, the metal bioaccessibility in the gastric phase (SBRC) followed the order: Pb (7.2%) > As (2.56%) for agricultural soils from Paracatu-MG, while for soils from the Deloro Site mining areas, the order was: Pb (9%) > As (7.55%). When comparing land uses, the Pb (%) bioaccessibility did not significantly differ between agricultural and mining soils. Meanwhile, the As (%) bioaccessibility was significantly higher in mining areas than in agricultural areas. The bioaccessibility values of As and Pb are relatively low compared to those recorded in soils contaminated with anthropogenic PTEs (Xia *et al.*, 2016; Mehta *et al.*, 2020). These values are like those found in chestnut soils developed in mineralized areas of southwestern Spain, characterized by their high concentrations of naturally occurring PTEs (Fernández-Landero *et al.*, 2021). In the present study, due to the low bioaccessibility of As and Pb, they are likely strongly bound to the soil matrix and may therefore not be available for gastric absorption after accidental soil ingestion.

3.4. ***Correlation between the As and Pb levels and soils physicochemical properties***

Table 5 shows the correlation between the chemical parameters and the pseudototal concentrations of As and Pb in the soil samples from Brazil. A significant positive correlation was observed between pseudototal As and extractable Fe (R = 0.64, P < 0.01) (Figure 1a). Brazilian soils, such as Latossolos and Argissolos, are predominantly rich in Fe and Mn oxides, thus exhibiting a greater capacity for adsorption of various PTEs (Feitosa *et al.*, 2021). For As, the presence of Fe oxides can reduce its mobility in the soil because the positive charges on the surfaces of the Fe oxides interact with the negative charges of AsO_4^{3-} and AsO_3^{3-} (Warren and Alloway, 2003; Komárek *et al.*, 2013). In the studied Brazilian soil samples, there was a significant positive correlation between pseudototal Pb and pH (R = 0.32, P < 0.01) (Figure 1a). As pseudototal Pb concentrations are significantly pH-dependent, this may enhance its solubilization in the soil for highly acidic gastric juice and consequently increase the bioaccessible Pb concentrations in these soils (Fernández-Landero *et al.*, 2021). A significant negative correlation was found between pseudototal Pb and OC (R = -0.29, P < 0.01) and extractable Fe (R = -0.22, P < 0.01) (Table 5 and Figure 1a). This is because these soils are used for agriculture and have low organic matter content. Furthermore, the source of Pb in these study areas is possibly derived from the local lithology, as anthropogenic Pb is often more accumulated near the soil surface due to its affinity with soil organic matter (CCME, 1999), whereas in these soils, Pb does not significantly change with depth (Table 1).

Table 6 shows the correlation between the chemical parameters and the pseudototal concentrations of As and Pb in the soil samples from Canada. A significant positive correlation was observed between pseudototal As and OC ($R = 0.70$, $P < 0.05$) (Figure 1b), indicating that OC had a greater impact on the distribution of As in the soils of the mine area in Canada. Langner *et al.* (2012) indicated that organic matter could completely sequester As through the formation of covalent bonds between As and organic sulfur (S) groups, and OC significantly affected the distribution of PTEs. Zou *et al.* (2023) reported a strong positive correlation of As with OC and concluded that elevated concentrations of dissolved organic carbon (DOC) promoted catabolic responses of iron-reducing microorganisms and triggered microbial As detoxification mechanisms, leading to more release of As into clay fractions, including As (III) and organic As. Chapagain *et al.* (2009) also reported a strong positive correlation of As with organic matter content, and the results were consistent with our findings. Moreover, due to the nearly hundred years of mining activity history, the processes of constant soil disturbance may have led to soil aggregate breakdown, which could increase OC decomposition and, consequently, enhance As release in the soil (Nie *et al.*, 2018). Tenkouano *et al.* (2019) reported a decrease in organic content and an increase in the carbonate content of sediments during the years of Deloro operation. This indicates that the residues were predominantly inorganic and contained large amounts of calcium and As carbonates (Azcue and Nriagu, 1995).

In the abandoned gold mine areas, a significant positive correlation was observed between pseudototal Pb and OC ($R = 0.77$, $p < 0.05$), clay ($R = 0.81$, $p < 0.05$), and pseudototal Fe ($R = 0.71$, $p < 0.05$) (Figure 1b). Chen *et al.* (2020) concluded that phenolic and carboxylic groups of SOM could complex Pb^{2+} with SOM, resulting in the formation of highly conjugated aggregates and elevation of molecular weight/size; however, this binding may be weakened by mining activity. Cai *et al.* (2016) found that the bioaccessibility of Pb decreased with increasing OM content due to their high affinity for each other. The correlations between pseudototal Pb and clay, and pseudototal Pb and pseudototal Fe confirm that the fine-grained soil fraction exhibits a greater tendency for PTEs adsorption than coarse-grained soils, due to the presence of soil particles with large surface areas, such as clay minerals, Fe and Mn oxyhydroxides, and humic acids (Dragovic *et al.*, 2008).

A Pearson analysis was performed for Brazilian and Canadian soils, and the correlations of As and Pb bioaccessibility with soil physicochemical properties are presented in Tables 5 and 6. Soil physicochemical properties, including soil pH, OC, and pseudototal As, Fe, and Mn contents, were reported to be important parameters controlling As bioaccessibility in As-enriched soils in previous studies (Juhasz *et al.*, 2007; Li *et al.*, 2014, Smith *et al.*, 2014; Sharmin *et al.*, 2020). A significant positive correlation was observed between As_{IVBA} and pseudototal As ($R = 0.86$, $P < 0.001$) and extractable Fe ($R = 0.57$, $P < 0.001$) in Brazilian agricultural soils (Table 5 and Figure 1a). Other authors also found a positive correlation between As bioaccessibility and its pseudototal level in the soil (Juhasz *et al.*, 2007; Sarkar *et al.*, 2007; Meunier *et al.*, 2010; Wang *et al.*, 2023). The positive correlation between As_{IVBA} and extractable Fe may indicate that the mineralogical properties of the soils in this area may be more important for As bioaccessibility than other physical and chemical soil properties (Ruby *et al.*, 1999; Juhasz *et al.*, 2007) and, thus, pose a health risk to animals and humans through accidental soil ingestion. While a significant positive correlation was observed between Pb_{IVBA} and pseudototal Pb ($R = 0.93$, $p < 0.001$), $\%Pb_{IVBA}$ ($R = 0.77$, $P < 0.01$), and pH ($R = 0.26$, $P < 0.01$) (Table 5 and Figure 1a). This indicates that pseudototal Pb is controlling bioaccessibility in these soils. Sanderson *et al.* (2012) also found a strong positive correlation between bioaccessible Pb and pseudototal Pb in soils with more acidic pH. Farmer *et al.* (2011) also found a strong significant correlation between gastric bioaccessible Pb concentrations and pseudototal Pb concentrations in soils. A significant negative correlation was found between Pb_{IVBA} and extractable Fe ($R = -0.20$, $P < 0.05$) (Figure 1a). This occurs mainly because Pb is a cationic element. Furthermore, Pb bound to Fe oxides is more potentially soluble (Lu *et al.*, 2011).

In Canadian soils, a significant negative correlation was observed between bioaccessible As and pseudototal Fe ($R = -0.64$, $p < 0.05$) and a positive correlation between bioaccessible As and pseudototal As ($R = 0.67$, $p < 0.05$) (Figure 1b). Hiller *et al.* (2022) also found a negative correlation between As_{IVBA} in the gastric phase and Fe oxides, due to the role of soil Fe/Mn oxides in sequestering these metals (loids) and reducing their bioaccessibility (Sun *et al.*, 2021). Meunier *et al.* (2010) reported that differences in As bioaccessibility in abandoned gold mine slag could be attributed to mineralogy and its dissolution tendency under low pH gastric conditions. There was a positive correlation between Pb_{IVBA} and OC ($R = 0.80$, $P < 0.05$), clay ($R = 0.72$, $P < 0.05$), and pseudototal Pb ($R = 0.84$, $P < 0.05$) (Figure 1b). Fernández-Landero *et al.* (2021) also found a strong positive correlation between pseudototal level and bioaccessible concentrations of As and Pb. This indicates that the amount of these geogenic PTEs that can be solubilized by gastric juice and, therefore, available to cause human health damage, significantly increased with increasing pseudototal concentrations of As and Pb in the soil.

Multivariate regression analysis was performed to describe As_{IVBA} as a function of soil properties, including pH, total As, Fe, Mn, OC, and clay. It was identified that pseudototal As and pseudototal Fe concentrations were the factors that best described the variation of As_{IVBA} (Eqs. 1). Juhasz *et al.* (2007) reported that total As concentration, as well as total and extractable Fe concentrations, were the factors that best described As bioaccessibility (mg kg^{-1}) in the soil.

Eqs. 1:

As_{IVBA} (mg kg^{-1}) = 9.953 + 0.060 AsT − 0.0002 FeT (mg kg-1) $R^2 = 0.7218$, $p < 0.05$

Table 5. Pearson correlation between pH, organic carbon (OC), extractable Fe and Mn contents, and total and bioaccessible levels of As and Pb in Brazilian soil samples, Paracatu-MG, Brazil.

	pH	*OC*	Extractable Fe	Extractable Mn	*AsT*	*AsIVBA*	*%AsIVBA*	*PbT*	*PbIVBA*	*%PbIVBA*
pH	1									
OC	0.26	1								
Extractable Fe	-0.30	0.16	1							
Extractable Mn	0.22	0.61	0.11	1						
AsT	0.04	0.01	**0.64****	0.05	1					
AsIVBA	0.11	0.05	**0.57****	0.09	**0.86****	1				
%AsIVBA	0.04	0.20	**-0.15****	0.01	**-0.31****	-0.17	1			
PbT	**0.32****	**-0.29****	**-0.22****	0.06	0.10	**0.18***	**-0.35****	1		
PbIVBA	**0.26***	-0.14	**-0.20***	0.16	0.05	0.15	**-0.30****	**0.93****	1	
%PbIVBA	0.13	0.13	**-0.20***	0.16	-0.03	0.08	**-0.21***	**0.55****	**0.77****	1

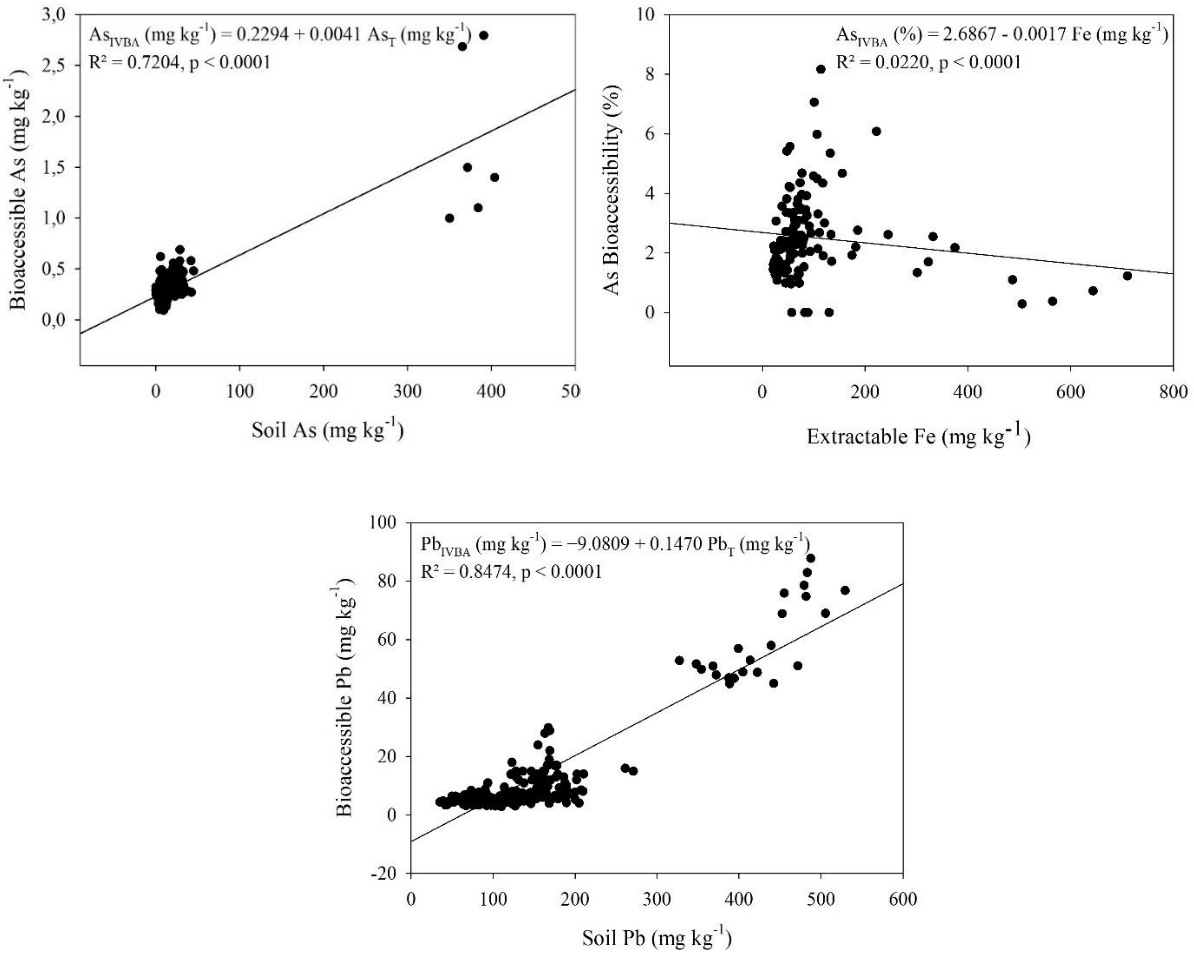
∗ Correlation is significant at the 0.05 level. ∗∗ Correlation is significant at the 0.01 level.

Table 6. Pearson correlation between pH, organic carbon (OC), extractable Fe and Mn contents, and total and bioaccessible levels of As and Pb in Canadian soil samples from the decommissioned Deloro Gold Mine in Marmora and Lake Municipality, Ontario, Canada.

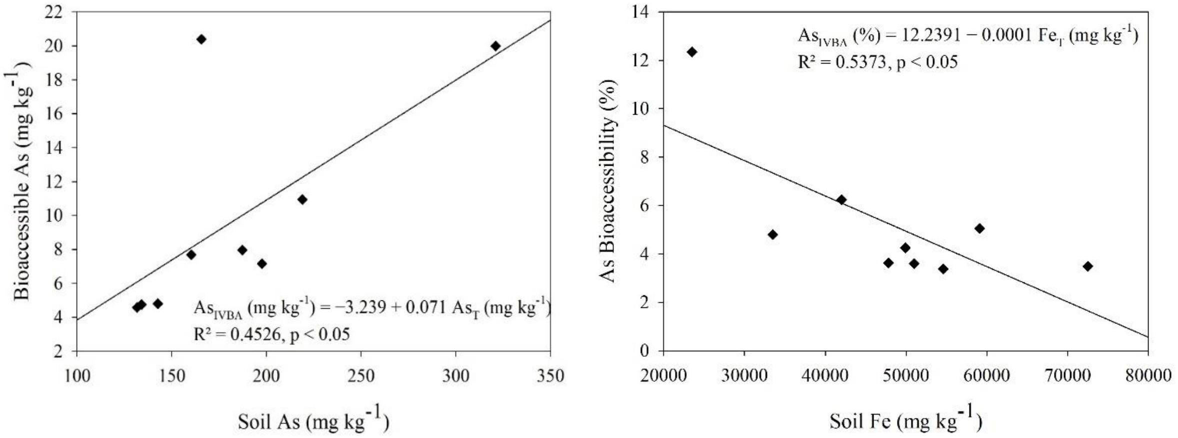
	pH	*OC*	*Clay*	*FeT*	*MnT*	*AsT*	*AsIVBA*	*%AsIVBA*	*PbT*	*PbIVBA*	*%PbIVBA*
pH	1										
OC	0.18	1									
Clay	-0.25	**0.79****	1								
FeT	0.11	0.31	0.52	1							
MnT	-0.01	0.24	0.43	**0.92****	1						
AsT	0.21	**0.70***	0.41	-0.20	-0.15	1					
AsIVBA	-0.13	0.08	-0.14	-0.64	-0.46	**0.67***	1				
%AsIVBA	-0.30	-0.37	-0. 49	**-0.73***	-0.54	0.18	**0.84***	1			
PbT	0.05	**0.77***	**0.81****	**0.71***	0.56	0.20	-0.49	**-0.78****	1		
PbIVBA	0.33	**0.80****	**0.72***	0.63	0.47	0.38	-0.28	-0.60	**0.84****	1	
%PbIVBA	0.14	-0.40	-0.60	-0.62	-0.50	0.09	0.63	**0.81****	**-0.78****	-0.36	1

∗ Correlation is significant at the 0.05 level. ∗∗ Correlation is significant at the 0.01 level.

a)


As$_{IVBA}$ (mg kg^{-1}) = 0.2294 + 0.0041 As$_T$ (mg kg^{-1})
R² = 0.7204, p < 0.0001
Bioaccessible As (mg kg^{-1})
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
100
200
300
400
50
Soil As (mg kg^{-1})
As$_{IVBA}$ (%) = 2.6867 - 0.0017 Fe (mg kg^{-1})
R² = 0.0220, p < 0.0001
As Bioaccessibility (%)
10
8
6
4
2
0
0
200
400
600
800
Extractable Fe (mg kg^{-1})
Pb$_{IVBA}$ (mg kg^{-1}) = −9.0809 + 0.1470 Pb$_T$ (mg kg^{-1})
R² = 0.8474, p < 0.0001
Bioaccessible Pb (mg kg^{-1})
100
80
60
40
20
0
-20
0
100
200
300
400
500
600
Soil Pb (mg kg^{-1})

b)


Bioaccessible As (mg kg^{-1})
22
20
18
16
14
12
10
8
6
4
2
As$_{IVBA}$ (mg kg^{-1}) = −3.239 + 0.071 As$_T$ (mg kg^{-1})
R² = 0.4526, p < 0.05
100
150
200
250
300
350
Soil As (mg kg^{-1})
As$_{IVBA}$ (%) = 12.2391 − 0.0001 Fe$_T$ (mg kg^{-1})
R² = 0.5373, p < 0.05
As Bioaccessibility (%)
14
12
10
8
6
4
2
0
20000
30000
40000
50000
60000
70000
80000
Soil Fe (mg kg^{-1})

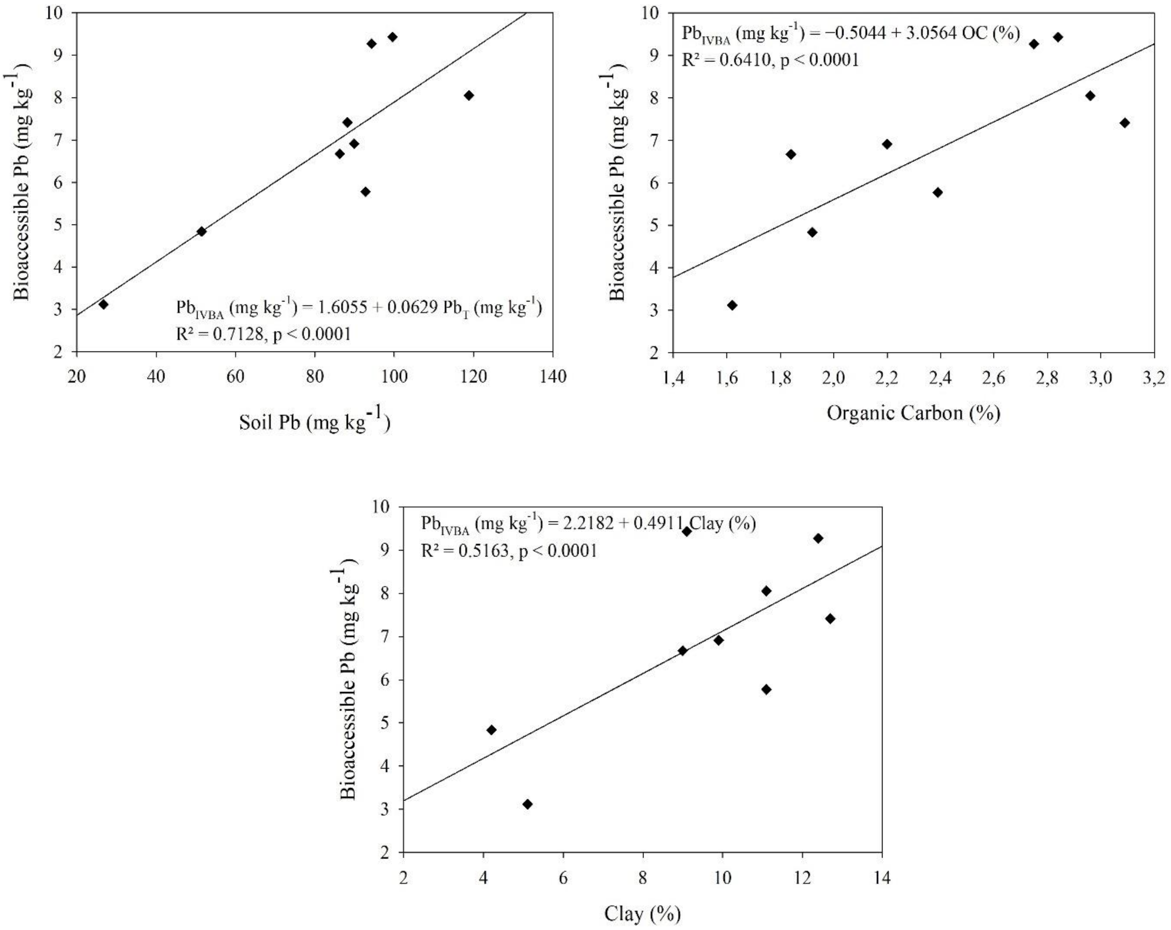


Figure 1 Linear regression (a) between bioaccessible As and soil pseudototal As. and bioaccessible Pb and soil pseudototal Pb in Brazilian soil samples. and (b) between bioaccessible As and soil pseudototal As and bioaccessible Pb and soil pseudototal Pb in Canadian soil samples. Where: circles represent Brazilian soil samples and diamonds represent Canadian soil samples.

3.5.Chronic daily intake and risk assessment

Values of CR > 10^{-5} and HQ > 1 indicate a significant risk of toxic outcomes from As (Bari *et al.*, 2021). CR was only calculated for As. The values of CDI and HQ for *in vitro* assays (SBRC) of As and Pb for each of the agricultural soils and the abandoned mine are presented in Table 7. The carcinogenic dose received by accidental ingestion of Brazilian agricultural soil ranged from 2.51x 10^{-6} to 1.80 x10^{-5} mg kg^{-1} day^{-1} for children and from 2.87 x10^{-7} to 2.06 x 10^{-6} mg kg^{-1} day^{-1} for adults. The CR values for agricultural soils were unacceptable only for children in RA2 and followed the following decreasing order: RA2 > CA3 > CA4 > RA3 > CA2 > CA6 > RA1 > CA1 > CA5 > RA4 (Figure 2). Feitosa *et al.* (2021) used only pseudototal

As concentrations in the calculations of carcinogenic risks for these same agricultural areas in Brazil and found high carcinogenic levels for children and adults in most of the areas studied. Thus, we can conclude that the incorporation of bioaccessible concentrations in risk calculations allows for a more accurate assessment of the risk resulting from oral exposure on a site-specific basis.

For the abandoned mine soils, the carcinogenic dose received by accidental soil ingestion ranged from 7.1×10^{-5} to 4.5×10^{-4} mg kg^{-1} day^{-1} for children and from 8.1×10^{-6} to 5.1×10^{-5} mg kg^{-1} day^{-1} for adults, resulting in occupational CR values exceeding the regulatory value of 1.0×10^{-5} at most sampling locations in the mine (Figure 2). The CR values for Canadian soils followed the following decreasing order: #4 > #21 > #23 > #5 > #3 > #28 > #11 > #2 > #10 > #1 (Figure 2). The CR values for Canadian mine soils were unacceptable for children and adults from all Canadian soil samples, except for adults from areas #1, #2, and #10. Bari *et al.* (2021) assessed As exposure risk levels in soils from an abandoned mine in Australia and confirmed that bioaccessible As levels also had the potential to cause both cancerous and non-cancerous diseases. However, they concluded that the relationship between bioaccessible concentrations and mineral form is an important factor in controlling risk and management pathways in abandoned mines. In the abandoned mine soils of the present study, the bioaccessibility of As is likely linked to Fe minerals, as seen in Figures 1a and 1b, where bioaccessible As concentrations are inversely proportional to total Fe concentrations in mine soil.

The Chronic Daily Intakes (CDIs) and Hazard Quotients (HQs) of As and Pb for oral exposure in children and adults in samples of agricultural and mine soils are presented in Table 7. For non-cancer effects, the HQ value for As in sample #4 (HQ = 1.00) from the abandoned mine was the only one among all areas that slightly reached the permissible risk in children (Table 7). Adverse health effects through Pb exposure should not occur, as the HQ value for this metal was within acceptable levels for toxic effects in all soil samples from Brazil and Canada. Fernández-Landero *et al.* (2021) assessed soils with As and Pb geological anomalies in Spain and found low levels of carcinogenic risk for these trace elements, suggesting that the standard exposure assumption may overestimate exposure to geogenic trace elements.

The results also indicated that the daily intake of As and Pb was significantly different among the different land uses sampled (Table 7). The CDI, HQ, and CR values for As were significantly higher in abandoned mine areas in Canada than in agricultural areas in Brazil. Therefore, the potential risk of As in soil to human health is higher in mining areas, mainly due to its material source and land use. However, CDI and HQ for Pb exhibited opposite behavior in different soil uses, with the highest values in agricultural areas. Overall, our data reveal that one area of Brazilian soils (RA2) and all Canadian mine areas confirm bioaccessible levels of As with the potential to trigger cancer, as the CR values exceeded the As threshold values (Figure 2a). Therefore, the overall risk of As causing cancer for children and adults when exposed to abandoned mine areas is high (Figure 2b). However, the population does not have free access to the area of this abandoned mine, and consequently, there is no risk to human health due to the absence of exposure. Meanwhile, for Pb, the non-carcinogenic risk is very low for both soils. Thus, we can conclude that differences in the geological origin of each soil and its type of use should be considered in risk assessment and remediation approaches.

Table 7. Average daily dose exposure to As and Pb via oral ingestion (CDI), and health risk quantification reported as non-carcinogenic hazard quotient (HQ) and hazard index (HI)

Canadian soil	**As**				**Pb**			
	Children		**Adult**		**Children**		**Adult**	
	CDI	**HQ**	**CDI**	**HQ**	**CDI**	**HQ**	**CDI**	**HQ**
#1	4.7E-05	0.16	5.4E-06	0.02	7.1E-05	0.003	8.1E-06	0.0003
#2	4.9E-05	0.16	5.6E-06	0.02	6.9E-05	0.003	7.8E-06	0.0003
#3	8.2E-05	0.27	9.3E-06	0.03	9.5E-05	0.004	1.1E-05	0.0004
#4	3.0E-04	**1.00**	3.4E-05	0.11	4.1E-05	0.002	4.7E-06	0.0002
#5	1.1E-04	0.38	1.3E-05	0.04	9.7E-05	0.004	1.1E-05	0.0004
#10	4.9E-05	0.16	5.6E-06	0.02	5.9E-05	0.002	6.8E-06	0.0003
#11	7.4E-05	0.25	8.4E-06	0.03	8.3E-05	0.003	9.5E-06	0.0004
#21	2.1E-04	0.70	2.4E-05	0.08	3.2E-05	0.001	3.7E-06	0.0001
#23	2.1E-04	0.68	2.3E-05	0.08	7.6E-05	0.003	8.7E-06	0.0003
#28	7.9E-05	0.26	9.0E-06	0.03	5.0E-05	0.002	5.7E-06	0.0002

Brazilian soil (0-5cm)	**As**				**Pb**			
	Children		**Adult**		**Children**		**Adult**	
	CDI	**HQ**	**CDI**	**HQ**	**CDI**	**HQ**	**CDI**	**HQ**
CA1	2.51E-06	0.01	2.87E-07	0.001	7.19E-05	0.003	8.22E-06	0.000
CA2	3.06E-06	0.01	3.50E-07	0.001	7.25E-05	0.003	8.29E-06	0.000
CA3	5.38E-06	0.02	6.15E-07	0.002	6.56E-04	0.026	7.49E-05	0.003
CA4	3.96E-06	0.01	4.53E-07	0.002	1.90E-04	0.008	2.17E-05	0.001
CA5	2.19E-06	0.01	2.50E-07	0.001	4.60E-05	0.002	5.26E-06	0.000
CA6	2.68E-06	0.01	3.07E-07	0.001	7.60E-05	0.003	8.69E-06	0.000
RA1	2.60E-06	0.01	2.97E-07	0.001	4.56E-05	0.002	5.21E-06	0.000
RA2	1.20E-05	0.04	1.37E-06	0.005	5.74E-05	0.002	6.56E-06	0.000
RA3	3.57E-06	0.01	4.08E-07	0.001	1.61E-04	0.006	1.84E-05	0.001
RA4	1.68E-06	0.01	1.92E-07	0.001	4.95E-05	0.002	5.66E-06	0.000

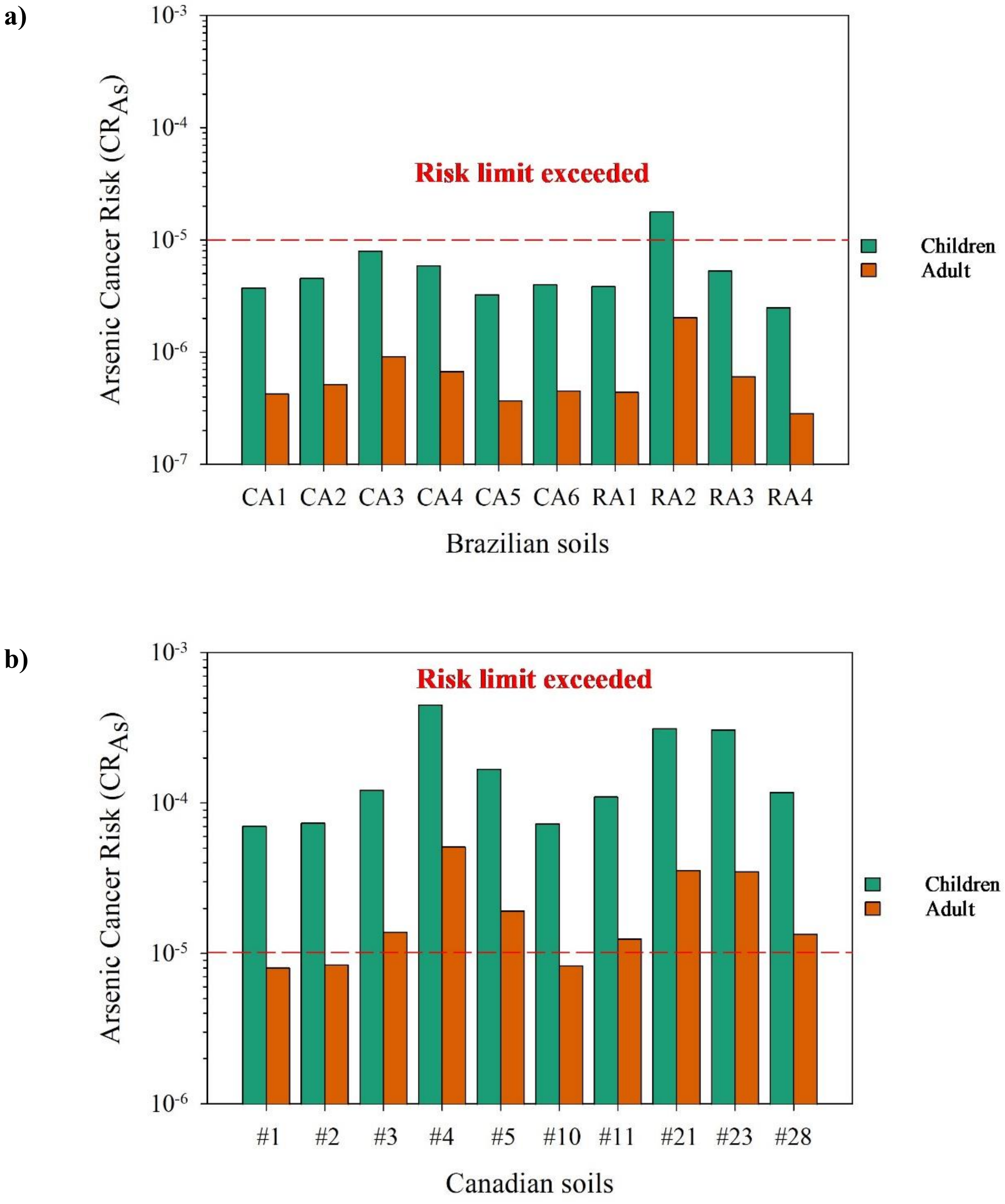


Figure 2 Occupational cancer risk values associated with As exposure (a) in Brazilian soil samples, and (b) in Canadian soil samples. The dashed lines indicate the regulatory limits to risk management.

4. Conclusions

The results presented in this study highlight that the bioaccessibility of As and Pb in soils is significantly low. Although the high pseudototal concentrations of As and Pb found in Brazilian agricultural soils and mining areas in Canada indicate extensive accumulation of these elements due to pedogenetic processes, these values do not adequately reflect the true risk to the health of the local population. The inclusion of bioaccessible data in risk calculations has allowed for a more precise assessment of the potential for oral exposure on a specific local basis.

The assumption that 100% of As and Pb present in the soil are bioavailable results in an overestimation of the potential risk of exposure to As and Pb in agricultural and mining soils, which can have a significant impact on remediation and management decisions. While the bioaccessibility of As and Pb can be predicted by soil properties in both land uses, all prediction equations should be subsequently validated.

Exposure to bioaccessible levels of As in relation to carcinogenic effects and As and Pb hazard indices for non-carcinogenic effects remains within acceptable levels, suggesting that no health risks are expected in any of the sampled areas. Therefore, *in vivo* bioavailability tests are essential to validate bioaccessibility tests, such as the SBRC, refining our understanding of human exposure and associated risks.

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THIRD PART - FINAL CONSIDERATIONS

This study aimed to evaluate the environmental and human health risks associated with elevated levels of arsenic (As) and lead (Pb) in soils from agricultural areas in Paracatu (MG), Brazil, and an abandoned gold mine in Marmora and Lake (ON), Canada. The results indicated that despite the high pseudototal concentrations of As and Pb, the bioaccessibility of these elements is relatively low. This suggests that assessments based solely on total concentrations may overestimate health risks, highlighting the importance of including bioaccessibility in risk calculations.

In Paracatu, As levels in plant tissues were below the detection limit, reinforcing the low mobility and bioaccessibility of As in these agricultural areas. However, in the mining areas in Canada, a carcinogenic risk of As was identified for both adults and children, demonstrating the need for continuous monitoring and specific interventions.

There was variation in the bioaccessibility of As and Pb between different areas and soil types, influenced by properties such as iron (Fe) content. This underscores the need to consider these variables in the development of risk management and mitigation strategies. The main limitation of the research was the mineralogical characterization of the soils, which is necessary for a deeper discussion of the data.

It is recommended to apply a correction factor of 10% for As bioaccessibility in Brazilian agricultural soils with high Fe content to adjust exposure and risk estimates more accurately. The next step in the research is to conduct *in vivo* bioavailability tests to validate oral bioaccessibility assays. These actions are essential for developing effective environmental management strategies and public health protection, contributing to a more precise risk assessment.