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

TESE DE DOUTORADO Nº 152

ELEMENTOS TERRAS RARAS, U, Th E ELEMENTOS POTENCIALMENTE TÓXICOS EM AGROECOSSISTEMAS COM USO DE FERTILIZANTES NO NORDESTE DO PARÁ

Tese apresentada por:

ANDERSON MARTINS DE SOUZA BRAZ
Orientador: Prof. Dr. Marcondes Lima da Costa (UFPA)

BELÉM
2020

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Sistema de Bibliotecas da Universidade Federal do Pará
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S719e Souza Braz, Anderson Martins de
Elementos terras raras, U, Th e elementos potencialmente tóxicos em agroecossistemas com uso de fertilizantes no nordeste do Pará / Anderson Martins de Souza Braz. — 2020.
xiv, 84 f. : il. color.

Orientador(a): Prof. Dr. Marcondes Lima da Costa
Tese (Doutorado) - Programa de Pós-Graduação em Geologia e Geoquímica, Instituto de Geociências, Universidade Federal do Pará, Belém, 2020.

1. Lantanídeos. 2. Química do Solo. 3. Fator de Enriquecimento. 4. Fator de Bioacumulação. 5. Amazônia Oriental. I. Título.

CDD 631.41

Universidade Federal do Pará
Instituto de Geociências
Programa de Pós-Graduação em Geologia e Geoquímica

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TESE APRESENTADA POR:

ANDERSON MARTINS DE SOUZA BRAZ

Como requisito parcial à obtenção do Grau de Doutor em Ciências na Área de GEOQUIMICA E PETROLOGIA, Linha de Pesquisa MINERALOGIA E GEOQUIMICA

Data da aprovação: 30 / 11 / 2020

Banca examinadora:

Prof. Dr. Marcondes Lima da Costa
(Orientador – UFPA)

Prof.ª Dr.ª Edna Santos de Souza
(Membro – UNIFESSPA)

Prof. Dr. Antonio Carlos de Azevedo
(Membro – USP)

Prof. Dr. Francisco de Assis Oliveira
(Membro – UFRA)

Prof. Dr. Rômulo Simões Angélica
(Membro – UFPA)

Dedico esse trabalho à minha mãe,
Maria Joana Martins da Silva,
fonte de inspiração e exemplo de vida,
amor, coragem e dedicação.

AGRADECIMENTOS

A **Deus** por ter abençoado e dado forças em todos os momentos dessa jornada.

À minha família que sempre me apoiou em todos os momentos.

Ao Prof. Dr. Marcondes Lima da Costa, pela orientação, por seus ensinamentos e amizade, por todos os momentos de descontrações e puxões de orelha. Tenho por ele um grande apreço e gratidão.

Ao Programa de Pós-Graduação em Geologia e Geoquímica da Universidade Federal do Pará (PPGG-UFPA), por meio dos seus professores e funcionários, pela oportunidade de crescimento profissional e apoio técnico em todas as fases do curso. Em especial à Cleida por sua amizade e paciência em toda as fases dessa vida acadêmica, facilitando tudo o que estava nas suas possibilidades e atribuições.

À Universidade Federal Rural da Amazônia pela liberação para o doutoramento e apoio por meio da Pró-Reitoria de Pesquisa e Desenvolvimento Tecnológico, Prodoutoral - 04/2017 (PROPED-UFRA).

Ao Prof. Dr. Antonio Rodrigues Fernandes, Universidade Federal Rural da Amazônia, pela amizade incondicional e imprescindível apoio para a realização deste trabalho.

Ao Dr. Silvio Junio Ramos, Instituto Tecnológico Vale, pela amizade, colaboração analítica e revisões dos artigos deste trabalho.

Às novas amizades adquiridas na Universidade Federal do Pará: Profa. Dra. Rosemery da Silva Nascimento, Srs. Ubirajara Fernandes Kimmemgs e Milson Edmar da Silva Xavier.

Aos amigos e membros do Grupo de Pesquisa em Geologia e Geoquímica Aplicada – GMGA/UFPA, pelo convívio.

"Tudo o que tenho (de valor) trago comigo."
(*Omnia Mea Mecum Porto*)
Bias de Priene (Séc. 6 a.C.)

RESUMO

A região amazônica é a última fronteira agrícola do Brasil e os aumentos da demanda por alimentos e fontes energéticas renováveis têm intensificado a pressão de uso do solo. O estado do Pará é um dos maiores produtores mundiais de dendê e pimenta do reino, sendo a mesorregião do Nordeste Paraense responsável pela produção anual de 1.634.476 toneladas de dendê, 39.577 toneladas de pimenta do reino e 286.768 toneladas de laranja, o que representa 97, 50 e 2% da produção nacional. Os solos da Amazônia, para expressarem o alto potencial agrícola, demandam altas taxas de aplicação de fertilizantes. Contudo, as matérias primas utilizadas na produção de insumos agrícolas também são fontes de contaminação do solo. Assim, estudos que facilitem o entendimento da dinâmica de elementos terras raras (ETRs) e outros metais/metaloides nos solos da região são relevantes. E, partindo da premissa que a ação antrópica, principalmente através das atividades agrícolas, tem provocado incrementos significativos nos teores destes elementos em solos, objetivou-se avaliar (i) as concentrações de ETRs e outros metais em agroecossistemas amazônicos de citricultura, dendeicultura e pipericultura, com 26, 10 e 5 anos de implantação, respectivamente; (ii) determinar os índices de contaminação como, o fator de enriquecimento e de bioacumulação e; (iii) estabelecer/discutir relações com as propriedades dos solos. Os resultados mostraram: (i) ETRs são extremamente correlacionados ao pH do solo; (ii) o európio (Eu) apresentou o maior fator de bioacumulação dentre os ETRs; (iii) as concentrações de atividade de ^{238}U e ^{232}Th no solo cultivado com pimenta do reino foram superiores à média mundial de ^{238}U (35 Bq kg^{-1}) e ^{232}Th (30 Bq kg^{-1}) conforme estabelecido pelo Comitê Científico das Nações Unidas sobre os Efeitos da Radiação Atômica (UNSCEAR); (iv) fatores de enriquecimento (FE) moderados de Ba, Pb e Zn (2 > FE < 5) e significativos para As e Cu (5 > FE < 20); (v) as seguintes ordens de bioacumulação: dendê - Cu > Zn > Hg > Ni > Ba > Co > As > Cr > Cd ≈ Pb; pimenta do reino - Zn > Hg > Cu > Ba > Ni > Co > Pb >> As > Cr > Cd; laranja - Hg > Ni > Ba > Zn > Co > Cu > As > Pb >> Cr > Cd. Nesse contexto, este é o primeiro estudo avaliando a absorção de ETRs por culturas amazônicas de grande importância para os mercados globais. Uma relevante contribuição para prever o acúmulo de contaminantes em solos resultante de atividades antrópicas, principalmente, em regiões de importância agrícola e de vulnerabilidade ambiental como o bioma Amazônia.

Palavras-chave: Lantanídeos. Química do Solo. Fator de Enriquecimento. Fator de Bioacumulação. Amazônia Oriental.

ABSTRACT

The Amazon region is the last agricultural frontier in Brazil and the increasing demand for food and renewable energy sources has intensified the pressure on land use. The Pará state is one of the world's largest producers of oil palm and black pepper, being the mesoregion Northeast Paraense responsible for the annual production of 1,634,476 tons of oil palm, 39,577 tons of black pepper and 286,768 tons of oranges, which represents 97, 50 and 2% of the Brazilian production. The Amazon soils, to express the high agricultural potential, demand high rates of fertilizer application. However, the raw materials used in the production of agricultural inputs are also sources of soil contamination. Thus, studies that facilitate the understanding of the dynamics of rare earth elements (REEs) and other metals / metalloids in the region's soils are relevant. And, based on the premise that anthropic action, mainly through agricultural activities, has caused significant increases in the levels of these elements in soils, the objective was to evaluate (i) the REEs concentrations and other metals in Amazon agroecosystems of orange, oil palm and black pepper, with 26, 10 and 5 years of implantation, respectively; (ii) determine the contamination rates, such as the enrichment and bioaccumulation factors and; (iii) establishing / discussing relationships with soil properties. The results showed: (i) REEs are extremely correlated to soil pH; (ii) the europium (Eu) presented the largest bioaccumulation factor among the REEs; (iii) the activity concentrations of ^{238}U and ^{232}Th in soil with black pepper cultivation were higher than the world average of ^{238}U (35 Bq kg^{-1}) and ^{232}Th (30 Bq kg^{-1}) according established by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR); (iv) moderate enrichment factors (EFs) for Ba, Pb and Zn (2> EF <5) and significant for As and Cu (5> EF <20); (v) the following orders of bioaccumulation: oil palm - Cu> Zn> Hg> Ni> Ba> Co> As> Cr> Cd ≈ Pb; black pepper - Zn> Hg> Cu> Ba> Ni> Co> Pb >> As> Cr> Cd; orange - Hg> Ni> Ba> Zn> Co> Cu> As> Pb >> Cr> Cd. In this context, this is the first study evaluating the absorption of REEs by Amazonian crops of great importance for global markets. A relevant contribution to predict the accumulation of contaminants in soils resulting from anthropic activities, especially in regions of agricultural importance and environmental vulnerability such as the biome Amazon.

Keywords: Lanthanides. Soil Chemistry. Enrichment Factor. Bioaccumulation Factor. Eastern Amazon.

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1.1 APRESENTAÇÃO

Os solos da região Amazônica são naturalmente heterogêneos devido à diferença na composição do material de origem e dos processos pedogenéticos que atuaram em sua formação (Quesada et al. 2010; 2020), resultando em alterações nos atributos morfológicos, físicos, químicos e mineralógicos (De Souza et al. 2018). As principais atividades econômicas no estado do Pará e na Amazônia incluem a agricultura, pecuária, produção de vegetais e extração mineral (Bowman et al. 2012; De Souza et al. 2013). Estas atividades podem causar distúrbios significativos no funcionamento dos ecossistemas e, além da contaminação dos solos, oferecer riscos à saúde pública (De Souza Braz et al. 2013; Birani et al. 2015).

A mesorregião do Nordeste do estado do Pará que compreende cinco microrregiões (Bragantina, Cametá, Guamá, Salgado e Tomé-Açu) e 49 municípios (Figura 1), corresponde a produção anual de 1.634.476 toneladas de dendê, 39.577 toneladas de pimenta do reino e 286.768 toneladas de laranja, o que representa 97, 50 e 2% da produção nacional (IBGE, 2017). E a demanda crescente em relação à produção de alimentos e geração de energia, associada ao apelo da sociedade contra o desflorestamento da Amazônia para abertura de novas áreas agrícolas, tem intensificado o uso de fertilizantes com vistas a aumentar a produtividade. As matérias-primas utilizadas na produção de adubos fosfatados e de micronutrientes podem conter diversos elementos químicos, os quais, dependendo da quantidade e do tempo de aplicação, podem ser tornar preocupação ambiental (Smidt et al. 2011; Bosco-Santos et al. 2017; Vieira da Silva et al. 2017; Michalak et al. 2018).

Os elementos terras raras (ETRs) se referem, literalmente, a um grupo de 17 elementos, incluindo os 15 lantanídeos, escândio e o ítrio (IUPAC, 2005). A importância econômica dos ETRs decorre da especificidade de suas propriedades químicas, magnéticas e de fluorescência (Mello et al. 1994). Considerando que a demanda pelos ETRs vem se intensificando, devido ao uso diversificado em setores de alta tecnologia, a contaminação ambiental pelo uso generalizado desses elementos tende a aumentar (Migaszewski; Gałuszka, 2015). E, devido a relação entre a adubação fosfatada com ETRs (Turra et al. 2011), pode-se supor acumulação destes no solo. Moreira et al. (2015), observaram que aplicações de fertilizantes fosfatados (560 kg P_2O_5 ha^{-1}), em solo cultivado com batata, foram suficientes para elevar as concentrações de La e Ce em 81% e 111%, respectivamente, quando comparados com os solos não cultivados (mata nativa).

A aplicação de adubos com ETRs vem sendo defendida para aumentar o crescimento e a produtividade das plantas (Diatloff et al. 1995; Challaraj et al. 2010), no entanto, este efeito ainda não é claro (Tyler, 2004; Shi et al. 2006). Por outro lado, a acumulação de ETRs no solo pode ter um efeito tóxico sobre a macrofauna (Li et al. 2010) e microfauna (Xu; Wang, 2001; Chu et al. 2001). Além disso, a aplicação excessiva na agricultura pode causar efeitos prejudiciais aos seres humanos por bioacumulação ao longo da cadeia alimentar (Kawagoe et al. 2005; Feng et al. 2006; Li et al. 2013).

No entanto, a composição química dos fertilizantes fosfatados também contêm radioelementos (Mazzilli et al. 2000; Yamazaki et al. 2003; Saueia et al. 2005). Becegato et al. (2008) observaram aumentos na concentração de Th (0,02 a 0,69 mg kg^{-1}) em solos agrícolas e relacionados ao uso de fertilizantes fosfatados. Aumento das concentrações de U no horizonte superficial do solo, devido às aplicações contínuas de fertilizantes químicos, foram observados em vários estudos (Rothbaum et al. 1979; Stojanovic et al. 2006; Takeda et al. 2006; Tunney et al. 2009; Yamaguchi et al. 2009). Além disso, a disposição de resíduos sólidos e a aplicação de pesticidas e fertilizantes podem aumentar a concentração dos chamados elementos potencialmente tóxicos (EPTs), por exemplo Pb, Cd e Hg, em solos e águas subterrâneas com potencial de risco e toxicidade ao ambiente e à saúde humana (Dutra et al. 2019; Jú et al. 2019; Parameswari et al. 2019; Qian et al. 2019). Embora os EPTs ocorram naturalmente, fontes antropogênicas contribuem para o aumento das taxas de redistribuição desses elementos entre os compartimentos do ambiente (Gong et al. 2019; Li et al. 2019).

Nesse sentido, agências comprometidas com a preservação ambiental fazem uso de modelos e técnicas de normalização com o propósito de distinguir as ocorrências naturais desses elementos químicos em solos e as fontes antropogênicas (Cetesb, 2005; Martinez-Lladó et al. 2008; Lado et al. 2008; Conama, 2009; Nael et al. 2009). Além disso, estudos científicos contribuem para estabelecer valores de background (naturais) e podem também ser utilizados para aferir se ocorre possíveis alterações antropogênica (Fernandes et al. 2018; Salomão et al. 2019; Sahoo et al. 2020).

O fator de enriquecimento (FE) é uma estimativa amplamente utilizada para avaliar os efeitos da atividade antrópica no aumento da concentração destes elementos químicos em solos, obtido a partir da razão entre a concentração do elemento químico de interesse em solo cultivado e a concentração natural ou nível de fundo (Loska et al. 1997; 2004; Blaser et al. 2000; Cortizas et al. 2003; Tijani et al. 2006; Dragovic´ et al. 2008; Nael et al. 2009; Muñoz-Barbosa et al. 2012; Likuku et al. 2013). E também o fator de bioacumulação (FBA) que correlaciona as concentrações de elementos químicos nos tecidos vegetais e o total no solo (Galhardi et al. 2020). Sendo o FBA considerado uma das variáveis de entrada mais importantes na avaliação de riscos para a saúde humana (Khan et al. 2015).

Nesse sentido, o estabelecimento de padrões de qualidade em solos, impõe-se no contexto como uma excelente ferramenta para identificar e monitorar áreas contaminadas, de modo a fornecer uma orientação quantitativa em estudos de avaliação de risco, e na tomada de decisão nas questões de remediação, reciclagem e disposição de resíduos em solos. Independentemente das questões técnicas e políticas, o tema poluição do solo vem, cada vez mais, tornando-se motivo de preocupação para a sociedade e para as autoridades, devido não só aos aspectos de proteção à saúde pública e ao meio ambiente, mas também à publicidade dada aos relatos de episódios críticos de poluição por todo o mundo.

Assim, partindo da hipótese que a ação antrópica, principalmente através das atividades agrícolas, tem provocado incrementos significativos na concentração de potenciais contaminantes químicos em solos, e que suas concentrações em solos cultivados são bons indicadores de alteração e vulnerabilidade ambiental.

1.2 OBJETIVOS

Geral:

Utilizar os ETRs, U, Th e EPTs como indicadores de qualidade do solo, em solos representativos da mesorregião do Nordeste Paraense, e estabelecer relações com o manejo, as culturas e os atributos dos solos.

Específicos:

i. Avaliar as concentrações de ETRs, U, Th e EPTs em solos agrícolas que receberam aplicações de fertilizantes por 26, 10 e 5 anos, nas lavouras de laranja, dendê e pimenta-do-reino, respectivamente;

ii. Estabelecer / discutir correlações entre ETRs, U, Th e EPTs com os atributos do solo e;

iii. Determinar os fatores de enriquecimento e bioacumulação nos agroecossistemas amazônicos de cultivo de laranja, pimenta-do-reino e dendê.

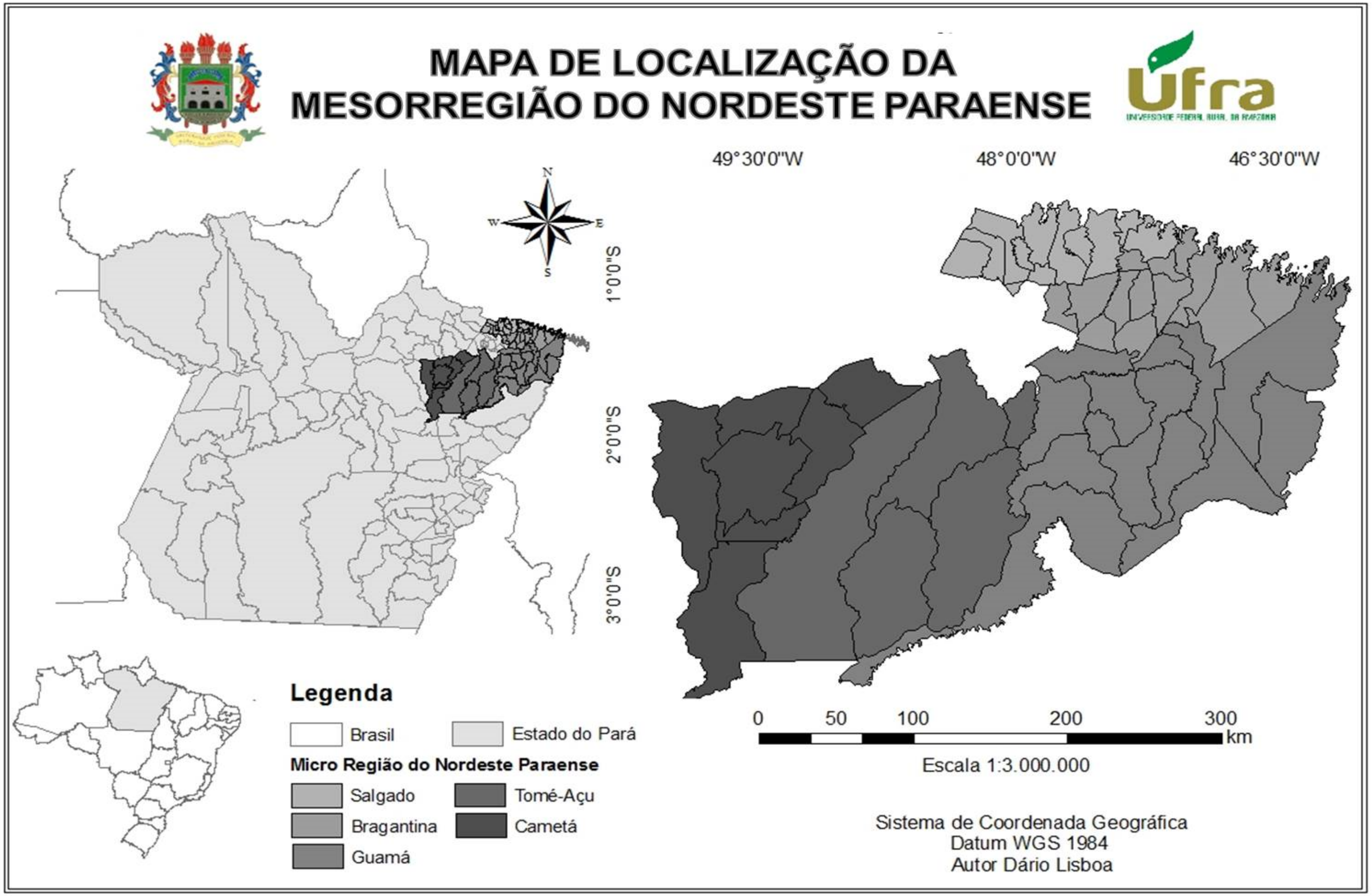


Figura 1. Mapa de localização do estado do Pará, destacando-se a mesorregião Nordeste Paraense com suas microrregiões.

CAPÍTULO 2 - MATERIAIS E MÉTODOS

2.1 ÁREA DE ESTUDO E AMOSTRAGEM DE SOLOS E PLANTAS

Para o desenvolvimento do presente trabalho foram amostrados solos (Argissolos e Latossolo) em plantios comerciais de laranja (*Citrus sinensis* (L.) Osbeck), com 26 anos de implantação; dendê (*Elaeis guineensis* Jacq.), com 10 anos de implantação e; pimento do reino (*Piper nigrum* L.), com 5 anos de implantação (Figuras 1 a 3).

Na implantação do pomar de laranja foram utilizados: 3 kg de esterco de ave e 60g de P_2O_5 (superfosfato simples), por cova, e 60g de N (uréia) e 30g K_2O (cloreto de potássio), por planta; do segundo ao quinto ano foram aplicados 200g de N, 90g de P_2O_5 e 180g de K_2O por planta; a partir do sexto ano teve início a adubação de produção com 80 kg ha^{-1} de N, 20 kg ha^{-1} de P_2O_5 e 40 kg ha^{-1} de K_2O; também foi aplicado o fungicida cúprico, conhecido como calda bordalesa ($CuSO_4$ + $Ca(OH)_2$).

Figura 1. Plantio de laranja, implantado em 1993, no município de Capitão Poço-PA (01°48'08,7"S e 47°11'55,7"W – elevação 69m).

O histórico da área de cultivo de dendê foi: aplicação no plantio de 23 kg ha^{-1} de fosfato natural reativo de Arad (33% de P_2O_5), seguido da formulação N-P-K (11-07-23) + 2,5% Mg +

0,5% B; com aplicações anuais da fórmula N-P-K (10-07-22). Para a implantação do cultivo de pimenta do reino foram utilizados 1,5 kg de esterco de ave + 500g de termofosfato (Yoorin), 17,5 % de P_2O_5, por cova; no primeiro e segundo ano foram aplicados 50g de uréia, 45g de superfosfato triplo e 30g de cloreto de potássio, por planta; a partir do terceiro ano foram aplicados 150g de uréia, 60g de superfosfato triplo e 100g de cloreto de potássio, por planta; a calda bordalesa também foi utilizada no controle de pragas na pipericultura.

Figura 2. Plantio de dendezeiro (A), fragmento de floresta remanescente (B) no município de Moju-PA (02°13'17,7"S e 48°47'52,4"W – elevação 21m).

Em cada área de plantio, os solos foram amostrados na camada de 0-20 cm de profundidade, em que 10 amostras simples foram realizadas para formar uma amostra composta, com três repetições, perfazendo um total de 30 amostras simples e 10 amostras compostas por plantio. Também, foram coletadas amostras de solos em áreas adjacentes aos plantios, composta por com vegetação nativa ou recuperada naturalmente (denominadas regionalmente de capoeiras), para fins de comparação e obtenção do fator de enriquecimento (FE).

Figura 3. Argissolo Amarelo distrófico com plantio de pimenta-do-reino (A) e (B), fragmento de floresta remanescente (C), (D) e (E) no município de Capitão Poço-PA (01°47'07,1"S e 47°04'06,8"W – elevação 59m)

Coletou-se amostras de plantas nos mesmos pontos da coleta de solo, para verificar a capacidade de bioacumulação pelas culturas. A amostragem de folhas nos plantios de pimenta-do-reino e laranja, consistiu em coletar folhas recém maduras, na porção do terço médio da copa por planta útil, no sentido Norte, Sul, Leste e Oeste (Oliveira; Cruz, 1999; Dias et al. 2013). Para as plantas de dendê, a partir do terceiro ou quarto ano de plantio, a amostragem foi realizada na folha nº 17 (do ápice para a base) (Figura 4), sendo considerada como a que melhor expressa o estado fisiológico ideal do dendezeiro (Rodrigues et al. 2006).

Figura 4. Amostragem de folíolos centrais da folha nº 17 de dendezeiro no município de Moju-PA (02°13'17,7"S e 48°47'52,4"W – elevação 21m).

2.2 CARACTERIZAÇÃO DO SOLO

As análises físico-químicas das amostras de solos foram realizadas de acordo com Embrapa (2011): pH em água e em solução de KCl 1 mol L^{-1} (1:2,5); Ca e Mg extraídos com solução de KCl 1 mol L^{-1} e quantificados por espectrofotometria de absorção atômica; K foi extraído com solução de HCl 0,05 mol L^{-1} e quantificado por fotometria de chama; P disponível extraído com solução de HCl 0,05 mol L^{-1} + H_2SO_4 0,0125 mol L^{-1} (Mehlich-1) e determinado por colorimetria; a determinação do carbono orgânico pelo método Walkley & Black de combustão por via úmida com dicromato de potássio; concentração de Al_2O_3 total no solo por ataque sulfúrico; e teor de argila (Gee; Bauder, 1986). A determinação de P_2O_5 foi por espectrômetro de fluorescência de raios-X, Rigaku modelo RIX 3000.

2.3 QUANTIFICAÇÃO E METODOLOGIA ANALÍTICA

2.3.1 Elementos terras raras

As amostras de solo e tecido das plantas foram secas ao ar e moídas para passar por uma peneira de náilon 150 mesh. Todas as amostras foram digeridas por meio de um método de fusão alcalina. Resumindo: uma alíquota de 0,1 g de cada amostra foi fundida com 1,4 g de metaborato de lítio em cadinhos de platina a 1000 °C em uma máquina de fusão (Fluxer BIS, Claisse, Québec, Canadá). Após o resfriamento, o grânulo resultante foi dissolvido em béqueres contendo 50 mL de uma solução de ácido tartárico a 2,5% e HNO_3 a 10%. Cada copo foi então transferido para uma placa quente a 120 ± 20 ° C com agitação magnética para solubilização completa. Em seguida, as amostras foram transferidas para frascos volumétricos de polipropileno de 100 mL e o volume foi completado com uma solução de ácido tartárico a 2,5% e HNO_3 a 10%. Amostras em branco e amostras de referência certificadas (OREAS-45c, GRE-3 e OREAS 146) foram adicionadas à série analítica. As concentrações totais de La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu e Y nas soluções digeridas foram determinados por espectrometria de massa com plasma acoplado indutivamente (ICP-MS, Modelo NexION 300D, Perkin Elmer, Waltham, MA, EUA). As recuperações ficaram consistentemente entre 90% e 110%. Todas as análises foram realizadas em duplicata. Para os resultados, a fim de eliminar a distribuição característica em ziguezague dos ETRs (conhecida como regra de Oddo-Harkins), foi aplicada a normalização de condritos (Boynton, 1984).

2.3.2 Urânio e tório

As amostras de solo e tecido vegetal foram extraídas de acordo com o método da água régia (3:1 HCl:HNO_3, v/v). Como procedimento: alíquotas de 0,5g das amostras peneiradas em malha 100 mesh foram transferidas para tubos de teflon, adicionando-se 9 mL de HCl (32%) e 3 mL de HNO_3 (65%), na proporção 3:1, com pureza analítica e concentrado, a seguir foi feito repouso para pré-digestão por 12h. O conjunto foi mantido em sistema fechado em micro-ondas (Mars Xpress, CEM Corporation) por 20’ a 180ºC. Após o resfriamento, as amostras foram transferidas para frascos certificados (NBR ISSO/IEC) de 25 mL, sendo o volume dos frascos preenchido com água ultrapura e os extratos filtrados em papel filtro. As análises foram realizadas em triplicatas e com testes em branco (controle). U e Th foram quantificados usando espectrometria de massa com plasma acoplado indutivamente (ICP-MS).

Os valores de U e Th em mg kg^{-1} (ppm) foram convertidos para concentração de atividade, em Bq kg^{-1}, usando os fatores de conversão fornecidos pela Agência Internacional de Energia Atômica (IAEA, 1989) e pelo Laboratório Central Polonês de Proteção Radiológica, conforme demonstrado em Malczewski et al. (2004): 1 ppm de ^{238}U corresponde a 12,35 Bq kg^{-1} e 1 ppm de ^{232}Th corresponde a 4,06 Bq kg^{-1}.

2.3.3 Elementos potencialmente tóxicos

Os elementos avaliados no estudo foram As, Ba, Cd, Co, Cu, Cr, Hg, Ni, Pb e Zn. A extração foi pelo método da água régia (3:1 HCl:HNO_3, v/v), reconhecido pela International Organization for Standardization como o padrão para certificação de solo na Europa (ISO, 1995). Como procedimento: transferiu-se alíquotas de 0,5g das amostras peneiradas em malha de 100 mesh para tubos de teflon, adicionando-se 9 mL de HCl (32%) e 3 mL de HNO_3 (65%), (3:1) concentrados e de pureza analítica, deixando em repouso para pré-digestão por 12h. O conjunto foi mantido em sistema fechado em forno de micro-ondas (Mars Xpress, CEM Corporation) por 20’ a 180ºC. Após o resfriamento, as amostras foram transferidas para balões certificados (NBR ISSO/IEC) de 25 mL, sendo o volume dos balões completados com água ultrapura e os extratos filtrados em papel filtro. As análises foram realizadas em triplicatas e com provas em branco (controle). Todos os elementos foram quantificados usando espectrometria de massa com plasma acoplado indutivamente (ICP-MS).

2.4 OBTENÇÃO DOS FATORES DE ENRIQUECIMENTO E BIOACUMULAÇÃO

Os fatores de enriquecimento (FE) foram calculados com o objetivo de verificar o grau de contaminação por incrementos de ETRs, U, Th e EPTs nas áreas em estudo. A obtenção do FE foi de acordo com Loska et al. (2004): FE = (Cn/Cref) / (Bn/Bref), onde Cn é concentração do elemento estudado no ponto em estudo (agroecossistemas) na amostra n, Cref é a concentração do elemento de referência no ponto em estudo (agroecossistemas), Bn é a concentração do elemento em estudo no ambiente de referência (floresta remanescente - controle) e Bref é a concentração do elemento de referência no ambiente de referência (floresta remanescente - controle).

Vários elementos químicos são comumente empregados como referência, tais como: Al, Ca, Fe, Mn, Ti e V (Loska et al. 2004). O elemento de referência utilizado neste estudo foi o alumínio, a partir dos resultados apresentados como Al_2O_3, por garantir mais robustez e confiabilidade aos resultados obtidos, pois a sua concentração tende a ser mais uniforme (Rubio et al. 2000; Alagarsamy; Zhang 2010; Islam et al. 2015). Sutherland (2000) propôs um sistema preliminar de classificação para avaliar o grau de poluição a partir dos FEs, dividido em 5 classes: FE <2, enriquecimento mínimo; $2 \geq$ FE <5, enriquecimento moderado; $5 \geq$ FE <20, enriquecimento significativo; $20 \geq$ FE <40, enriquecimento muito alto e FE ≥ 40, enriquecimento extremamente alto.

Para o cálculo dos fatores de enriquecimento, os teores basais tanto do elemento de referência adotado, quanto dos elementos em estudo foram reportados como a média da concentração destes elementos para amostras coletadas em áreas caracterizadas com o mínimo impacto antrópico (florestas remanescentes - controle) e adjacentes aos agroecossistemas. O fator de bioacumulação (FBA) foi calculado de acordo com Khan et al. (2015): FBA= [C planta / C solo], onde: [C planta] = concentração do elemento no tecido vegetal e; [C solo] = concentração do elemento no solo.

CAPÍTULO 3 - EFFECTS OF LONG-TIME FERTILIZERS APPLICATION ON RARE EARTH ELEMENTS IN AGROECOSYSTEMS FROM THE EASTERN AMAZON, BRAZIL.

Anderson Martins de Souza Braz[1]*, Marcondes Lima da Costa[2], Antonio Rodrigues Fernandes[3], Sílvio Junio Ramos[4].

[1]Geosciences, Federal Rural University of Amazon - UFRA, Capanema - PA, Brazil.

[2]Geosciences Museum, Institute of Geosciences, Federal University of Pará - UFPA, Brazil.

[3]Institute of Agricultural Sciences, Federal Rural University of Amazon - UFRA, Belém - PA, Brazil.

[4]Instituto Tecnológico Vale, Belém - PA, 66055-090, Brazil.

*Corresponding author: abrazgeo@gmail.com; anderson.braz@ufra.edu.br

ABSTRACT

Brazilian Amazon is the new agricultural frontier and intensive P-fertilizer use to attain and maintain satisfactory soil fertility, can have high concentrations of rare earth elements (REEs) and their entry into the soil via fertilizers has generated concern about environmental impacts and human health risks. This study aimed at REEs in Oxisol and Ultisols were evaluated, cultivated with orange (*Citrus sinensis* (L.) Osbeck), oil palm (*Elaeis guineensis* Jacq.) and black pepper (*Piper nigrum* L.), with 26, 10 and 5 years, respectively. The potential risk of contamination was estimated by the enrichment (EF) and bioaccumulation (BAF) factors. The results showed that pH, K and P-available significantly affected REEs concentrations. Europium bioaccumulation was the more significant among REEs. Black pepper crop showed the greater EF and BAF factors. The REEs increase, for the time being, do not represent risks to the environment and for human health.

Keywords: Lanthanides; Oxisol; Ultisol; Soil chemistry; Plant uptake; Environmental safety.

3.1 INTRODUCTION

Rare earth elements (REEs) are a group of 17 elements, comprising the 15 lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), with successive atomic numbers from 57 (lanthanum) to 71 (lutetium) along with yttrium (39) and scandium (21), which are recognized by the International Union of Pure and Applied Chemistry (IUPAC) due to the similar chemical, toxicological behavior and are often found in the same mineral origin. The lanthanide series are commonly divided into two groups by their atomic number and masses: light REE (LREEs: La-Eu) and heavy REE (HREEs: Gd-Lu). The LREEs are found in greater contents in the environment, have smaller atomic masses, in addition to greater solubility and alkalinity (Migaszewski and Galuszka, 2015). On the other hand, the Ministry of Land and Resources of China refers to Sm, Eu and Gd (atomic numbers 62 to 64, respectively) as medium elements (Medium Rare Earth Elements) (Liu, 2016). Promethium is the only one that has no natural occurrence, it is a product of uranium fission (Müller et al. 2016).

In agricultural areas, the main REEs entrance is caused by application of fertilizers (Otero et al. 2005; Turra et al. 2011; Waheed et al. 2011), and indirect application of REEs to agricultural soils is widespread due to their presence in the phosphate fertilizers (Ramos et al. 2016a). In addition, since the 1980s in China, REEs have been widely applied as fertilizers in agriculture to improve crop yield and quality (Hu et al. 2004; Tyler, 2004; Wang et al. 2008). Several studies have shown positive effects of REEs in plants and animals (Guo et al. 2013; Ma et al. 2014; Giraldo et al. 2014; Wu et al. 2014; Zhang et al. 2014; Shtangeeva, 2014; Cai et al. 2016; Vilela et al. 2018). On the other hand, it was reported that high concentrations of REEs decrease significantly the photosynthetic rate and chlorophyll content, slowing growth rate and even cause cell death (Shyam and Aery, 2012; Thomas et al. 2014; Chaturvedi et al. 2014; Carpenter et al. 2015; Pošćić et al. 2017; Jiang et al. 2017; Xu et al. 2017). And also, Rim et al. (2013) linked REEs contamination to occupational poisoning and human diseases. In thi way, it is necessary to exercise caution when introducing them into the ecosystem, either intentionally or involuntarily, since they are liable to bioaccumulate if transferred from the soil to living organisms and water bodies (Ramos et al. 2016a). The addition of REEs by the applications in large-scale of the P-fertilizers to Brazilian soils may represent a potential risk to agricultural and environmental sustainability, since 10.5 to 13.0 thousand tons of REEs are incorporated annually to soils (Ramos et al. 2016b; Silva et al. 2019).

Nowadays, the Brazilian Amazon is a new agricultural frontier, it has a major food producing area, exporting soy and beef to global markets (Vale et al. 2019), and is a pressing challenge to reconcile competing demands on land systems for food production and conservation of natural ecosystems, such as in Amazon biome (Cortner et al. 2019). Pará state is the second largest Brazilian state in area, with 1,247,955 km^2, of which approximately 57% consists of indigenous territories and protected areas, and this represents 29.73% of the Brazilian Amazon (4,196,943 km^2) and 14.65 % of Brazilian territory. The main economic activities in the state of Pará and the Amazon include agriculture, principally cattle rearing, vegetable production and mineral extraction (Bowman et al. 2012; De Souza et al. 2013). In the state of Pará there is an annual production of 286,768 tons of oranges, 1,634,476 tons of oil palm, and 39,577 tons of black pepper, which represents 2, 97 and 50% of the Brazilian production (IBGE, 2017).

To assess the effects of anthropic activity, on the increase of REEs in environmental compartments, the enrichment factor (FE) can be used (Galhardi et al. 2020), which is obtained from the ratio between the concentration of the element chemical of interest in cultivated soil and the natural concentration or background level (Loska et al. 1997; 2004), and also the bioaccumulation factor (BAF) that correlates the concentrations of chemical elements in plant tissues and the total in the soil (Galhardi et al. 2020). BAF is considered one of the most important input variables in the assessment of risks to human health (Khan et al. 2015).

Considering that the determination of the levels of REEs in agricultural soils can provide qualitative and quantitative guidance in studies of environmental risk assessment and human health. However, such assessments are scarce at the agricultural frontiers in the Amazon, which demand high applications of agricultural inputs, mainly P-fertilizers. In this way, the present study aimed to evaluate (i) the concentrations of REEs in agricultural soils that received fertilizer applications for 26, 10 and 5 years, in orange, oil palm and black pepper crops, respectively; (ii) establish / discuss relations of the levels of REEs with the soil attributes and; (iii) determine the enrichment and bioaccumulation factors in the Amazonian agroecosystems of orange, black pepper and oil palm cultivation.

3.2 MATERIAL AND METHODS

3.2.1 Study site, soil and leaf sampling

For the development of this study, samples were collected in the Brazilian Amazon of Oxisol and Ultisol (Soil Survey Staff, 2014), which are predominant in the region. Soils were sampled in commercial plantations of orange (*Citrus sinensis* (L.) Osbeck), with 26 years of implantation; oil palm (*Elaeis guineensis* Jacq.), with 10 years of implantation and; pepper (*Piper nigrum* L.), with 5 years of implantation (Figure 1).

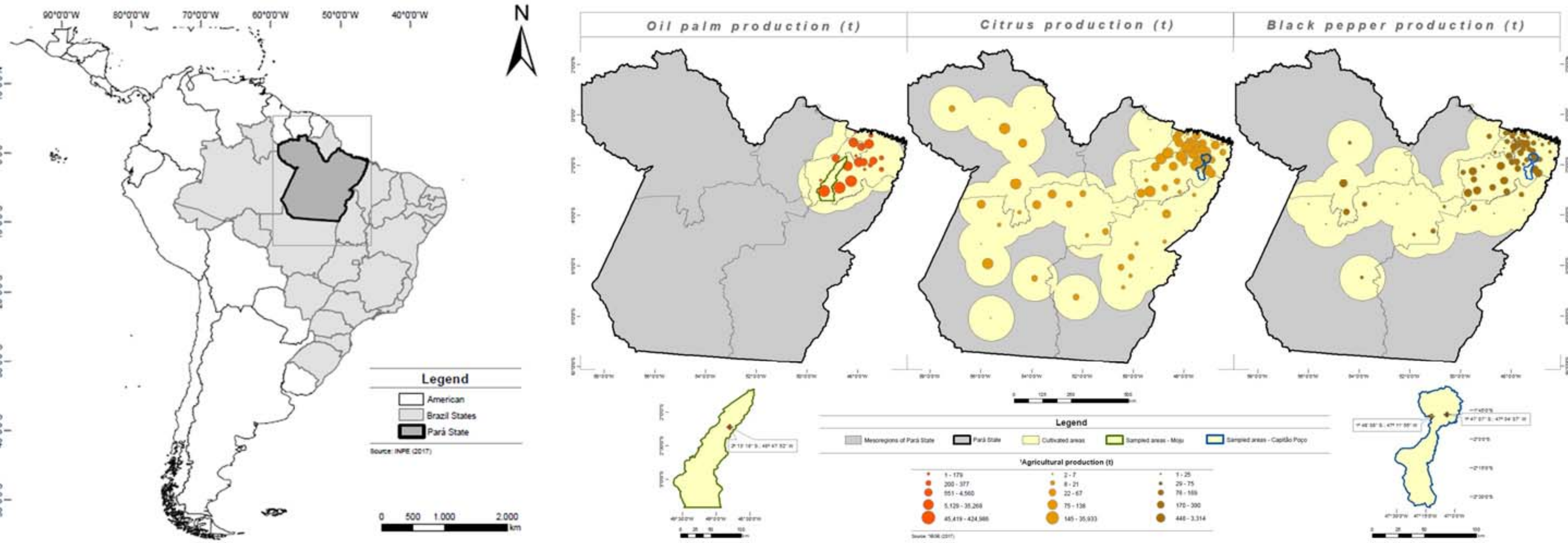


Figure 1. Study site and soil and leaf sampling from Pará State, Brazilian Amazon.

In the implantation of the orange orchard, were used 3 kg of chicken manure and 60 g of P_2O_5 (*single superphosphate*) per pit, and 60 g of N (urea) and 30 g K_2O (potassium chloride), per plant. From the second to the fifth year, 200g of N, 90g of P_2O_5 and 180g of K_2O were applied per plant. And from the sixth year on, the production fertilization started with 80 kg ha^{-1} of N, 20 kg ha^{-1} of P_2O_5 and 40 kg ha^{-1} of K_2O. The cupric fungicide, known as Bordeaux mixture ($CuSO_4$ + Ca $(OH)_2$), was also applied.

In the oil palm cultivation area was application of 23 kg ha^{-1} of natural phosphate reactive from Arad (33% P_2O_5), followed by the formulation NPK (11-07-23) + 2.5% Mg + 0.5% B; with annual applications of the N-P-K formula (10-07-22). For the implementation of black pepper cultivation, were used 1.5 kg of chicken manure + 500 g of thermophosphate (Yoorin - 17.5% of P_2O_5), per pit. In the first and second year were applied 50g of urea, 45g of triple superphosphate and 30g of potassium chloride, per plant. From the third year onwards were applied 150g of urea, 60g of triple superphosphate and 100g of potassium chloride, per plant. The Bordeaux mixture was also used to control pests in black pepper cultivation.

In each crop area, the soils were sampled in the 0 – 0.2 m deep, were taken 10 simple samples to form one composite sample, with three replications, making a total of 30 simple samples and 10 samples composed by crop. Soil samples were also collected in areas adjacent to the plantations, composed of native or naturally recovered vegetation (regionally called capoeiras), for the purpose of comparison and obtaining the enrichment factor (EF).

The physical-chemical analyzes of soil samples were carried out according to Embrapa (2011): pH H_2O and 1 mol L^{-1} KCl solution (1: 2.5); Ca and Mg in 1 mol L^{-1} KCl solution and quantified by atomic absorption spectrophotometry; K extracted with 0.05 mol L^{-1} HCl solution and quantified by flame photometry; Available P extracted with HCl solution 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1} (Mehlich-1) and determined by colorimetry; the organic carbon by the Walkley & Black method (wet combustion) with potassium dichromate; the Al_2O_3 total by sulfuric attack; and clay content (Gee et al. 1986).

X-ray fluorescence spectrometry (FRX) was used for the quantitative evaluation of the P_2O_5. Soil samples were placed in an oven to dry at 110 °C and then taken to a muffle, at 1000 °C, for two hours, for the determination of fire-exposed loss. The soil were analyzed in the X-ray fluorescence spectrometer, Rigaku model RIX 3000, equipped with Rh, by the calibration curves method, which were constructed using international reference materials.

Plant samples were collected at the same points of soil collection to verify the REEs bioaccumulation capacity by cultivation. Leaf sampling in black pepper and orange plantations consisted of collecting freshly ripe leaves, in the middle third portion of the crown per useful plant, in way the North, South, East and West (Oliveira and Cruz, 1999; Dias et al. 2013). For oil palm, the leaf sampling from the third or fourth year of cultivation was performed on leaf nº 17 (the apex to based), being considered as the best expression or the ideal physiological state for the oil palm (Rodrigues et al. 2006).

3.2.2 REEs methods and measurements techniques

The soil and plants tissue samples were air-dried and ground to pass through a 150-mesh nylon sieve. All samples were digested by means of an alkaline fusion method. In brief, an aliquot of 0.1 g from each sample was fused with 1.4 g of lithium metaborate in platinum crucibles at 1000 °C in a fusion machine (Fluxer BIS, Claisse, Québec, Canada). After cooling, the resulting beadwas dissolved in beakers containing 50 mL of a 2.5% solution of tartaric acid and 10% HNO_3. Each beaker was then transferred to a hot plate at 120 ± 20 °C with magnetic stirring for complete solubilization. After that, the samples were transferred to 100-mL polypropylene volumetric flasks and the volume was completed with a 2.5% solution of tartaric acid and 10% HNO_3. Blank and certified reference samples (OREAS-45c, GRE-3 and OREAS 146) were added to the analytical series. The REE contents in the digested solutions were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Model NexION 300D, Perkin Elmer, Waltham, MA, USA). Recoveries were consistently between 90% and 110%. All the analyzes were performed in duplicate.

Total REEs concentrations (ΣREE) were calculated as the sum of the concentrations of each individual REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and yttrium (Y). At the same time, in order to eliminate the characteristic zigzag distribution of REEs (known as the Oddo-Harkins rule) was applied the chondrite-normalization (Boynton, 1984).

3.2.3 Enrichment and bioaccumulation factors calculation

The enrichment factor (EF) was calculated in order to verify the degree of contamination by increment of REEs in the areas study. The calculation of the enrichment factor was done using the following Eq. 1 (Loska et al. 2004).

$$EF = (Cn/Cref) / (Bn/Bref) \qquad (1)$$

Where Cn is the concentration of the element studied at the point under study (agroecosystems) in sample n, Cref is the concentration of the reference element at the point under study (agroecosystems), Bn is the concentration of the element under study in the reference environment (remaining forest - control) and Bref is the concentration of the reference element in the reference environment (remaining forest - control).

Several chemical elements are commonly used as a reference, such: Al, Ca, Fe, Mn, Ti and

V (Loska et al. 2004). The reference element used in this study was Al_2O_3, this guarantees more robustness and reliability to the results obtained, the its concentration tends to be more uniform (Rubio et al. 2000; Alagarsamy and Zhang, 2010; Islam et al. 2015). Sutherland (2000) proposed a preliminary classification system to assess the degree of pollution with the EFs, divided into 5 class: EF < 2, deficient to minimal enrichment; 2 ≥ EF < 5, moderate enrichment; 5 ≥ EF < 20, significant enrichment; 20 ≥ EF < 40, very high enrichment; EF ≥ 40, extremely high enrichment.

For the calculation of the enrichment factors, the baseline levels of reference element and the elements under study were reported as the average concentration from collected in characterized areas with the least anthropic impact (remaining forests - control) and adjacent to agroecosystems. The bioaccumulation factor (BAF) was obtained using the following Eq. 2 (Khan et al. 2015).

$$BAF= [C\ plant / C\ soil] \quad (2)$$

Where: [C plant] = REEs concentration in the plant tissue and; [C soil] = REEs concentration in the soil.

3.3 RESULTS

3.3.1 Soil attributes

Descriptive characteristics of the soils are presented as mean values in Table 1. The soils in oil palm and citrus cultivation showed values of pH H_2O 4.6 and 4.7, respectively, indicating high acidity, while the soil cultivated with black pepper showed medium acidity (pH H_2O 5.2). The Ca^{2+} exchangeable in the oil palm areas was 9.6 mmol$_c$ kg^{-1}, considered low. The Ca^{2+} exchangeable of 13.7 and 34 mmol$_c$ kg^{-1} for citrus and black pepper areas can be considered medium and high, respectively, according to the classification by Alvarez et al. (1999). The Mg^{2+} exchangeable in soils: 2.5 mmol$_c$ kg^{-1} (oil palm), 15 mmol$_c$ kg^{-1} (black pepper) and 9 mmol$_c$ kg^{-1} (citrus) are classified as low, high and medium, respectively (Alvarez et al. 1999). The K^+ exchangeable was considered low in soils with oil palm and citrus (0.9 and 0.5 mmol$_c$ kg^{-1}, respectively). Only the soil cultivated with black pepper, showed a high concentration of K^+ exchangeable (4.2 mmol$_c$ kg^{-1}).

Table 1. Identification, location and attributes of soils (n[a] = 30)

Soils[b]	Geographical coordinates	pH		Ca^{2+}	Mg^{2+}	K^{+}	P	Al_2O_3	OC[c]	Clay	Silt	Sand
		H_2O	KCl	.........$mmol_c$ kg^{-1}.......			mg kg^{-1}	............................g kg^{-1}.............................				
				Elaeis guineensis Jacq.								
Typic Hapludox	2°13′ 18″ S 48° 47′ 52″ W	4.6	4.3	9.6	2.5	0.9	5	54.1	11.6	277	133	590
Control[d] (Oxisol)		4.0	3.7	1.3	1.7	0.6	2.6	54.0	13.5	303	98	599
				Piper nigrum L.								
Typic Hapludult - 1	1°47′ 07″ S 47° 04′ 07″ W	5.2	4.7	34	15	4.2	234	71.7	16	171	117	712
Control (Ultisol 1)		4.1	3.7	11.3	10	0.5	1	52.9	11	168	74	758
				Citrus sinensis (L.) Osbeck								
Typic Hapludult - 2	1°48′ 08″ S 47° 11′ 56″ W	4.7	4.1	13.7	9	0.5	8	53.6	6.9	60	21	919
Control (Ultisol 2)		4.4	3.8	5.1	1.2	0.1	1.5	48.8	9.7	63	58	879

[a]Number of samples, [b]USDA Soil Taxonomy (2014), [c]Organic carbon, [d]non-agricultural

The P-available (Mehlich-1) in oil palm, black pepper and citrus soils were 5, 234 and 8 mg kg^{-1}, respectively. These values are considered: very low, very high and low, according to the classification by Alvarez et al. (1999). The organic carbon content in soils cultivated with oil palm (11.6 g kg^{-1}) and orange (6.9 g kg^{-1}) were low, while in black pepper (16 g kg^{-1}) was considered medium (Alvarez et al. 1999). The clay content in the studied soils was considered low. Furthermore, the soils have a predominance of the sand fraction (Table 1), the characteristic observed in most of the soils in this region.

3.3.2 REEs, EF and BAF in agricultural soils-plants

The REE concentrations obtained for soils cultivated with black pepper and oil palm were higher than those of remaining forest fragments (control), while the citrus cultivation showed concentrations of REE lower than the control area (Table 2). REE concentrations in the soils and plants generally decreased from the light to heavy elements (Figure 2). Indeed, the LREE represented about 77% of the REE in the soils and 91% in plant tissues. All the soils and crops presented similar distribution patterns, with a clear enrichment of REE in relation to chondrite (Figure 3). The REE concentrations of plant tissues are at least one order of magnitude lower than for soils, but vary over several orders of magnitude as a function of plant species and soil concentrations (Table 2).

The enrichment factors for all HREE were less than 2 (EF < 2), considered as minimal, and the soil cultivated with citrus (Typic Hapludult-2) showed low EF (EF < 2) for LHREE and HREE (Figure 4). The soil cultivated with oil palm (Typic Hapludox) showed EF moderate (EF > 2) for Ce and Sm, while in the black pepper cultivation (Typic Hapludult-1) showed EF > 2 for La, Ce, Pr and Sm (Figure 4). The bioaccumulation factors in the plant tissues generally follow the order: Black Pepper > Citrus > Oil Palm, and the Eu bioaccumulation was the more significant (Figure 5).

Table 2. REEs in soils and plants (mean - dry weight) and agricultural inputs applied to soils

Samples	REEs ($mg\ kg^{-1}$)														
	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Soils															
Oxisol (Typic Hapludox)[a]	13.80	11.20	21.80	2.03	5.90	1.37	0.28	1.48	0.28	1.92	0.49	1.59	0.29	2.32	0.37
Control[b] (Oxisol)	10.50	5.60	9.60	1.02	3.10	0.61	0.17	1.03	0.22	1.48	0.39	1.20	0.21	1.76	0.27
Ultisol (Typic Hapludult)[a] - 1	20.70	15.80	29.20	2.84	8.80	1.85	0.34	2.17	0.37	2.86	0.78	2.53	0.48	3.48	0.59
Control (Ultisol 1)	11.20	5.50	10.60	0.98	3.30	0.54	0.17	1.04	0.17	1.57	0.42	1.37	0.26	2.00	0.29
Ultisol (Typic Hapludult)[a] - 2	14.10	6.80	12.80	1.25	3.90	0.73	0.19	1.33	0.25	1.86	0.52	1.76	0.30	2.50	0.40
Control (Ultisol 2)	23.70	9.10	17.50	1.60	4.70	1.01	0.24	1.86	0.40	3.07	0.83	2.72	0.49	4.09	0.59
Plants															
Oil palm (Leaf)	0.13	0.40	0.67	0.06	0.23	0.08	0.03	0.06	0.01	0.06	0.01	0.03	0.03	< 0.03	0.01
Black pepper (Leaf)	0.60	1.77	4.00	0.34	1.33	0.23	0.09	0.20	0.02	0.20	0.02	0.06	0.02	0.09	0.02
Citrus (Leaf)	0.33	0.77	1.47	0.14	0.43	0.05	0.04	0.11	0.02	0.09	0.02	0.03	0.03	0.04	0.02
Soil inputs in Brazil[c]															
Single superphosphate (SSP)	3.5 - 123.7	8.1 - 604.6	6.3 - 1098.5	1.2 - 135.3	3.4 - 442.9	0.7 - 61.0	0.2 - 14.6	1.2 - 45.2	0.1 - 6.6	1.0 - 31.0	0.1 - 4.7	0.3 - 7.7	(0.5 - 3.5)[d]	0.4 - 5.7	0.1 - 0.9
Triple superphosphate (TSP)	4.2 - 35.6	6.2 - 10.4	4.7 - 11.0	1.3 - 2.6	2.2 - 3.5	0.9 - 25.3	0.1 - 0.3	3.6 - 20.3	1.3 - 1.6	1.1 - 1.9	0.3 - 0.5	0.1 - 1.5	(0.5 - 1.5)[d]	0.4 - 2.2	0.1 - 0.4
Gypsum	0.2 - 1.0	0.4 - 2.1	0.2 - 3.3	0.3 - 0.8	< 0.007 - 0.5	0.5 - 1.2	< 0.006	0.2 - 0.9	0.5 - 0.8	0.1 - 0.4	0.1 - 0.2	< 0.013	-	< 0. 009 - 0.1	< 0.005
Limestones	0.6 - 3.1	1.2 - 5.9	1.3 - 9.7	1.1 - 2.1	< 0.007 - 6.7	1.8 - 3.1	< 0.006 - 0.2	3.0 - 16.3	0.9 - 2.0	0.1 - 1.8	0.2 - 0.3	< 0.013 - 0.4	-	0.1 - 0.3	< 0.005

[a]Agricultural fields. [b]non-agricultural. [c]Silva et al. (2019). [d]Ramos et al. (2016b).

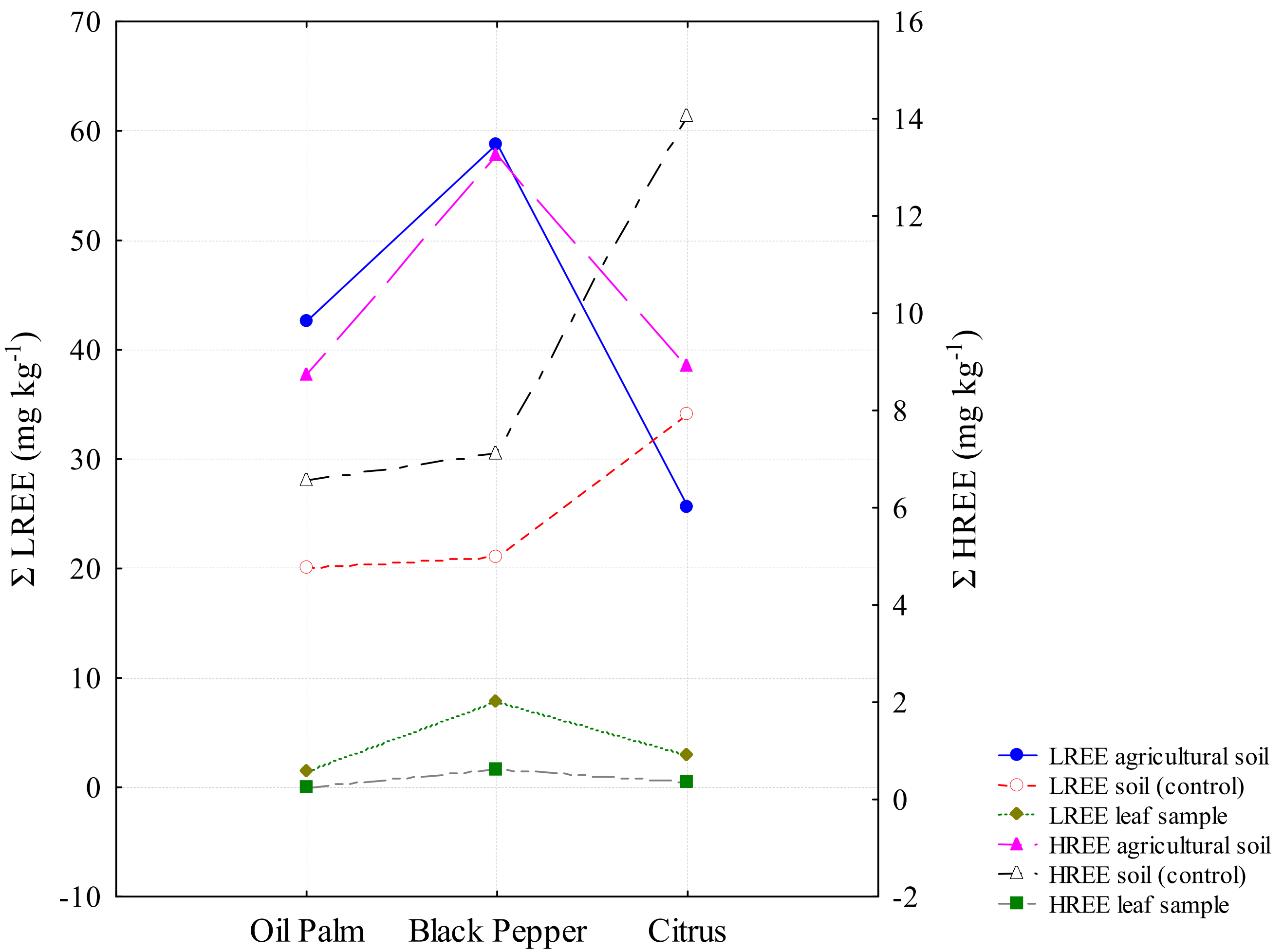


Figure 2. Light rare earth elements (LREEs) and heavy (HREEs) in agricultural soils and of reference (control) and in plants tissue of the oil palm, black pepper and citrus cultivation.

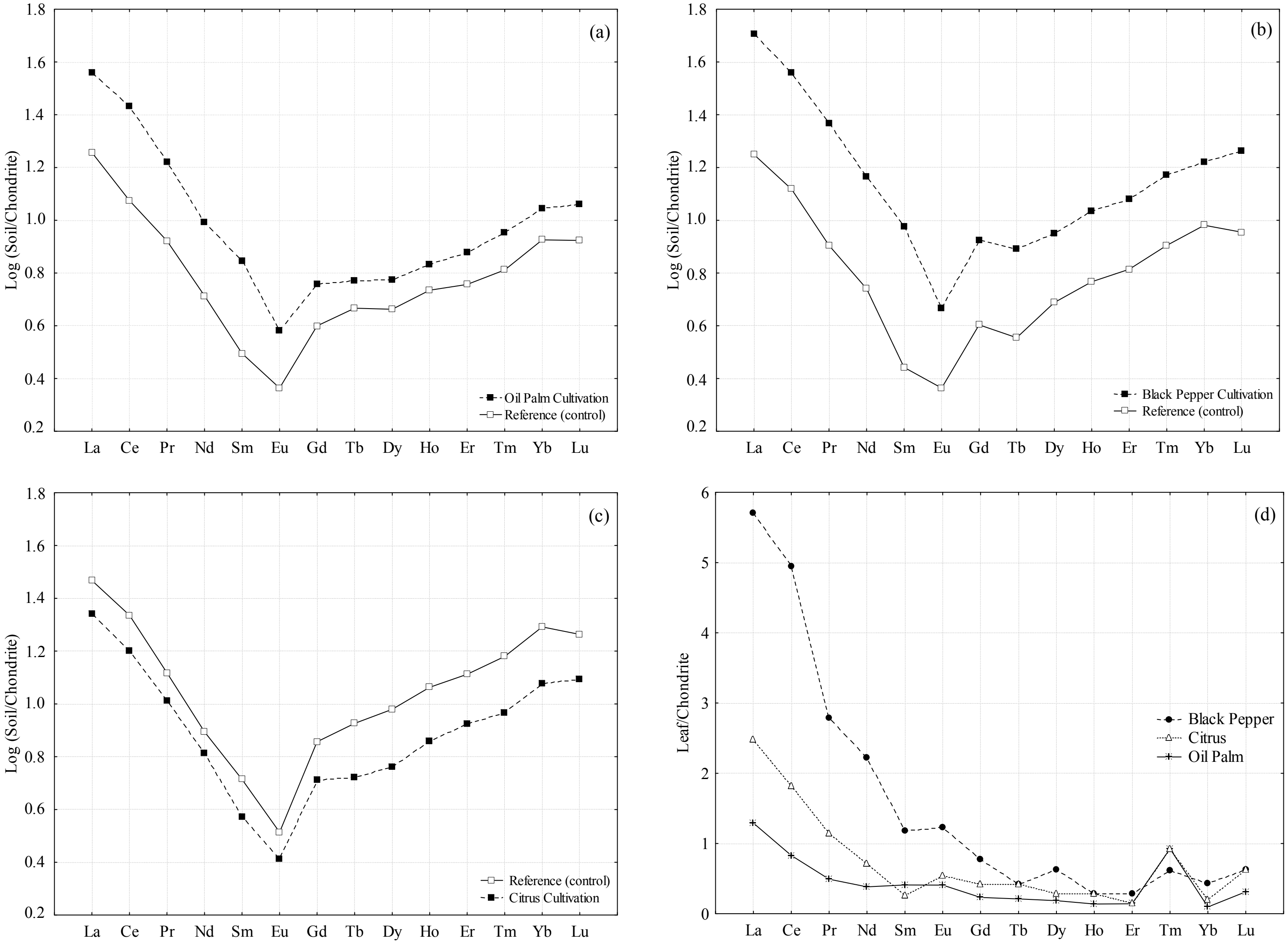


Figure 3. REEs in agricultural soil and plant (a) oil palm soil (b) black pepper soil (c) citrus soil and (d) plants tissue, normalized to the concentrations in chondrite.

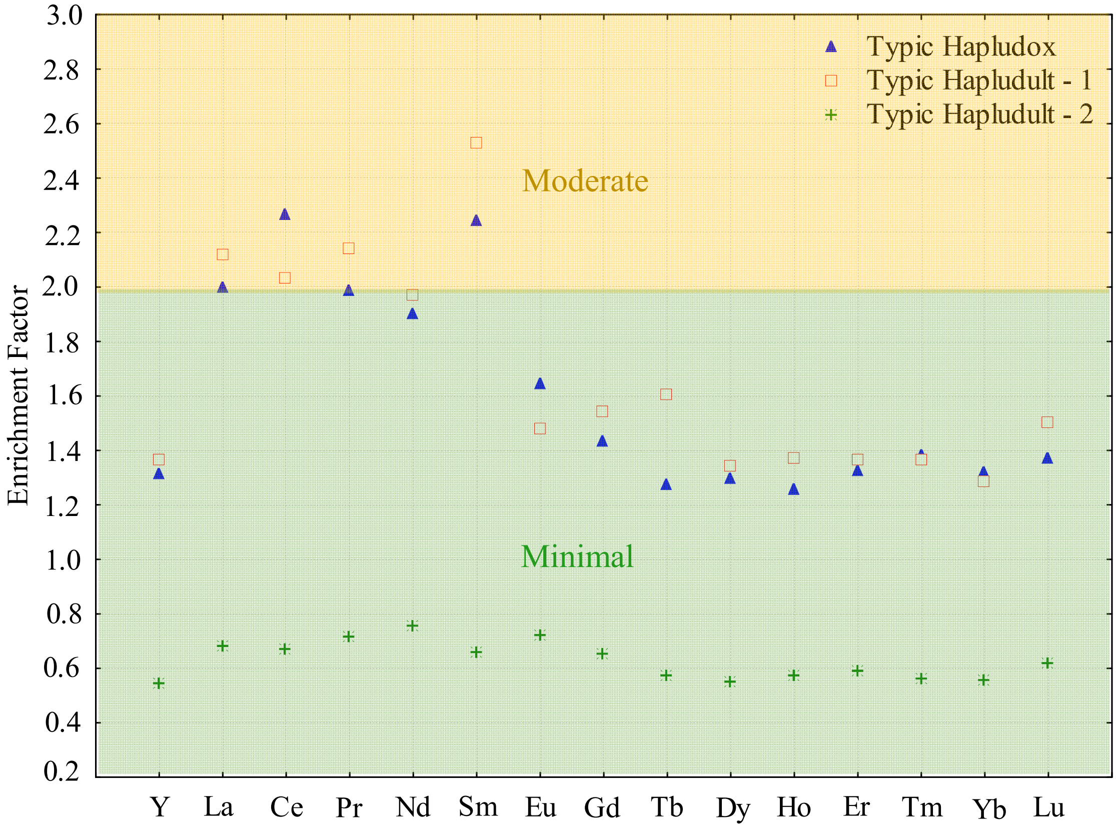


Figure 4. Enrichment factors of REEs in the cultivated soils.

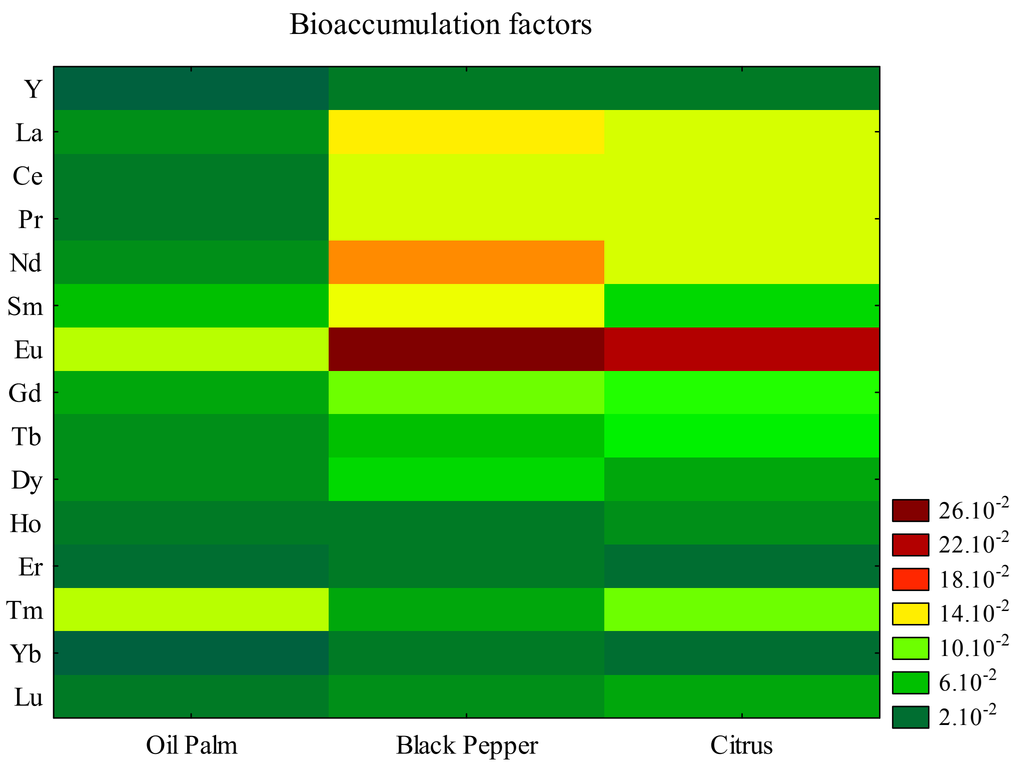


Figure 5. Bioaccumulation factors of REEs in plants tissue of the oil palm, black pepper and citrus cultivation.

The contents of LREE were positively correlated very tightly and significantly with pH, K and P in the cultivated soils (Table 3 and Figure 6). On the other hand, there was a relatively poor correlation between HREE concentrations with the soils properties (Table 3). The ΣREE were positively and significantly correlated with the soil pH.

Table 3. Pearson's correlation coefficients of REEs concentrations with the soil properties

	pH	Ca	Mg	K	P	Al_2O_3	P_2O_5	OC	Clay	Silt	Sand
Y	0.564	0.379	0.086	0.348	0.458	0.246	0.401	0.085	-0.570	-0.058	0.442
La	**0.872***	0.785	0.419	**0.843***	**0.837***	0.780	0.793	0.572	0.014	0.556	-0.176
Ce	**0.869***	0.764	0.398	0.807	0.799	0.738	0.765	0.526	-0.009	0.548	-0.157
Pr	**0.879***	0.787	0.425	**0.848***	**0.838***	0.787	0.794	0.571	0.026	0.559	-0.186
Nd	**0.891***	**0.842***	0.510	**0.889***	**0.882***	**0.834***	**0.850***	0.591	0.005	0.537	-0.164
Sm	**0.858***	0.747	0.369	**0.820***	0.804	0.757	0.754	0.571	0.068	0.595	-0.228
Eu	**0.846***	0.725	0.342	0.786	0.777	0.715	0.731	0.538	0.025	0.576	-0.191
Gd	**0.817***	0.668	0.320	0.673	0.737	0.587	0.682	0.341	-0.353	0.219	0.198
Tb	0.614	0.359	-0.018	0.405	0.488	0.306	0.387	0.190	-0.380	0.110	0.250
Dy	0.604	0.441	0.135	0.426	0.529	0.325	0.471	0.170	-0.515	0.021	0.377
Ho	0.616	0.463	0.179	0.432	0.541	0.336	0.488	0.142	-0.566	-0.042	0.434
Er	0.630	0.468	0.195	0.411	0.522	0.317	0.480	0.085	-0.613	-0.090	0.483
Tm	0.647	0.527	0.254	0.480	0.585	0.384	0.549	0.173	-0.562	-0.010	0.421
Yb	0.544	0.362	0.092	0.307	0.432	0.206	0.377	0.025	-0.625	-0.122	0.502
Lu	0.710	0.538	0.241	0.494	0.594	0.404	0.545	0.140	-0.563	-0.028	0.427
LREE	**0.875***	0.782	0.421	**0.832***	**0.825***	0.767	0.787	0.552	0.003	0.552	-0.167
HREE	0.639	0.469	0.171	0.435	0.539	0.338	0.488	0.136	-0.553	-0.018	0.417
Σ REE	**0.872***	0.762	0.395	0.799	0.811	0.725	0.769	0.502	-0.098	0.474	-0.068

***Significant at** $p < 0.05$

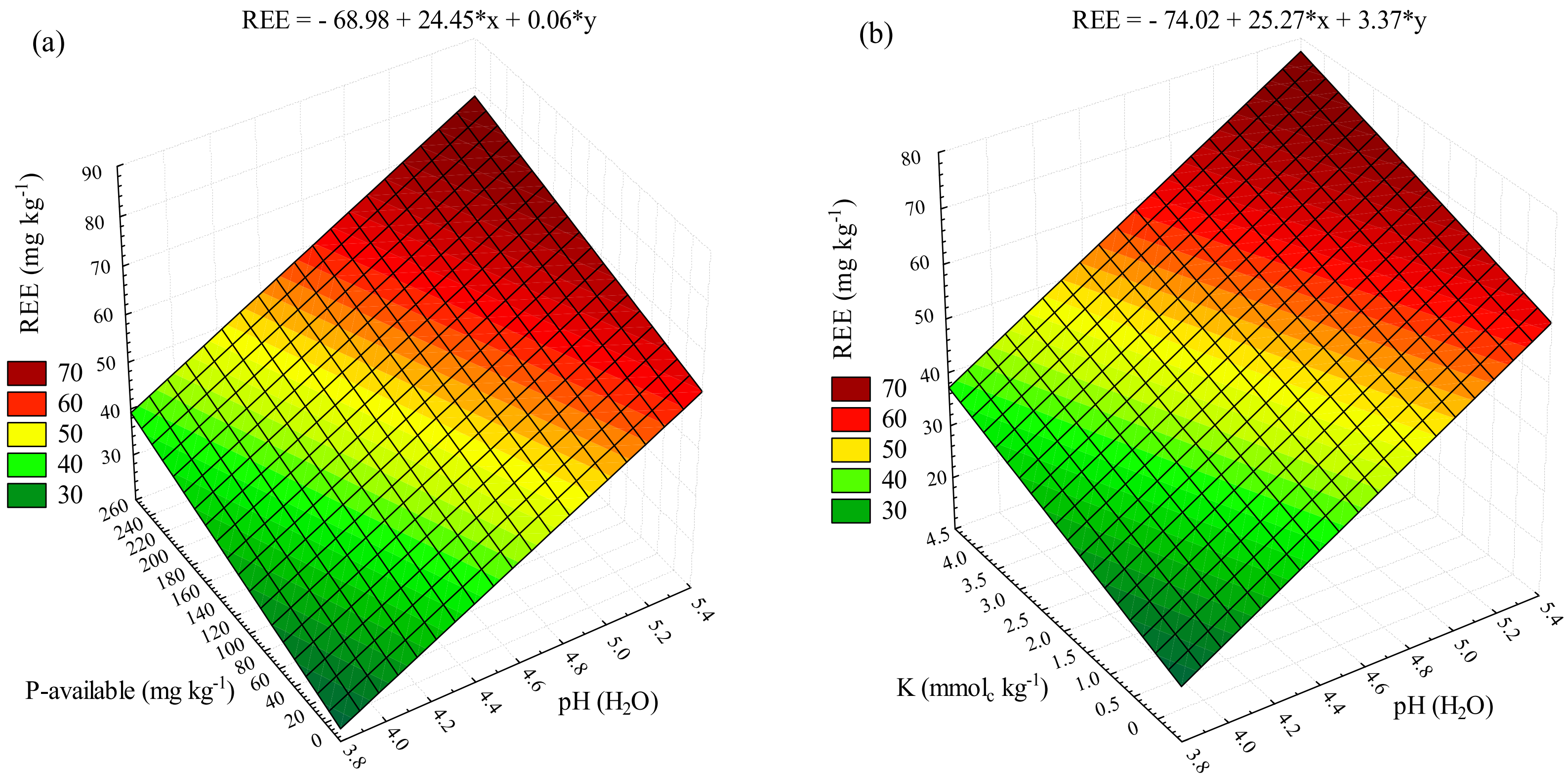


Figure 6. Response surface of REE concentration in the cultivated soils (a) P-available and pH (b) K and pH.

3.4 DISCUSSION

3.4.1 Soil attributes

The soils of this study, except for the black pepper cultivation, even following the criteria and recommendations for the use of limestone and fertilizers, have high acidity (pH H_2O <5). In tropical regions, the climatic conditions further the loss of bases by leaching, increasing acidity, even in areas that have received liming. Study in the Eastern Amazon showed that Oxisols and Ultisols have high acidity (Birani et al. 2015; De Souza et al. 2018). In the Western Amazon, Moreira and Fageria (2009) studied 3340 soil samples collected in primary forest, secondary forest, native forest, fallow area, polyculture and monoculture areas, and observed that more than 94% have acidity values in ranges considered high to very high, according to the classification by Alvarez et al. (1999).

The total organic carbon (TOC) in soils with oil palm and citrus were low, compared to black pepper cultivation, due to the longer time of implantation of these crops and the climatic conditions with intense rains and high temperatures that prevail in this part of the Amazon. These conditions contribute to the rapid decomposition of organic matter (De Souza et al. 2018). The organic carbon lower observed in soil cultivated with citrus, may be related to the longer cultivation time of the soil. Bayer and Mielniczuk (1997) observed that the organic matter content in Ultisol was reduced from 31 g kg^{-1}, under natural conditions, to 18 g kg^{-1} as result of successive crops. Bowman et al. (1990) observed reductions of 55 to 63% in TOC of the soil (0-15 cm) in sixty years of cultivation. De Souza Braz et al. (2013) found decrease in organic carbon of soil Typic Hapludox from the Eastern Amazon, after 15 years of use of land with pasture.

The clay contents of the soils in this study were low, but within the range observed by Birani et al. (2015), in soils, Typic Hapludox (38 to 931 g kg^{-1}) and Typic Hapludult (53 to 719 g kg^{-1}), from the Eastern Amazon. The results obtained indicate the predominance of sand fraction, the characteristic observed in most of the soils in the Pará state (De Souza et al. 2018).

The soils cultivated with citrus and oil palm showed low of the P, while in the black pepper cultivation the values were very high. Frazão et al. (2013) evaluated oil palm plantations in Amazon soils, with 4, 8 and 25 years of implantation, and observed P content in the soil of 4.3, 3.9 and 4.2 mg kg^{-1}, respectively. The higher P content of the soil in the area cultivated with black pepper may be related to the residual effect of fertilization with thermophosphate (Withers et al. 2018).

3.4.2 REEs, EF and BAF in agricultural soils-plants

In the environment where Oxisols and Ultisols are formed, i.e. high temperature and precipitation and consequently high weathering-leaching, losses of cations are expected, with a consequent pH decrease, removal of weatherable minerals and accumulation of kaolinite and oxides (De Souza et al. 2018). This fact may explain the lower levels of REEs in topsoil due weathering-leaching (Laveuf and Cornu, 2009). In this study, the anthropogenic activities also may explain the lower and higher levels of REEs in agricultural soils when compared with the areas non-agricultural (control). The P-fertilizers are main the anthropogenic source of REEs, and generally lead to enhance of REEs contents in soils, due to the high affinity of phosphates to REEs (Ramos et al. 2016a; 2016b). In Brazilian tropical soils/agroecosystems the average annual rate of P mineral fertilizer applied to crops is 25 kg P ha^{-1} yr^{-1} (Withers et al. 2018). The continuous application of high doses of P fertilizers and soil correctives to Brazilian soils represent 13,000 tons of REEs are incorporated annually to soils (Silva et al. 2019). However in the orange orchard (this study), sandy soil and longer time of the soil use possibly contributed to the low REEs due the loss by leaching. The sandy and peaty soils tends to low REE contents than clayey soils (Mihajlovic et al. 2019). The pH decrease in soils causes leaching of REEs (Pang et al. 2002).

In general (this study), the LREEs were more abundant than HREEs, agreement with results in topsoil observed by Wiche et al. (2017). In black pepper and oil palm cultivation, enrichment factors (EF > 2.0) suggests a anthropogenic contribution of La, Ce, Pr and Sm in the cultivated soils. Wang and Liang (2014) proposes values EF >1.5 as significant enrichment caused by anthropogenic sources. The EF values, ranged from 1.1 for La to 2.1 for Gd, were considered low in the natural wetland soil of China (Cheng et al. 2012). Plants can solubilize LREEs from soil by roots and then uptake and transport to leaves and carboxylate groups in plant tissues can bind with LREE ions easier than HREE effectively (Miao et al. 2008; Brioschi et al. 2013). The REE typically exhibit trivalent oxidation states, except europium and cerium, which may also occur respectively as Eu^{2+} and Ce^{4+} (Aide and Aide, 2012). In plant tissues (this study), the highest bioaccumulation factor was to Eu with following order: black pepper, citrus and oil palm. This higher bioaccumulation could be due to the interchangeability of Eu with Ca during physiological processes of plant growth occurring in soil or to protein binding in photosystem II (Zeng et al. 2003; Kruk et al. 2003). The Eu is considered as an indicator of biogeochemical processes due to change of its valence state under different environmental conditions and also for similarity to chemical characteristics of Ca (Shtangeeva and Ayrault, 2007).

The REE bioaccumulation, also referred to as transfer factors, in the present study varied from 0.02 to 0.26. In contrast, Turra et al. (2013) observed transfer factors of La in citrus plants, ranged from 0.62 to 1.09, is mentioned among species with a high ability to accumulate REE.

In a recent study by the same author, the highest transfer factor of REE was observed for La (0.0047) in Rangpur lime (*Citrus limonia* Osbeck) plants (Turra el al. 2019). This differences can be attributed to the soil properties, soil management, orchard age and cultivation environments (Tyler, 2004; Brioschi et al. 2013; Turra et al. 2020). In another study, Cheng et al. (2015) reported that low pH in different types of orchard soils from a typical Chinese area of orange planting induced higher uptake of REEs by the orange trees. Uptake of REE by plants tends to be higher at a low pH (Cao et al. 2001). A significant linear correlation between REE content from sandy soil to palms has been observed (Wahid et al. 2003). Moreover, the REEs can be accelerates growth of plant tissues (Kovaříková et al. 2019). The positive effects of La in bell pepper quality by enhancing some growth parameters and biomolecule concentrations was found (García-Jiménez et al. 2017).

In our study, for tillage amazon conditions, the pH, K and P-available were the main factors influencing the REEs contents in soils. Other study indicate that the organic acids, redox potential, and soil pH are important factors affecting REE bioavailability (Shan et al. 2002; 2003). On the other hand, a higher affinity between REE and inorganic ligands, such as phosphate (PO_4^{3-}), plays important roles in REE bioaccumulation (Ding et al. 2005; Liang et al. 2008). In Mollisol (US) and Oxisol (Brazil), Dinali et al. (2019) showed that soil REE sorption is influenced by soil pH especially for tropical soil (Oxisol), and the Eu was the most sorbed element among REE.

3.5 CONCLUSIONS

It is important to understand REEs accumulation, especially those in high weathered soils, as were examined here. In that context, this is the first study evaluating the uptake of REE by amazon crops of great importance for global markets. The results indicate that under field conditions the REEs concentrations is extremely influenced by pH soil, especially in tropical soils. Also, Eu was the most bioaccumulated in black pepper, orange and oil palm crops among REEs. The longer time of the soil use with the orange cultivation, compared to the other crops, was not decisive to establish cause/effect relations with the REEs concentrations. These findings will be relevant and useful to predict REEs accumulation in soils resulting from anthropogenic activities, which is valuable in agriculturally important regions, and of environmental vulnerability such the Amazon biome.

Data availability

All data used in the analysis here are made available in the tables and figures, with the exception of the chondrite values for REEs normalizing, which are available in Boynton (1984).

Author contributions

AMSB and MLC conducted field sampling. AMSB, MLC, ARF and SJR performed laboratory analysis. AMSB, MLC, ARF and SJR contributed to the elaboration of the methodology and discussion of the results. All authors reviewed and commented on the manuscript.

Acknowledgements

The first author thank the Pro-Rectory of Research and Technological Development (PROPED/UFRA) for Support (Prodoutoral - 04/2017). The second (Grant 305015/2016-8) and the last (Grant 307166/2019-8) authors thank the CNPQ for the financial support.

Conflict of Interest

The authors declare that they have no conflict of interest.

CAPÍTULO 4 - LONG-TIME FERTILIZERS APPLICATION IN EASTERN AMAZON: EFFECTS OF URANIUM AND THORIUM LEVELS IN SOIL CULTIVATED WITH BLACK PEPPER, ORANGE AND OIL PALM.

Anderson Martins de Souza Braz[1]*, Marcondes Lima da Costa[2], Antonio Rodrigues Fernandes[3], Sílvio Junio Ramos[4].

[1]Geosciences, Federal Rural University of Amazon - UFRA, Capanema - PA, Brazil.

[2]Geosciences Museum, Institute of Geosciences, Federal University of Pará - UFPA, Brazil.

[3]Institute of Agricultural Sciences, Federal Rural University of Amazon - UFRA, Belém - PA, Brazil.

[4]Instituto Tecnológico Vale, Belém - PA, 66055-090, Brazil.

*Corresponding author: abrazgeo@gmail.com; anderson.braz@ufra.edu.br

Highlights

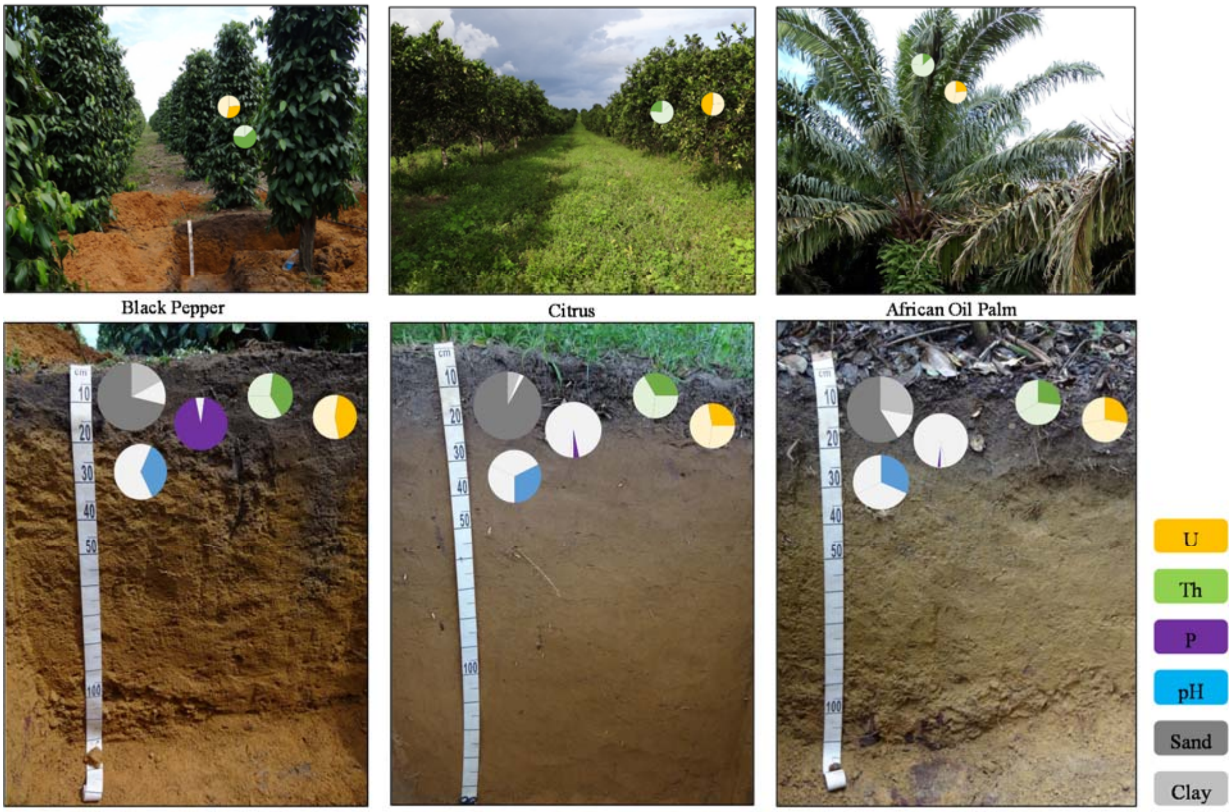
- The low enrichment factors of U and Th was mainly because the soils are sandy.
- ^{238}U activity concentration was greatest in plant tissue of the orange cultivation.
- ^{232}Th activity concentration was greatest in plant tissue of the black pepper cultivation.
- The lowest levels of ^{238}U and ^{232}Th activity were in plant tissue of the oil palm cultivation.
- The activity concentrations of ^{238}U and ^{232}Th in the soil with black pepper cultivation were higher than the world average.

ABSTRACT

Agriculture in the Brazilian Amazon has intensified, along with the use of fertilizers. The phosphate fertilizers routinely used can have high concentrations of radioelements. In the present study the elemental and activity concentrations of U and Th in Oxisols and Ultisols were evaluated, cultivated with orange (*Citrus sinensis* (L.) Osbeck), oil palm (*Elaeis guineensis* Jacq.) and black pepper (*Piper nigrum* L.), with 26, 10 and 5 years of implantation, respectively. The potential risk of contamination was estimated by the enrichment (EF) and bioaccumulation (BAF) factors. Correlations between pH, Ca, Mg, K, P and the sand fraction of the soils with the concentrations of U and Th in the soil / plant relationship they were obtained. The enrichment (EFs < 2) and bioaccumulation (0.01 < BAF < 0.05) factors were considered low. In plant tissues the orders of magnitudes were: ^{238}U (mBg kg^{-1}) - Orange > Black pepper > Oil palm; ^{232}Th (mBg kg^{-1}) - Black pepper >> Orange > Oil palm. The activity concentrations of ^{238}U and ^{232}Th in the soil cultivated with black pepper and in the soil of the reference environment of the orange orchard (remaining forest - control) were higher than the world average of ^{238}U (35 Bq kg^{-1}) and ^{232}Th (30 Bq kg^{-1}) as established by the United Nations Scientific Committee on Effects of Atomic Radiation. Perennial crops that are fertilized annually must be monitored by environmental agencies for the accumulation of chemical elements that offer potential risks to human health.

Keywords: Radioelements; elemental concentration; soil chemistry; plant uptake.

Graphical Abstract



4.1 INTRODUCTION

Brazilian agriculture, in the last 20 years, aiming to increase the productivity of crops, has intensified the use of new technologies, concomitant with applications in large-scale of the P-fertilizers (Withers et al. 2018). However, the chemical composition of P-fertilizers contains radioelements (Mazzilli et al. 2000; Yamazaki et al. 2003; Saueia et al. 2005). Uranium (U) exists naturally in the earth's crust with an average concentration of 2.5 mg kg^{-1}, and thorium (Th) is almost three times more abundant than U (Shtangeeva, 2008). The concentration range of Th in soils is 2 to 12 mg kg^{-1} with an average value of 6 mg kg^{-1} (Kabata-Pendias and Pendias, 2001). And the concentration of U in soils, without anthropic action, 0.4 to 6.0 mg kg^{-1} (Shacklette and Boerngen, 1984). Despite the natural occurrence in soils and plants, the increase in the concentrations of U and Th in these environmental compartments may indicate areas affected by agricultural, industrial or mining activities (Ebyan, 2019).

The impact of P-fertilizers on uranium and thorium concentrations in agricultural soils has been the subject of environmental monitoring and risk assessment of human exposure (Kant et al. 2006; Ünak et al. 2007; Yamaguchi et al. 2009; Shtangeeva, 2010; Wetterlind et al. 2012; Khan et al. 2020). The concentrations of U and Th are often higher in soils rich in phosphate (Shtangeeva, 2008). Becegato et al. (2008) observed increases in Th concentration (0.02 to 0.69 mg kg^{-1}) in agricultural soils and related to the use of phosphate fertilizers. Increased of U concentrations in the surface horizon of the soil, due to continuous applications of chemical fertilizers, were observed for several studies (Rothbaum et al. 1979; Stojanovic et al. 2006; Takeda et al. 2006; Tunney et al. 2009; Yamaguchi et al. 2009).

The soil properties such as pH, clay minerals, Ca, K and organic matter, correlated with the bedrock composition and weathering intensity (Ribeiro et al. 2018), as well its management (application of fertilizers) (Vogel et al. 2020), can related with the retention and absorption of the radioelements by plants (Tagami and Uchida, 2020). To assess the effects of pedogenetic processes and other non-lithogenic factors, such as for example the anthropic influence, on the increase of radioelements in environmental compartments, the enrichment factor (FE) can be used, which is obtained from the ratio between the concentration of the element chemical of interest in cultivated soil and the natural concentration or background level (Loska et al. 1997; 2004), and also the bioaccumulation factor (BAF) that correlates the concentrations of chemical elements in plant tissues and the total in the soil. BAF is considered one of the most important input variables in the assessment of risks to human health (Khan et al. 2015; Ebyan, 2019).

Pará state is the second largest Brazilian state in area, with 1,247,955 km^2, of which approximately 57% consists of indigenous territories and protected areas, and this represents

29.73% of the Brazilian Amazon (4,196,943 km^2) and 14.65 % of Brazilian territory. The main economic activities in the state of Pará and the Amazon include agriculture, principally cattle rearing, vegetable production and mineral extraction (Bowman et al. 2012; De Souza et al. 2013). In the state of Pará there is an annual production of 286,768 tons of oranges, 1,634,476 tons of oil palm, and 39,577 tons of black pepper, which represents 2, 97 and 50% of the Brazilian production (IBGE, 2017). The growing demand in relation to food production and energy generation, coupled with society's call against deforestation in the Amazon to open new agricultural areas, has intensified the use of fertilizers in order to increase productivity (Vale et al., 2019; Cortner et al., 2019).

Considering that the determination of the levels of radioelements in agricultural soils can provide qualitative and quantitative guidance in studies of environmental risk assessment and human health. However, such assessments are scarce at the agricultural frontiers in the Amazon, which demand high applications of agricultural inputs, mainly P-fertilizers. In this way, the present study aimed to evaluate (i) the concentrations of U and Th in agricultural soils that received fertilizer applications for 26, 10 and 5 years, in orange, oil palm and black pepper crops, respectively; (ii) establish / discuss relations of the levels of radioelements with the soil attributes and; (iii) determine the enrichment and bioaccumulation factors in the Amazonian agroecosystems of orange, black pepper and oil palm cultivation.

4.2 MATERIAL AND METHODS

4.2.1 Study site, soil and leaf sampling

For the development of this study, samples were collected in the Brazilian Amazon of Oxisol and Ultisol (Soil Survey Staff, 2014), which are predominant in the region (Fig. 1). Soils were sampled in commercial plantations of orange (*Citrus sinensis* (L.) Osbeck), with 26 years of implantation; oil palm (*Elaeis guineensis* Jacq.), with 10 years of implantation and; pepper (*Piper nigrum* L.), with 5 years of implantation.

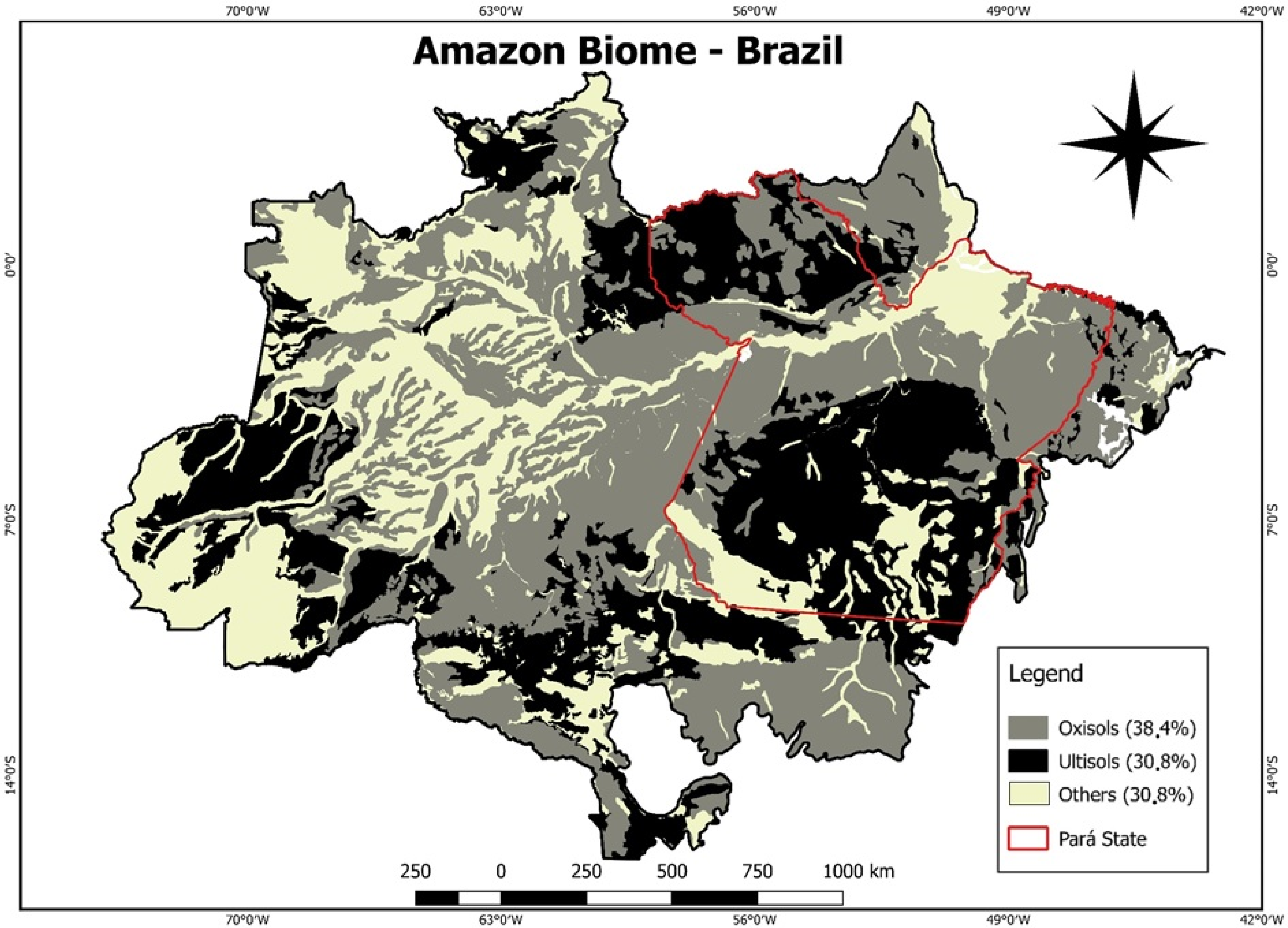


Figure 1. Study site and soil and leaf sampling from Oxisol and Ultisol in the Pará State, Brazilian Amazon.

In the implantation of the orange orchard, were used 3 kg of chicken manure and 60 g of P_2O_5 (*single superphosphate*) per pit, and 60 g of N (urea) and 30 g K_2O (potassium chloride), per plant. From the second to the fifth year, 200g of N, 90g of P_2O_5 and 180g of K_2O were applied per plant. And from the sixth year on, the production fertilization started with 80 kg ha^{-1} of N, 20 kg ha^{-1} of P_2O_5 and 40 kg ha^{-1} of K_2O. The cupric fungicide, known as Bordeaux mixture ($CuSO_4$ + Ca $(OH)_2$), was also applied.

In the oil palm cultivation area was application of 23 kg ha^{-1} of natural phosphate reactive from Arad (33% P_2O_5), followed by the formulation NPK (11-07-23) + 2.5% Mg + 0.5% B; with annual applications of the N-P-K formula (10-07-22). For the implementation of black pepper cultivation, were used 1.5 kg of chicken manure + 500 g of thermophosphate (Yoorin - 17.5% of P_2O_5), per pit. In the first and second year were applied 50g of urea, 45g of triple superphosphate and 30g of potassium chloride, per plant. From the third year onwards were applied 150g of urea, 60g of triple superphosphate and 100g of potassium chloride, per plant. The Bordeaux mixture was also used to control pests in black pepper cultivation.

In each crop area, the soils were sampled in the 0 – 0.2 m deep, were taken 10 simple samples to form one composite sample, with three replications, making a total of 30 simple samples and 10 samples composed by crop. Soil samples were also collected in areas adjacent to the plantations, composed of native or naturally recovered vegetation (regionally called capoeiras), for the purpose of comparison and obtaining the enrichment factor (EF).

The physical-chemical analyzes of soil samples were carried out according to Embrapa (2011): pH H_2O and 1 mol L^{-1} KCl solution (1: 2.5); Ca and Mg in 1 mol L^{-1} KCl solution and quantified by atomic absorption spectrophotometry; K extracted with 0.05 mol L^{-1} HCl solution and quantified by flame photometry; Available P extracted with HCl solution 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1} (Mehlich-1) and determined by colorimetry; the organic carbon by the Walkley & Black method (wet combustion) with potassium dichromate; the Al_2O_3 total by sulfuric attack; and clay content (Gee et al. 1986).

X-ray fluorescence spectrometry (FRX) was used for the quantitative evaluation of the P_2O_5. Soil samples were placed in an oven to dry at 110 ^oC and then taken to a muffle, at 1000 ^oC, for two hours, for the determination of fire-exposed loss. The soil were analyzed in the X-ray fluorescence spectrometer, Rigaku model RIX 3000, equipped with Rh, by the calibration curves method, which were constructed using international reference materials.

Plant samples were collected at the same points of soil collection to verify the U and Th bioaccumulation capacity by cultivation. Leaf sampling in black pepper and orange plantations consisted of collecting freshly ripe leaves, in the middle third portion of the crown per useful plant, in way the North, South, East and West (Oliveira and Cruz, 1999; Dias et al. 2013). For oil palm, the leaf sampling from the third or fourth year of cultivation was performed on leaf nº 17 (the apex to based), being considered as the best expression or the ideal physiological state for the oil palm (Rodrigues et al. 2006).

4.2.2 U and Th methods and measurements techniques

The soil and plants tissue samples were extracted according to Aqua Regia (AR) method (3:1 $HCl:HNO_3$, v/v). As procedure: 0.5 g aliquots of the sieved samples in 100 mesh mesh were transferred to teflon tubes, adding 9 mL of HCl (32%) and 3 mL of HNO_3 (65%), in ratio 3:1, with analytical purity and concentrated, next was rest for pre-digestion for 12h. The set was kept in a closed system in a microwave (Mars Xpress, CEM Corporation) for 20' at 180ºC. After cooling, the samples were transferred to certified flasks (NBR ISSO/IEC) of 25 mL, the volume of the flasks being completed with ultrapure water and the extracts filtered on filter paper. The analysis were performed in triplicates and with blank tests (control). U and Th were quantified using inductively coupled plasma mass spectrometry (ICP-MS).

Values of U and Th in ppm were converted to activity concentration, in Bq kg^{-1}, using the conversion factors given by the International Atomic Energy Agency (IAEA, 1989) and by the Polish Central Laboratory for Radiological Protection, as shown in Malczewski et al. (2004). The specific parent activity of a sample containing 1 mg kg^{-1}, by weight, of ^{238}U is 12.35 Bq kg^{-1} and 1 mg kg^{-1} of ^{232}Th is 4.06 Bq kg^{-1}.

4.2.3 Enrichment and bioaccumulation factors calculation

The enrichment factor (EF) was calculated in order to verify the degree of contamination by increment of radioelements in the areas study. The calculation of the enrichment factor was done using the following Eq. 1 (Loska et al. 2004).

$$EF = (Cn/Cref) / (Bn/Bref) \quad (1)$$

Where Cn is the concentration of the element studied at the point under study (agroecosystems) in sample n, Cref is the concentration of the reference element at the point under study (agroecosystems), Bn is the concentration of the element under study in the reference environment (remaining forest - control) and Bref is the concentration of the reference element in the reference environment (remaining forest - control).

Several chemical elements are commonly used as a reference, such: Al, Ca, Fe, Mn, Ti and V (Loska et al. 2004). The reference element used in this study was Al_2O_3, this guarantees more robustness and reliability to the results obtained, the its concentration tends to be more uniform (Rubio et al. 2000; Alagarsamy and Zhang, 2010; Islam et al. 2015). Sutherland (2000) proposed a preliminary classification system to assess the degree of pollution with the EFs, divided into 5 class: EF < 2, deficient to minimal enrichment; 2 ≥ EF < 5, moderate enrichment; 5 ≥ EF < 20, significant enrichment; 20 ≥ EF < 40, very high enrichment; EF ≥ 40, extremely high enrichment.

For the calculation of the enrichment factors, the baseline levels of reference element and the elements under study were reported as the average concentration from collected in characterized areas with the least anthropic impact (remaining forests - control) and adjacent to agroecosystems. The bioaccumulation factor (BAF) was obtained using the following Eq. 2 (Khan et al. 2015).

$$BAF= [C\ plant / C\ soil] \quad (2)$$

Where: [C plant] = radioelement concentration in the plant tissue and; [C soil] = radioelement concentration in the soil.

4.3 RESULTS

4.3.1 Soil attributes

Physical and chemical properties of the soil samples are in Table 1. The soils in oil palm and citrus cultivation showed values of pH H_2O 4.6 and 4.7, respectively, indicating high acidity, while the soil cultivated with black pepper showed medium acidity (pH H_2O 5.2). The Ca^{2+} exchangeable in the oil palm areas was 9.6 $mmol_c\ kg^{-1}$, considered low. The Ca^{2+} exchangeable of 13.7 and 34 $mmol_c\ kg^{-1}$ for orange and black pepper areas can be considered medium and high, respectively, according to the classification by Alvarez et al. (1999). The Mg^{2+} exchangeable in soils: 2.5 $mmol_c\ kg^{-1}$ (oil palm), 15 $mmol_c\ kg^{-1}$ (black pepper) and 9 $mmol_c\ kg^{-1}$ (orange) are classified as low, high and medium, respectively (Alvarez et al. 1999). The K^{+} exchangeable was considered low in soils with oil palm and orange (0.9 and 0.5 $mmol_c\ kg^{-1}$, respectively). Only the soil cultivated with black pepper, showed a high concentration of K^{+} exchangeable (4.2 $mmol_c\ kg^{-1}$).

The labile P (Mehlich-1) in oil palm, black pepper and citrus soils were 5, 234 and 8 mg kg^{-1}, respectively. These values are considered: very low, very high and low, according to the classification by Alvarez et al. (1999). The organic carbon content in soils cultivated with oil palm (11.6 g kg^{-1}) and orange (6.9 g kg^{-1}) were low, while in black pepper (16 g kg^{-1}) was considered medium (Alvarez et al. 1999). The clay content in the studied soils was considered low. Furthermore, the soils have a predominance of the sand fraction (Table 1), the characteristic observed in most of the soils in this region.

Table 1. Identification, location and attributes of soils ($n^a = 30$)

Soils[b]	Geographical coordinates	pH		Ca^{2+}	Mg^{2+}	K^+	P	Al_2O_3	OC[c]	Clay	Silt	Sand
		H_2O	KCl	.........$mmol_c\ kg^{-1}$.......			$mg\ kg^{-1}$	............................$g\ kg^{-1}$............................				
				Elaeis guineensis Jacq.								
Typic Hapludox	2°13′ 18″ S 48° 47′ 52″ W	4.6	4.3	9.6	2.5	0.9	5	54.1	11.6	277	133	590
Control[d] (Oxisol)		4.0	3.7	1.3	1.7	0.6	2.6	54.0	13.5	303	98	599
				Piper nigrum L.								
Typic Hapludult - 1	1°47′ 07″ S 47° 04′ 07″ W	5.2	4.7	34	15	4.2	234	71.7	16	171	117	712
Control (Ultisol 1)		4.1	3.7	11.3	10	0.5	1	52.9	11	168	74	758
				Citrus sinensis (L.) Osbeck								
Typic Hapludult - 2	1°48′ 08″ S 47° 11′ 56″ W	4.7	4.1	13.7	9	0.5	8	53.6	6.9	60	21	919
Control (Ultisol 2)		4.4	3.8	5.1	1.2	0.1	1.5	48.8	9.7	63	58	879

[a]Number of samples, [b]USDA Soil Taxonomy (2014), [c]Organic carbon, [d]non-agricultural

4.3.2 Uranium and Thorium in soils and plants

The average concentrations of U and Th obtained for soils cultivated with black pepper (3.48 and 10.70 mg kg^{-1}) and oil palm (2.15 and 7.25 mg kg^{-1}), respectively, were higher than those of remaining forest fragments (control), while the orange cultivation showed concentrations of U (2.19 mg kg^{-1}) and Th (9.0 mg kg^{-1}) lower than the control area: U (2.99 mg kg^{-1}) and Th (10.30 mg kg^{-1}), Fig. 2. In the agricultural soils in this study, the concentrations of U and Th showed positive correlations with the levels of P_2O_5 (Fig. 3). The enrichment factors were less than 2 (EF < 2), were obtained the following orders: U - black pepper > oil palm > orange; Th - oil palm > black pepper > orange. The soil cultivated with orange showed low EF (Fig. 4A).

The average concentrations of U and Th in plant tissues were, respectively, 0.08 and 0.18 mg kg^{-1} for orange, 0.05 and 0.48 mg kg^{-1} for black pepper and 0.04 and 0.10 mg kg^{-1} for oil palm (Fig. 2). The bioaccumulation factors of U and Th for the three cultivated plants were extremely low, BAF < 0.05 (Fig. 4B). The activity concentration of ^{232}Th (Table 2) in the plant tissue of the black pepper was extremely high (1,948.8 mBq kg^{-1}). For activity concentrations in the plant tissues were obtained the following orders: ^{238}U (mBg kg^{-1}) - orange > black pepper > oil palm; ^{232}Th (mBg kg^{-1}) - black pepper >> orange > oil palm.

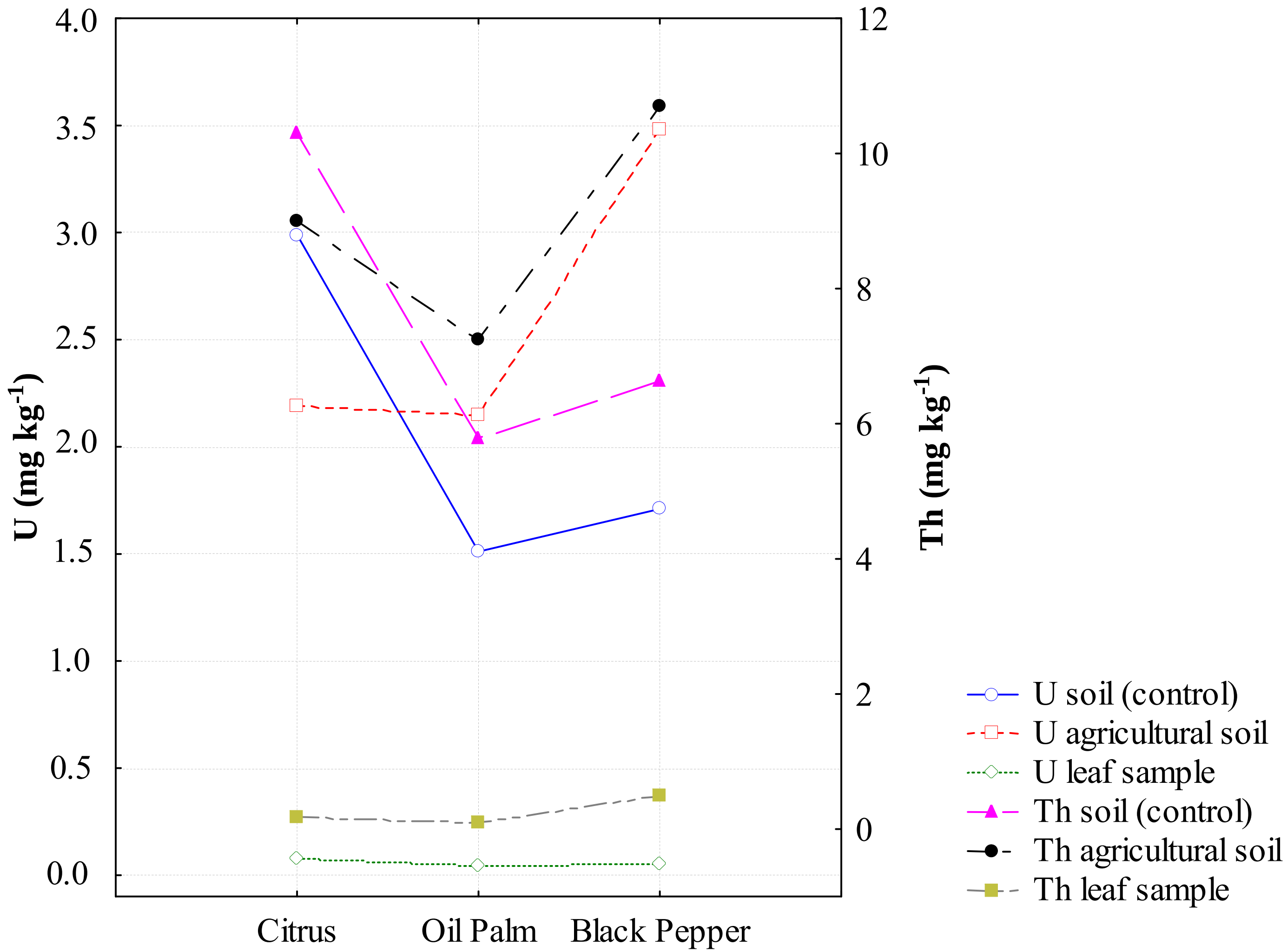


Figure 2. Uranium and Thorium in agricultural soils and of reference (control) and in plants tissue of the citrus, pepper and oil palm cultivation.

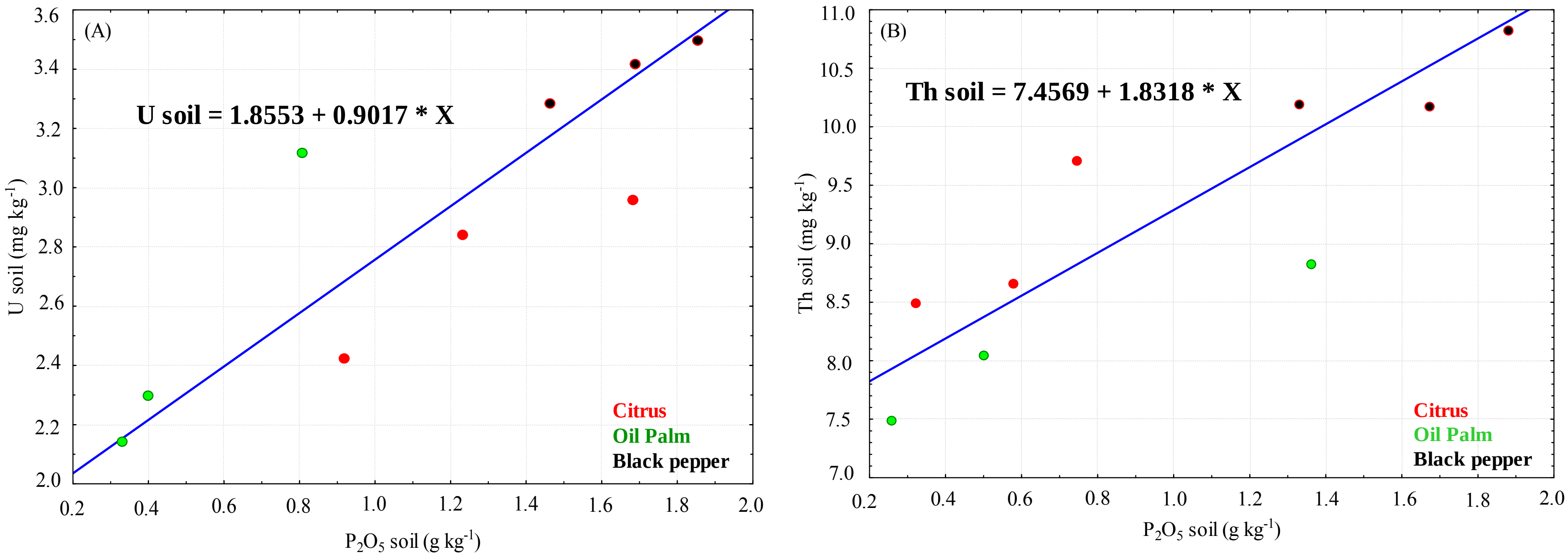


Figure 3. Elemental concentration ratio of U (A) and Th (B) with P_2O_5 content in the cultivated soils.

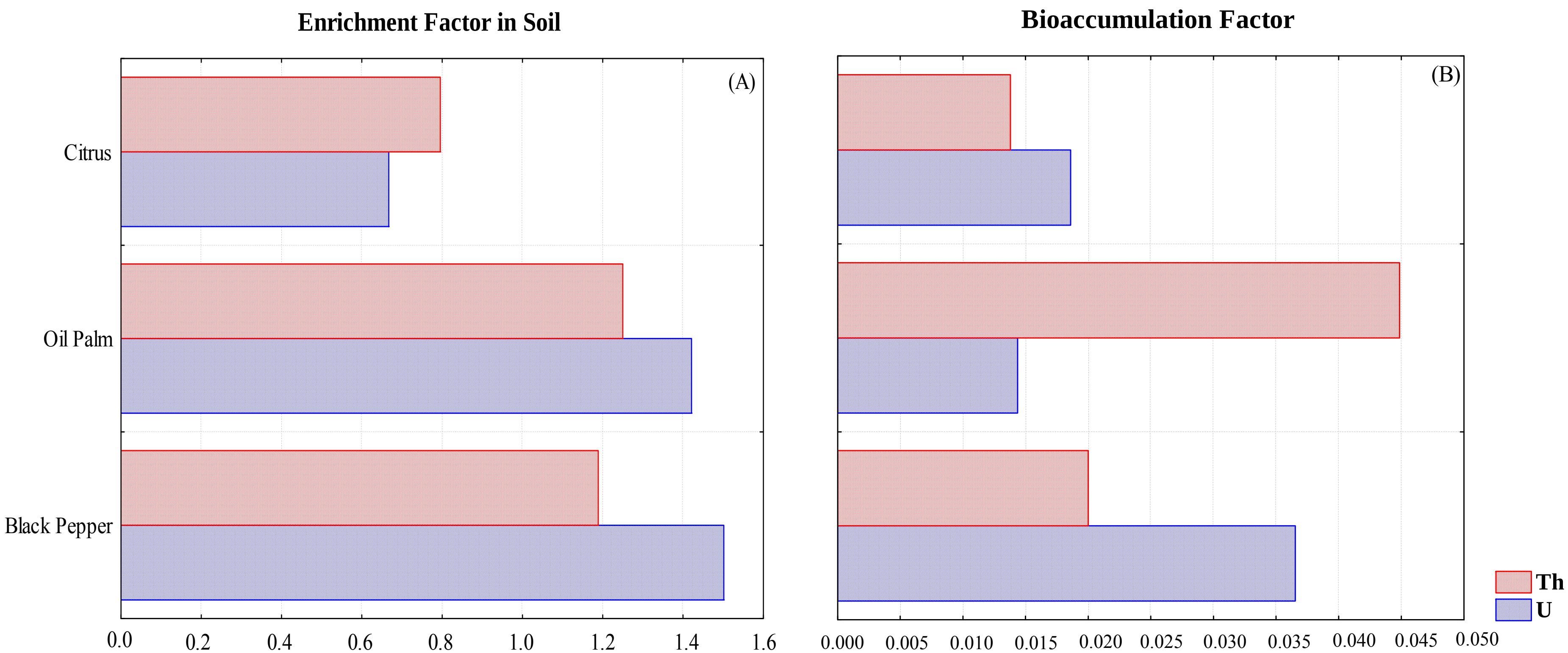


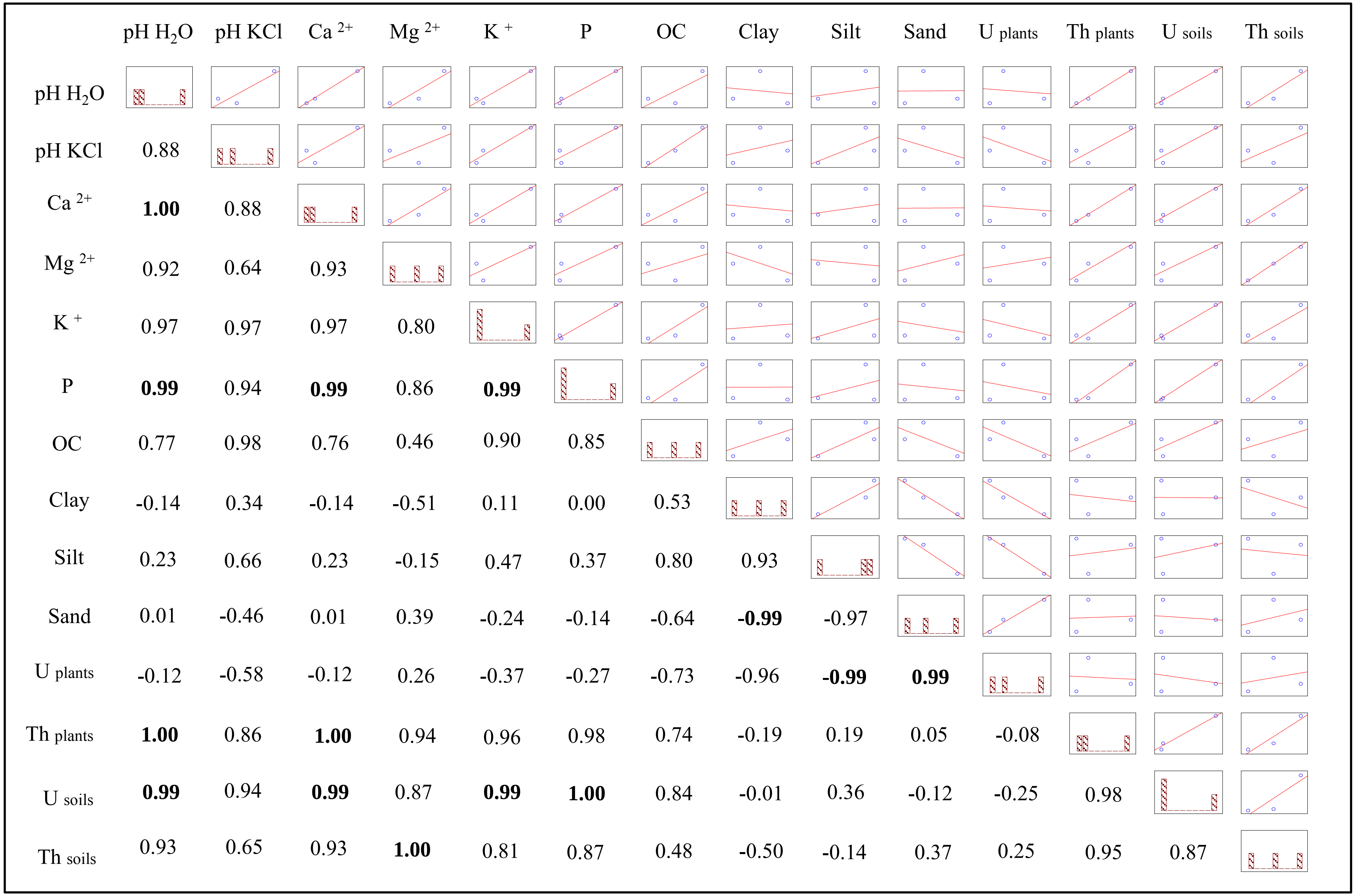
Figure 4. Enrichment (A) and bioaccumulation (B) factors of the U and Th in the cultivated soils and plants.

Pearson's correlation between the concentrations of U and Th with the properties of the soils in the cultivated areas proved to be strongly positive of the U with pH, Ca, K and P, while the most significant of Th was with Mg (Fig. 5). The U in plant tissues showed a negative correlation with the silt content and a strong positive correlation with the sand content of the soils. Regarding the Th concentration in the plants, showed a strong positive correlation with the pH and Ca of the soils (Fig. 5).

Table 2. Activity concentrations of uranium and thorium in soil and plant samples (dry weight) compared with existing literature data

Samples	^{238}U	^{232}Th	Th/U	References
Soils/Countries	.... Bq kg^{-1}	....		
Typic Hapludox[a]	26.55	29.43	1.11	This study (n = 30)
Typic Hapludult[a] -1	42.99	43.44	1.01	-
Typic Hapludult[a] -2	27.05	36.54	1.35	-
Control[b] (Oxisol)	18.65	23.51	1.26	-
Control (Ultisol 1)	21.12	26.96	1.28	-
Control (Ultisol 2)	36.93	41.82	1.13	-
Brazil (n = 15)	9.63	33.90	3.52	Pérez et al., 1998
Brazil (n = 153)	57.30	60.70	1.06	Peixoto et al., 2016
Brazil (n = 25)	-	86.30	-	Nascimento et al., 2019
USA	18.28	5.89	0.32	Myrick et al., 1983
Turkey	29.90	36.70	1.23	Cengiz, 2017
South Africa	28.28	31.55	1.12	Masok et al., 2018
Indian	37.70	75.30	1.99	Selvasekarapandian et al., 2000
China	112.00	71.50	0.64	Yang et al., 2005
Italy	41.37	50.59	1.22	Guagliardi et al., 2020
Spain	153.14	71.86	0.47	Taboada et al., 2006
Portugal	49	51	1.04	UNSCEAR, 2000
Greece	25	21	0.84	-
Worldwide	35	30	0.86	-
Plants	...... mBq kg^{-1}	....		
Oil Palm (Typic Hapludox)	494.0	406.0	0.82	This study (diagnostic leaf)
Black pepper (Typic Hapludult -1)	617.5	1,948.8	3.16	-
Citrus (Typic Hapludult -2)	988.0	730.8	0.74	-
Oil Palm (seed)	64.20	59.91	0.93	Ramli et al., 2009
Cassava (leaf)	35.54	22.45	0.63	-
Papaya (fruit)	6.22	2.33	0.37	-
Jackfruit (fruit)	5.44	4.26	0.78	-
Banana (fruit)	< 0.49	< 0.21	-	-
Moss	599.50	820.29	1.37	-
Tomato (fruit) - Black sand	16,660.00	1,540.00	0.09	Hegazy et al., 2013
Tomato (fruit) - Clay soil	2,220.00	490.00	0.22	-
Mango (fruit) - Black sand	14,310.00	970.00	0.07	-
Mango (fruit) - Clay soil	9,390.00	490.00	0.05	-
Wheat (flour)	5,700.00	1,900.00	0.33	Khan et al., 2020
Reference values:				UNSCEAR, 2000
Root vegetables and fruits	3	0.5	0.17	-
Leafy vegetables	20	15	0.75	-
Grain products	20	3	0.15	-

[a]Agricultural fields, [b]non-agricultural



	pH H_2O	pH KCl	Ca^{2+}	Mg^{2+}	K^{+}	P	OC	Clay	Silt	Sand	U plants	Th plants	U soils	Th soils
pH H_2O														
pH KCl	0.88													
Ca^{2+}	**1.00**	0.88												
Mg^{2+}	0.92	0.64	0.93											
K^{+}	0.97	0.97	0.97	0.80										
P	**0.99**	0.94	**0.99**	0.86	**0.99**									
OC	0.77	0.98	0.76	0.46	0.90	0.85								
Clay	-0.14	0.34	-0.14	-0.51	0.11	0.00	0.53							
Silt	0.23	0.66	0.23	-0.15	0.47	0.37	0.80	0.93						
Sand	0.01	-0.46	0.01	0.39	-0.24	-0.14	-0.64	**-0.99**	-0.97					
U plants	-0.12	-0.58	-0.12	0.26	-0.37	-0.27	-0.73	-0.96	**-0.99**	**0.99**				
Th plants	**1.00**	0.86	**1.00**	0.94	0.96	0.98	0.74	-0.19	0.19	0.05	-0.08			
U soils	**0.99**	0.94	**0.99**	0.87	**0.99**	**1.00**	0.84	-0.01	0.36	-0.12	-0.25	0.98		
Th soils	0.93	0.65	0.93	**1.00**	0.81	0.87	0.48	-0.50	-0.14	0.37	0.25	0.95	0.87	

Figure 5. Pearson's correlation coefficient between U and Th concentrations with the attributes of soils ($p \leq 0.05$).

4.4 DISCUSSION

4.4.1 Soil attributes

The soils of this study, except for the black pepper cultivation, even following the criteria and recommendations for the use of limestone and fertilizers, have high acidity (pH H_2O <5). In tropical regions, the climatic conditions further the loss of bases by leaching, increasing acidity, even in areas that have received liming. The soil acidity has a strong influence on the dynamics of cationic ions, making them more available under high acidity conditions (Rieuwerts et al. 2006). Study in the Eastern Amazon showed that Oxisols and Ultisols have high acidity (Birani et al. 2015; De Souza et al. 2018). In the Western Amazon, Moreira and Fageria (2009) studied 3340 soil samples collected in primary forest, secondary forest, native forest, fallow area, polyculture and monoculture areas, and observed that more than 94% have acidity values in ranges considered high to very high, according to the classification by Alvarez et al. (1999).

The organic carbon in soils with oil palm and orange were low, compared to black pepper cultivation, due to the longer time of implantation of these crops and the climatic conditions with intense rains and high temperatures that prevail in this part of the Amazon. These conditions contribute to the rapid decomposition of organic matter (De Souza et al. 2018). The organic carbon lower observed in soil cultivated with orange, may be related to the longer cultivation time of the soil. Bayer and Mielniczuk (1997) observed that the organic matter content in Ultisol was reduced from 31 g kg^{-1}, under natural conditions, to 18 g kg^{-1} as result of successive crops. Bowman et al. (1990) observed reductions of 55 to 63% in organic carbon of the soil (0-15 cm) in sixty years of cultivation. De Souza Braz et al. (2013) found decrease in organic carbon of soil Typic Hapludox from the Eastern Amazon, after 15 years of use of land with pasture.

The clay contents of the soils in this study were low, but within the range observed by Birani et al. (2015), in soils, Typic Hapludox (38 to 931 g kg^{-1}) and Typic Hapludult (53 to 719 g kg^{-1}), from the Eastern Amazon. The results obtained indicate the predominance of sand fraction, the characteristic observed in most of the soils in the Pará state (De Souza et al. 2018).

The soils cultivated with orange and oil palm showed low of the P, while in the black pepper cultivation the values were very high. Frazão et al. (2013) evaluated oil palm plantations in Amazon soils, with 4, 8 and 25 years of implantation, and observed P content in the soil of 4.3, 3.9 and 4.2 mg kg^{-1}, respectively. This variation of P in agricultural areas is usually due to the amounts applied in fertilization and soil management, which can provide greater productivity and therefore greater export of the nutrient. The higher P content of the soil in the area cultivated with black pepper may be related to the residual effect of fertilization with thermophosphate

(Withers et al. 2018).

4.4.2 Uranium and Thorium in soils and plants

The U and Th concentrations in agricultural soils showed a positive correlation with the increase in the P_2O_5 content, resulting from the use of P-fertilizers in these areas. Thus, the results in the present study show a direct relationship between phosphate fertilization and an increase of U and Th in the soils. The U concentration is higher than the Th in P-fertilizers, however in the soils of the present study, this did not reflect a higher U concentration in relation to Th. Takeda el al. (2006) obtained in superphosphate samples an average concentration of 31 mg kg^{-1} and 0.8 mg kg^{-1} for U and Th, respectively. The U and Th concentrations are 5.6 and 2.6 times higher in triple superphosphate (TSP) than single superphosphate (SSP), with average 172.8 mg kg^{-1} of U and 2.1 mg kg^{-1} of Th (Vogel et al. 2020). It is important to observe, addition to the U and Th concentrations in P-fertilizers, their bioavailability in soils (Souza and Ferreira, 2005).

In oxidizing environments, common in superficial horizons of the soils, predominate the U-soluble and Th-insoluble form (Malikova et al. 2020). This may explain, in the studied areas, the higher levels of Th than U in the soils. In addition, the presence of CO_3^{2-} and HCO_3^- ions contributes to the permanence of U-soluble form (Malikova et al. 2020). Under such conditions, are also the soils of the present study. And, the high acidity and sandy texture of the soils, favored the solubility, mobility and leaching of these radioelements, resulting in EFs < 2 in the evaluated soils. Rodríguez et al. (2008) observed that the activity concentrations of radioelements in the soil decreased as the particle size (particle size fractions) increased.

Among the most important drivers of the U mobility is the soil pH (Echevarria et al. 2001). Low pH increase U mobility and its availability for absorption by plants (Stojanović et al. 2012). It is known that U can be more mobile in the soil than Th and more bioavailable compared to Th (Morton et al. 2002). However, it has been reported that Th in the rhizosphere can form soluble complexes with humic acids, and in this form plants can easily absorb the Th (Reiller et al. 2002). Comparing the bioaccumulation of U and Th for the three plant species in the present study, we can observe BAF (U > Th) in orange and black pepper cultivation. The bioaccumulation of Th in oil palm leaves was three times greater than that of U (BAF Th >>> BAF U). In addition to the edaphoclimatic factors that control the bioavailability of radioelements in the rhizosphere, there is a natural difference in the absorption capacity of plants (Shtangeeva, 2010).

The low bioaccumulation factors (0.01 < BAF < 0.05) obtained for U and Th in the studied species, are above the soil-plant transfer factors for the Tropical Regions: U ($TF = 4.9 \times 10^{-3}$)

and Th (TF = 8.2 x 10^{-3}), established by the International Atomic Energy Agency (IAEA, 2010). This suggests that, despite small concentrations found, orange and oil palm and black pepper plants have the capacity to accumulate U and Th.

The activity concentrations of U and Th in the soils and plants in this study show that the concentrations in the plant tissues are not based only on the quantitative properties of the soils. As reported by Tuovinen et al. (2011), the relationship between the concentration of radioelements from soils to plants is not linear. Pulhani et al. (2005) demonstrated that the availability of essential nutrients for absorption by plants, like as calcium and potassium, regulates the absorption of non-essential elements, like as U and Th.

The activity concentrations of U and Th in the soil cultivated with black pepper and in the soil of the remaining forest fragment (control), adjacent to the orange cultivation, ^{238}U (42.99 e 36.93 Bq kg^{-1}) and ^{232}Th (43.44 e 41.82 Bq kg^{-1}), respectively, were higher than the world average: ^{238}U (35 Bq kg^{-1}) and ^{232}Th (30 Bq kg^{-1}), shown that established by the United Nations Scientific Committee on Effects of Atomic Radiation (UNSCEAR, 2000). However, ^{238}U and ^{232}Th concentrations in the Amazon soils, of the present study, were well below the averages obtained by Peixoto et al. (2016) in Ultisols of the Minas Gerais state – Brazil, which may be related to the bedrock richer in these elements and the subtropical climate conditions, in which the loss by leaching is less than in the areas of this study. The higher activity concentration of ^{238}U in orange leaves may be related to soil be more sandy, that facilitated the plant uptake, and the higher activity concentration of ^{232}Th in Black pepper leaves may be related to the higher pH and Ca values of the soil (Pulhani et al. 2005).

4.5 CONCLUSIONS

The important soil properties to understand the dynamics of U and Th in the soil/plant relationship were: pH, Ca, Mg, K, P and the sand fraction;

The longer time of the soil use with the orange cultivation, compared to the other crops, was not decisive to establish cause/effect relations with the radioelements;

The soils in the present study are sandy, and possibly this contributed to the low concentrations of U and Th in the soils and plants, and also in the low enrichment and bioaccumulation factors, and the possible that losses of U and Th by leaching in crops;

The enrichment and bioaccumulation factors obtained indicate that the concentrations of U and Th in orange, black pepper and oil palm crops, for the time being, do not represent risks to the environment and for human health. However, the increments monitoring of radioelements in agricultural soils it necessary to continue.

Acknowledgements

The first author thank the Pro-Rectory of Research and Technological Development (PROPED/UFRA) for Support (Prodoutoral - 04/2017). The second (Grant 305015/2016-8) and the last (Grant 307166/2019-8) authors thank the CNPQ for the financial support.

Conflict of Interest

The authors declare that they have no conflict of interest.

CAPÍTULO 5 - ENVIRONMENTAL IMPACT OF POTENTIALLY TOXIC ELEMENTS ON TROPICAL SOILS USED FOR LARGE-SCALE CROP COMMODITIES IN THE EASTERN AMAZON, BRAZIL.

Anderson Martins de Souza Braz[1]*, Marcondes Lima da Costa[2], Antonio Rodrigues Fernandes[3], Sílvio Junio Ramos[4].

[1]Geosciences, Federal Rural University of Amazon - UFRA, Capanema - PA, Brazil.

[2]Geosciences Museum, Institute of Geosciences, Federal University of Pará - UFPA, Brazil.

[3]Institute of Agricultural Sciences, Federal Rural University of Amazon - UFRA, Belém - PA, Brazil.

[4]Instituto Tecnológico Vale, Belém - PA, 66055-090, Brazil.

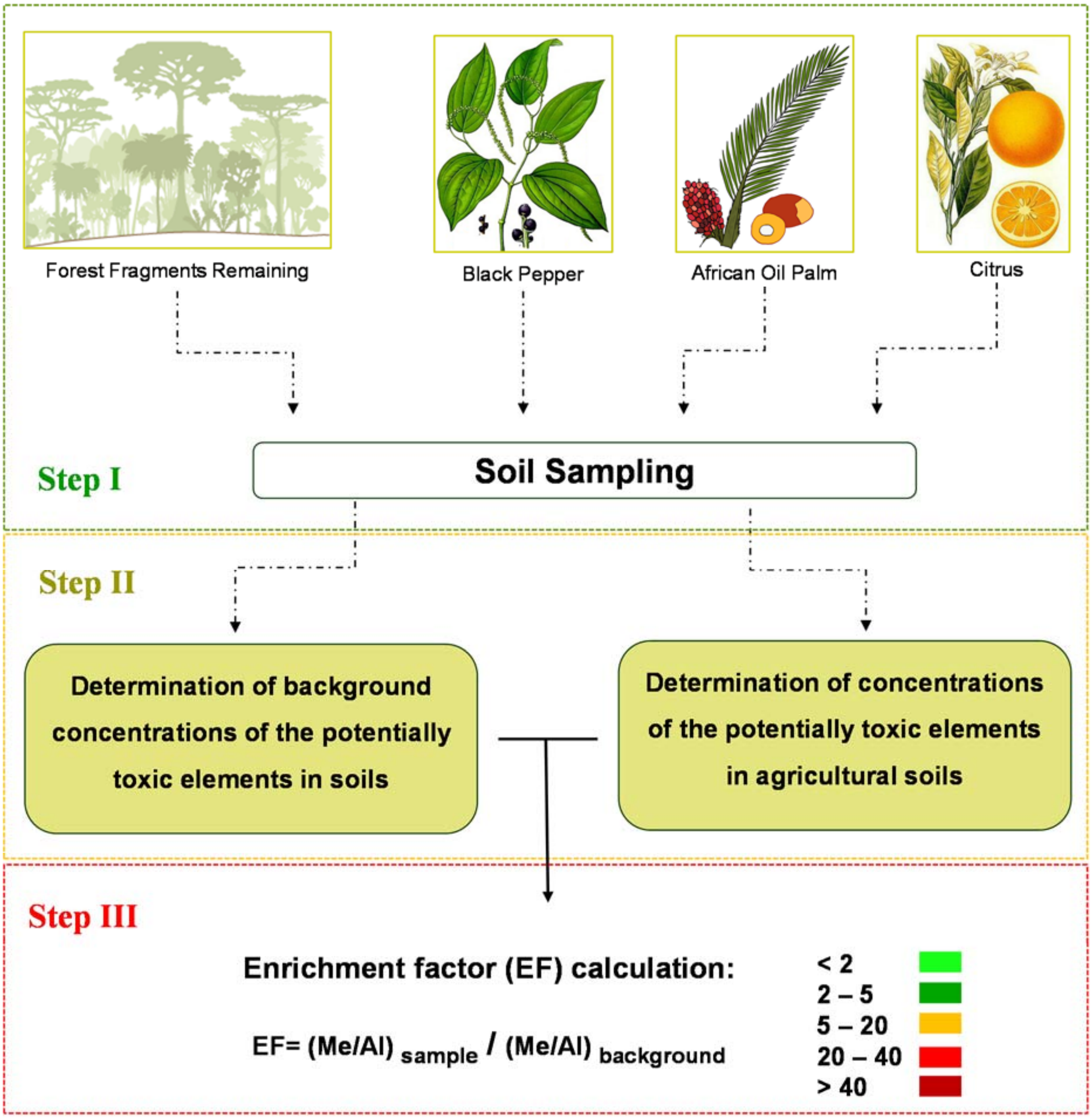
*Corresponding author: abrazgeo@gmail.com; anderson.braz@ufra.edu.br

ABSTRACT

The Amazon soils, in order to express the high agricultural potential, demand high rates of fertilizer application, making it necessary to carry out constant monitoring of ecological functions and biogeochemical processes in this important biome. The concentrations of As, Ba, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn and contamination indexes were studied in Oxisol and Ultisol, cultivated with orange (*Citrus sinensis* (L.) Osbeck), oil palm (*Elaeis guineensis* Jacq.) and black pepper (*Piper nigrum* L.), with 26, 10 and 5 years of implantation, respectively. The potential risk of contamination was estimated by the enrichment (EF) and bioaccumulation (BAF) factors. Moderate enrichment of Ba, Pb and Zn (2> EF <5) and significant for As and Cu (5> FE <20) was observed. In addition, the following orders of bioaccumulation were found: BAF oil palm: Cu > Zn > Hg > Ni > Ba > Co > As > Cr > Cd ≈ Pb; BAF black pepper: Zn > Hg > Cu > Ba > Ni > Co > Pb >> As > Cr > Cd; BAF orange: Hg > Ni > Ba > Zn > Co > Cu > As > Pb >> Cr > Cd. However, concentrations of potentially toxic elements (PTEs) in soils, except for Cr in black pepper cultivation, remained within the quality reference values (QRVs) established by environmental legislation, in all cultivation areas.

Keywords: Soil chemistry. Enrichment factor. Soil pollution. Risk assessment.

Graphical Abstract



5.1 INTRODUCTION

Nowadays, the Brazilian Amazon is a new agricultural frontier, it has a major food producing area, exporting soy and beef to global markets (Vale et al. 2019), and is a pressing challenge to reconcile competing demands on land systems for food production and conservation of natural ecosystems, such as in Amazon biome (Cortner et al. 2019). Pará is the second largest Brazilian state in area, with 1,247,955 km^2, of which approximately 57% consists of indigenous territories and protected areas, and this represents 29.73% of the Brazilian Amazon (4,196,943 km^2) and 14.65 % of Brazilian territory. The main economic activities in the state of Pará and the Amazon include agriculture, principally cattle rearing, vegetable production and mineral extraction (Bowman et al. 2012; De Souza et al. 2013). In the state of Pará there is an annual production of 286,768 tons of oranges, 1,634,476 tons of oil palm, and 39,577 tons of black pepper, which represents 2, 97 and 50% of the Brazilian production (IBGE 2017).

The growing demand in relation to food production and energy generation, coupled with society's call against deforestation in the Amazon to open new agricultural areas, has intensified the use of fertilizers in order to increase productivity. The raw materials used in the production of phosphate fertilizers and micronutrients can contain several chemical elements, which, depending on the amount and time of application, can become an environmental concern (Smidt et al. 2011; Ramos et al. 2016; Bosco-Santos et al. 2017; Vieira da Silva et al. 2017; Michalak et al. 2018). In addition, the disposal of waste and the application of pesticides and fertilizers can increase the concentration of potentially toxic elements (PTEs), for example, Pb, Cd and Hg, in soils and groundwater with potential for risk and toxicity in the environment and in human health (Dutra et al. 2019; Jú et al. 2019; Parameswari et al. 2019; Qian et al. 2019). Although PTEs occur naturally, anthropogenic sources contribute to the increased rates of redistribution of these elements among the compartments of the environment (Gong et al. 2019; Li et al. 2019).

In this way, agencies committed to environmental preservation use standardization models and techniques in order to distinguish natural occurrences of PTEs in soils and anthropogenic sources (Cetesb 2005; Martinez-Lladó et al. 2008; Lado et al. 2008; Conama 2009; Nael et al. 2009). In addition, scientific studies contribute to establish background values (natural) and can also be used to assess whether possible anthropogenic changes occur (Fernandes et al. 2018; Salomão et al. 2019; Sahoo et al. 2020).

The enrichment factor (EF) obtained from the ratio between the concentration of the element in the cultivated soil and the concentration of its level of natural base or background is an widely used estimate to assess the effects of pedogenetic processes and other non-lithogenic factors , for example, anthropic influence, on the concentration of the chemical elements and the PTEs in the environment (Loska et al. 1997; 2004; Blaser et al. 2000; Cortizas et al. 2003; Tijani et al. 2006; Dragovic´ et al. 2008; Nael et al. 2009; Muñoz-Barbosa et al. 2012; Likuku et al. 2013). Alagarsamy and Zhang (2010) classified the EF of an element as natural EF = 1, enriched when EF> 1 and depleted when EF <1. Rubio et al. (2000) consider EF values between 1 and 3 to be moderate, strong EF from 3 to 6 and severe EF> 6. EF values> 2 are strong indications of anthropic action (Fachinelli et al. 2001). The ratio between the concentrations of PTEs in plant tissues and the total in soils, called the bioaccumulation factor (BAF), is considered one of the most important input variables in the assessment of risks to human health (Sipter et al. 2009; Oti 2015).

Considering that the determination of the levels of potentially toxic elements in agricultural soils, as well as the achievement of standardization indexes, with a view to the evaluation of soil quality, can provide a qualitative and quantitative guidance in studies of environmental risk assessment. However, such assessments are scarce at the agricultural frontiers in the Amazon, which demand high applications of agricultural inputs, mainly phosphate fertilizers. In this way, the present study aimed to evaluate (i) the concentrations of PTEs of soils in Amazonian agroecosystems of citriculture, pipericulture and oil palm; (ii) determine the contamination rates, such as the enrichment and bioaccumulation factor and; (iii) establish / discuss relations with natural values and safety standards of environmental protection agencies.

5.2 MATERIAL AND METHODS

5.2.1 Study site, soil and plant sampling

For the development of this study, samples were collected in the Brazilian Amazon of Latossolo and Argissolo, in the Brazilian soil classification (Embrapa 2018) or Oxisols and Ultisols, respectively, in the Soil Taxonomy classification system (Soil Survey Staff 2014), which are predominant in the region (Fig. 1) and, in general, are characterized by having high acidity, low availability of nutrients and the sand fraction dominating the granulometry of the surface layer (Table 1), with predominance of kaolinite (De Souza et al. 2018). Soils were sampled in commercial plantations of orange (*Citrus sinensis* (L.) Osbeck), with 26 years of implantation; oil palm (*Elaeis guineensis* Jacq.), with 10 years of implantation and; pepper (*Piper nigrum* L.), with 5 years of implantation (Fig. 1).

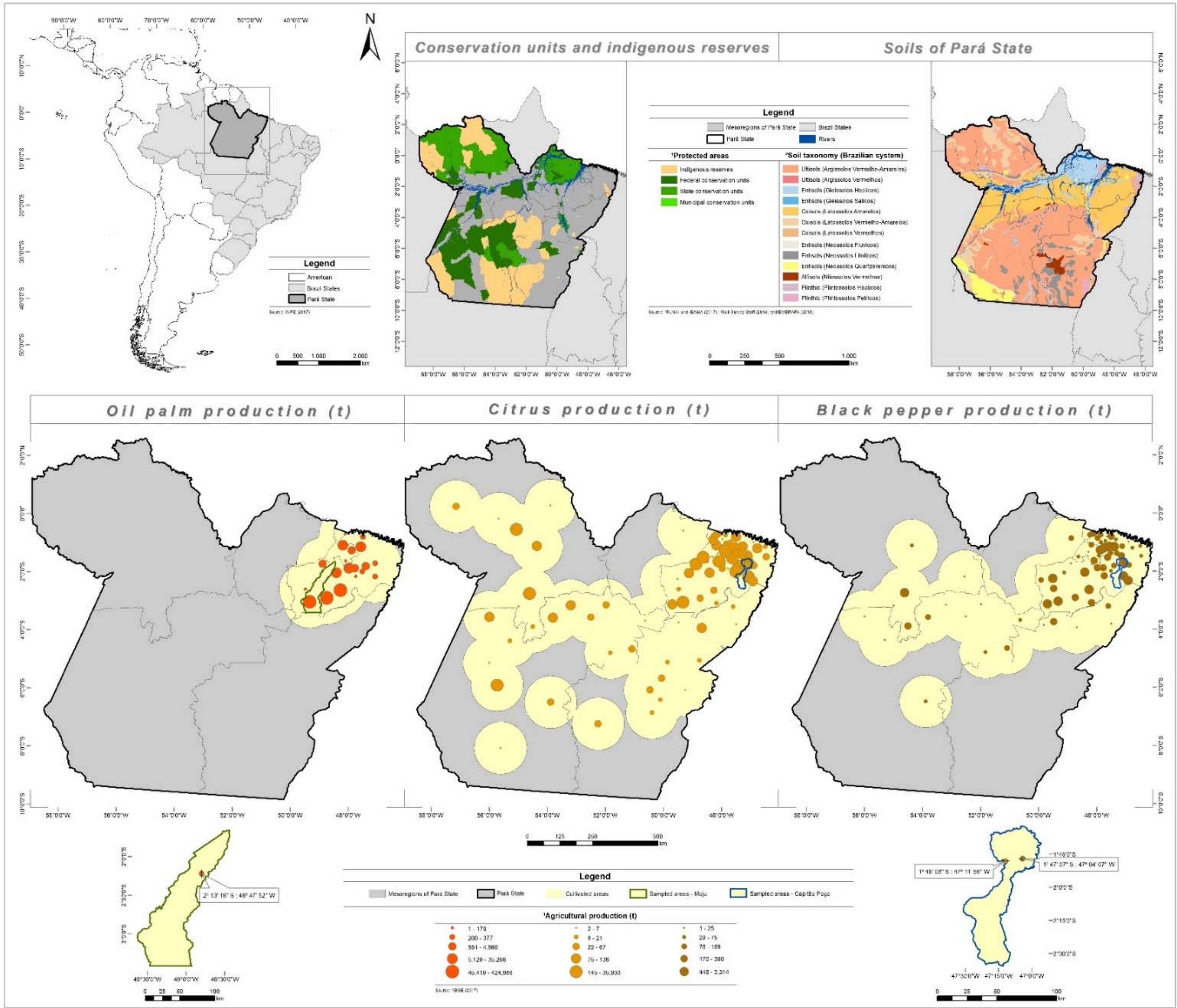


Figure 1. Study site and sampling of Oxisols and Ultisols from Pará State, Brazil.

In the implantation of the orange orchard, were used 3 kg of chicken manure and 60 g of P_2O_5 (*single superphosphate*) per pit, and 60 g of N (urea) and 30 g K_2O (potassium chloride), per plant. From the second to the fifth year, 200g of N, 90g of P_2O_5 and 180g of K_2O were applied per plant. And from the sixth year on, the production fertilization started with 80 kg ha^{-1} of N, 20 kg ha^{-1} of P_2O_5 and 40 kg ha^{-1} of K_2O. The cupric fungicide, known as Bordeaux mixture ($CuSO_4$ + Ca $(OH)_2$), was also applied.

In the oil palm cultivation area was application of 23 kg ha^{-1} of natural phosphate reactive from Arad (33% P_2O_5), followed by the formulation NPK (11-07-23) + 2.5% Mg + 0.5% B; with annual applications of the N-P-K formula (10-07-22). For the implementation of black pepper cultivation, were used 1.5 kg of chicken manure + 500 g of thermophosphate (Yoorin - 17.5% of P_2O_5), per pit. In the first and second year were applied 50g of urea, 45g of triple superphosphate and 30g of potassium chloride, per plant. From the third year onwards were applied 150g of urea, 60g of triple superphosphate and 100g of potassium chloride, per plant. The Bordeaux mixture was also used to control pests in black pepper cultivation.

In each crop area, the soils were sampled in the 0 – 0.2 m deep, were taken 10 simple samples to form one composite sample, with three replications, making a total of 30 simple samples and 10 samples composed by crop. Soil samples were also collected in areas adjacent to the plantations, composed of native or naturally recovered vegetation (regionally called capoeiras), for the purpose of comparison and obtaining the enrichment factor (EF).

The physical-chemical analyzes of soil samples were carried out according to Embrapa (2011): pH H_2O and 1 mol L^{-1} KCl solution (1: 2.5); Ca and Mg in 1 mol L^{-1} KCl solution and quantified by atomic absorption spectrophotometry; K extracted with 0.05 mol L^{-1} HCl solution and quantified by flame photometry; Available P extracted with HCl solution 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1} (Mehlich-1) and determined by colorimetry; the organic carbon by the Walkley & Black method (wet combustion) with potassium dichromate; the Al_2O_3 total by sulfuric attack; and clay content (Gee et al. 1986).

Plant samples were collected at the same points of soil collection to verify the bioaccumulation capacity of PTEs by cultivation. Leaf sampling in black pepper and orange plantations consisted of collecting freshly ripe leaves, in the middle third portion of the crown per useful plant, in way the North, South, East and West (Oliveira and Cruz 1999; Dias et al. 2013). For oil palm, the leaf sampling from the third or fourth year of cultivation was performed on leaf nº 17 (the apex to based), being considered as the best expression or the ideal physiological state for the oil palm (Rodrigues et al. 2006).

5.2.2 Potentially toxic elements analyses

The elements evaluated in the study were As, Ba, Cd, Co, Cu, Cr, Hg, Ni, Pb and Zn. The metal content in the samples was extracted according to Aqua Regia (AR) method (3:1 $HCl:HNO_3$, v/v). This method has been used by the International Organization for Standardization as the standard for soil certification in Europe (ISO 1995). As procedure: 0.5 g aliquots of the sieved samples in 100 mesh mesh were transferred to teflon tubes, adding 9 mL of HCl (32%) and 3 mL of HNO_3 (65%), in ratio 3:1, with analytical purity and concentrated, next was rest for pre-digestion for 12h. The set was kept in a closed system in a microwave (Mars Xpress, CEM Corporation) for 20' at 180ºC. After cooling, the samples were transferred to certified flasks (NBR ISSO / IEC) of 25 mL, the volume of the flasks being completed with ultrapure water and the extracts filtered on filter paper. The analysis were performed in triplicates and with blank tests (control). All elements were quantified using inductively coupled plasma mass spectrometry (ICP-MS).

5.2.3 Enrichment and bioaccumulation factors calculation

The enrichment factor (EF) was calculated in order to verify the degree of contamination by increment of PTEs in the areas study. The calculation of the enrichment factor was done using the following Eq. 1 (Loska et al. 2004).

$$EF = (Cn/Cref) / (Bn/Bref) \quad (1)$$

Where Cn is the concentration of the element studied at the point under study (agroecosystems) in sample n, Cref is the concentration of the reference element at the point under study (agroecosystems), Bn is the concentration of the element under study in the reference environment (remaining forest - control) and Bref is the concentration of the reference element in the reference environment (remaining forest - control).

Several chemical elements are commonly used as a reference, such: Al, Ca, Fe, Mn, Ti and V (Loska et al. 2004). The reference element used in this study was Al_2O_3, this guarantees more robustness and reliability to the results obtained, the its concentration tends to be more uniform (Rubio et al. 2000; Alagarsamy and Zhang 2010; Islam et al. 2015). Sutherland (2000) proposed a preliminary classification system to assess the degree of pollution with the EFs, divided into 5 class: $EF < 2$, deficient to minimal enrichment; $2 \geq EF < 5$, moderate enrichment; $5 \geq EF < 20$, significant enrichment; $20 \geq EF < 40$, very high enrichment; $EF \geq 40$, extremely high enrichment.

For the calculation of the enrichment factors, the baseline levels of reference element and the elements under study were reported as the average concentration from collected in characterized areas with the least anthropic impact (remaining forests - control) and adjacent to agroecosystems. The bioaccumulation factor (BAF) was obtained using the following Eq. 2

(Khan et al. 2015).

BAF= [C plant / C soil] (2)

Where: [C plant] = concentration of PTE in plant tissue and; [C soil] = concentration of PTE in the soil.

5.3 RESULTS

5.3.1 Soil attributes

The soils of areas cultivated with oil palm and orange, showed values of pH H_2O 4.6 and 4.7, respectively (Table 1), indicating high acidity. The soil cultivated with black pepper, with pH H_2O 5.2, presents medium acidity (Alvarez et al. 1999). The ΔpH (pH KCl - pH H_2O) values of the soils in this study: -0.3 (oil palm); -0.5 (black pepper) and -0.6 (orange), show the predominance of negative charges compared to the Acric soils that present positive charges (Mekaru and Uehara 1972).

The Ca^{2+} exchangeable in the oil palm areas was 9.6 $mmol_c\ kg^{-1}$, considered low. The Ca^{2+} exchangeable of 13.7 and 34 $mmol_c\ kg^{-1}$ for orange and black pepper areas can be considered medium and high, respectively, according to the classification by Alvarez et al. (1999). The Mg^{2+} exchangeable in soils: 2.5 $mmol_c\ kg^{-1}$ (oil palm), 15 $mmol_c\ kg^{-1}$ (black pepper) and 9 $mmol_c\ kg^{-1}$ (orange) are classified as low, high and medium, respectively (Alvarez et al. 1999). The K^+ exchangeable was considered low in soils with oil palm and orange (0.9 and 0.5 $mmol_c\ kg^{-1}$, respectively). Only the soil cultivated with black pepper, showed a high concentration of K^+ exchangeable (4.2 $mmol_c\ kg^{-1}$).

The labile P (Mehlich-1) in oil palm, black pepper and citrus soils were 5, 234 and 8 mg kg^{-1}, respectively. These values are considered: very low, very high and low, according to the classification by Alvarez et al. (1999). The organic carbon content in soils cultivated with oil palm (11.6 g kg^{-1}) and orange (6.9 g kg^{-1}) were low, while in black pepper (16 g kg^{-1}) was considered medium (Alvarez et al. 1999).

The clay content in the studied soils was considered low. Furthermore, the soils have a predominance of the sand fraction (Table 1), the characteristic observed in most of the soils in this region.

Table 1. Identification, location and attributes of agricultural soils (n[a] = 30)

Soils[b]	Geographical coordinates	pH		Ca^{2+}	Mg^{2+}	K^{+}	P	Al_2O_3	OC[c]	Clay	Silt	Sand
		H_2O	KCl	.........$mmol_c$ kg^{-1}.......			mg kg^{-1}	............................g kg^{-1}............................				
Oil palm (*Elaeis guineensis* Jacq.)												
Typic Hapludox	2°13′ 18″ S 48° 47′ 52″ W	4.6	4.3	9.6	2.5	0.9	5	54.1	11.6	277	133	590
Control[d] (Oxisol)		4.0	3.7	1.3	1.7	0.6	2.6	54.0	13.5	303	98	599
Black pepper (*Piper nigrum* L.)												
Typic Hapludult - 1	1°47′ 07″ S 47° 04′ 07″ W	5.2	4.7	34	15	4.2	234	71.7	16	171	117	712
Control (Ultisol 1)		4.1	3.7	11.3	10	0.5	1	52.9	11	168	74	758
Citrus (*Citrus sinensis* (L.) Osbeck)												
Typic Hapludult - 2	1°48′ 08″ S 47° 11′ 56″ W	4.7	4.1	13.7	9	0.5	8	53.6	6.9	60	21	919
Control (Ultisol 2)		4.4	3.8	5.1	1.2	0.1	1.5	48.8	9.7	63	58	879

[a]Number of samples, [b]USDA Soil Taxonomy (2014), [c]Organic carbon, [d]non-agricultural

5.3.2 PTEs, EF and BAF in agricultural soils-plants

The average of EPTs concentrations obtained for the soils in this study, both in the plantations and in remaining forest fragments (natural values), are showed in table 2. In general, the soil cultivated with oil palm exceeded the values found in the native area for the elements, As, Ba, Cr and Pb. The soil cultivated with black pepper was superior to the native for Ba, Cr, Cu, Ni, Pb and Zn. While in the soil cultivated with orange, this behavior was observed only for Cu and Zn. The Cd values were similar for all sampled areas, and small variations were observed for Co and Hg. In soils cultivated with oil palm and black pepper, occurred enrichment by As, Ba and Pb (Fig. 2). The soils cultivated with black pepper and orange, showed enrichment by Cu, and only in the soil cultivated with orange occurred enrichment by Zn (Fig. 2).

The PTEs in plant tissues showed great variation for crop (except for the Cd which was identical) and, in general, highest levels were observed for the orange, except the Zn which was higher in black pepper (Table 2). High bioaccumulation factor (BAF) of Cu and Zn, were obtained for oil palm (Fig. 3). The black pepper was obtained high bioaccumulation factor only for the Zn. Ba, Hg and Ni showed high bioaccumulation in orange cultivation (Fig. 3). In general, were obtained the following orders for bioaccumulation: BAF oil palm: Cu > Zn > Hg > Ni > Ba > Co > As > Cr > Cd ≈ Pb; BAF black pepper: Zn > Hg > Cu > Ba > Ni > Co > Pb >> As > Cr > Cd; BAF orange: Hg > Ni > Ba > Zn > Co > Cu > As > Pb >> Cr > Cd.

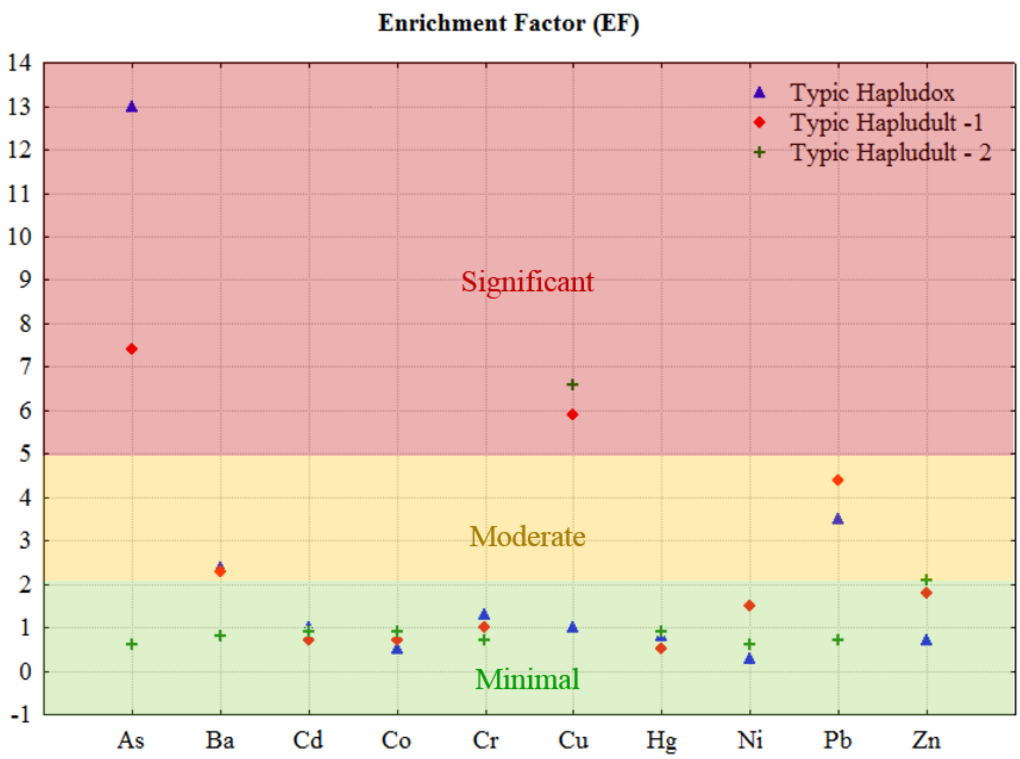


Figure 2. Enrichment factors of PTEs in the cultivated soils.

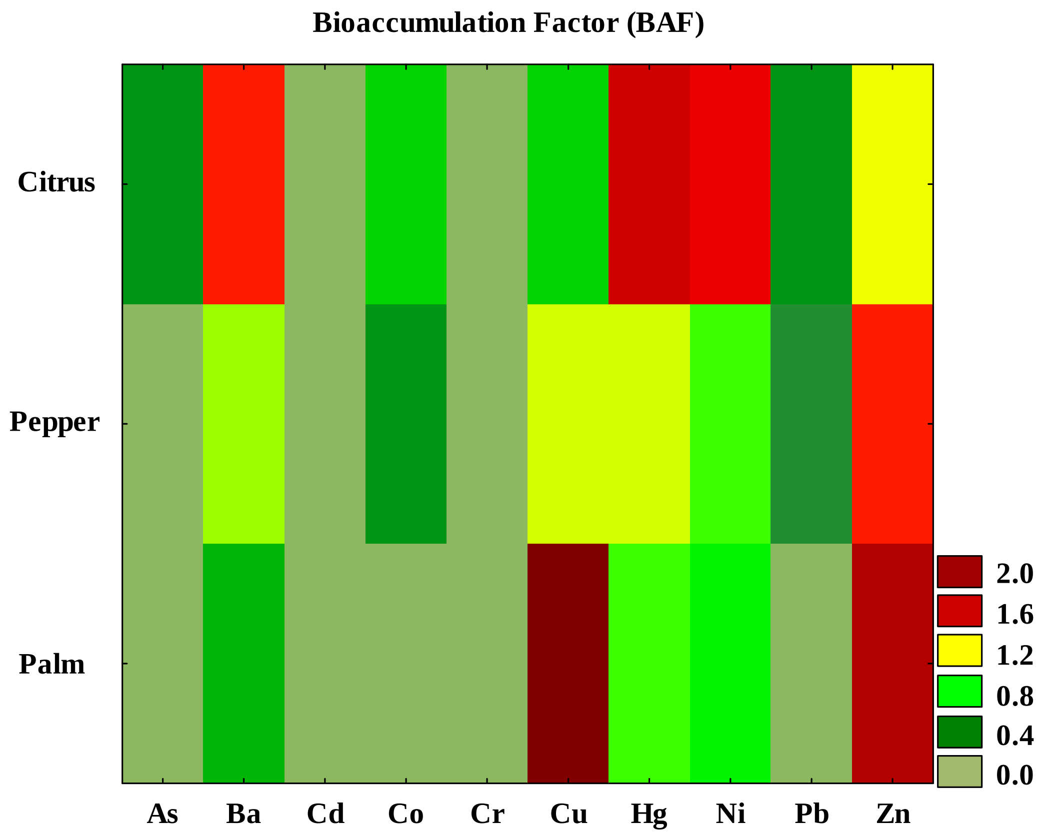


Figure 3. Bioaccumulation factors based on the mean of PTEs in plants tissue of the Citrus (Orange), Pepper (Black Pepper) and Oil Palm cultivation.

The PTEs in the studied soils did not reach the values of prevention and research (with the exception of Cr in the black pepper cultivation), fig. 4, established and regulated by the Environmental Protection Agency, as a criterion for identifying polluted or contaminated areas and assessing the potential risk to the environment and human health.

Table 2. Potentially toxic elements in soils, plants and agricultural inputs applied to soils

Samples	PTEs (mg kg^{-1})									
	As	Ba	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Soils										
Typic Hapludox[a]	1.3	24.8	0.4	1.0	50.0	2.0	0.05	2.0	7.0	8.0
Control[b] (Oxisol)	0.1	10.3	0.4	2.0	40.0	2.0	0.06	6.0	2.0	11.0
Typic Hapludult[a] - 1	2.0	32.3	0.4	2.0	70.0	16.0	0.05	4.0	6.0	19.0
Control (Ultisol 1)	0.2	10.3	0.4	2.0	50.0	2.0	0.07	2.0	1.0	8.0
Typic Hapludult[a] - 2	0.6	17.0	0.4	2.0	40.0	36.0	0.05	2.0	4.0	21.0
Control (Ultisol 2)	0.9	18.9	0.4	2.0	50.0	5.0	0.05	3.0	5.0	9.0
Plants										
Oil palm	0.09	9.00	0.01	0.10	3.00	4.10	0.03	1.03	0.23	13.33
Black pepper	0.09	23.33	0.01	0.57	2.67	13.50	0.04	2.70	0.70	25.00
Citrus	0.16	23.33	0.01	0.97	3.33	16.57	0.08	2.83	1.03	20.67
Soil inputs[c]										
Phosphate fertilizers	2 - 1200	200	0.1 - 170	1 - 12	66 - 245	1 - 300	0.01 - 1.2	7 - 38	7 - 225	50 - 1450
Nitrogen fertilizers	2 - 120	-	0.05 - 8.5	5 - 12	3 - 19	1 - 15	0.3 - 3	7 - 38	2 - 1450	1 - 42
Manure	3 - 25	270	0.3 - 0.8	0.3 - 24	5.2 - 55	2 - 60	0.09 - 0.2	7.8 - 30	6.5 - 15	15 - 250
Limestones	0.1 - 24	120	0.04 - 0.1	0.4 - 3	10 - 15	2 - 125	0.05	10 - 20	20 - 1250	10 - 450

[a]Agricultural fields, [b]non-agricultural, [c]Kabata-Pendias and Pendias (2001).

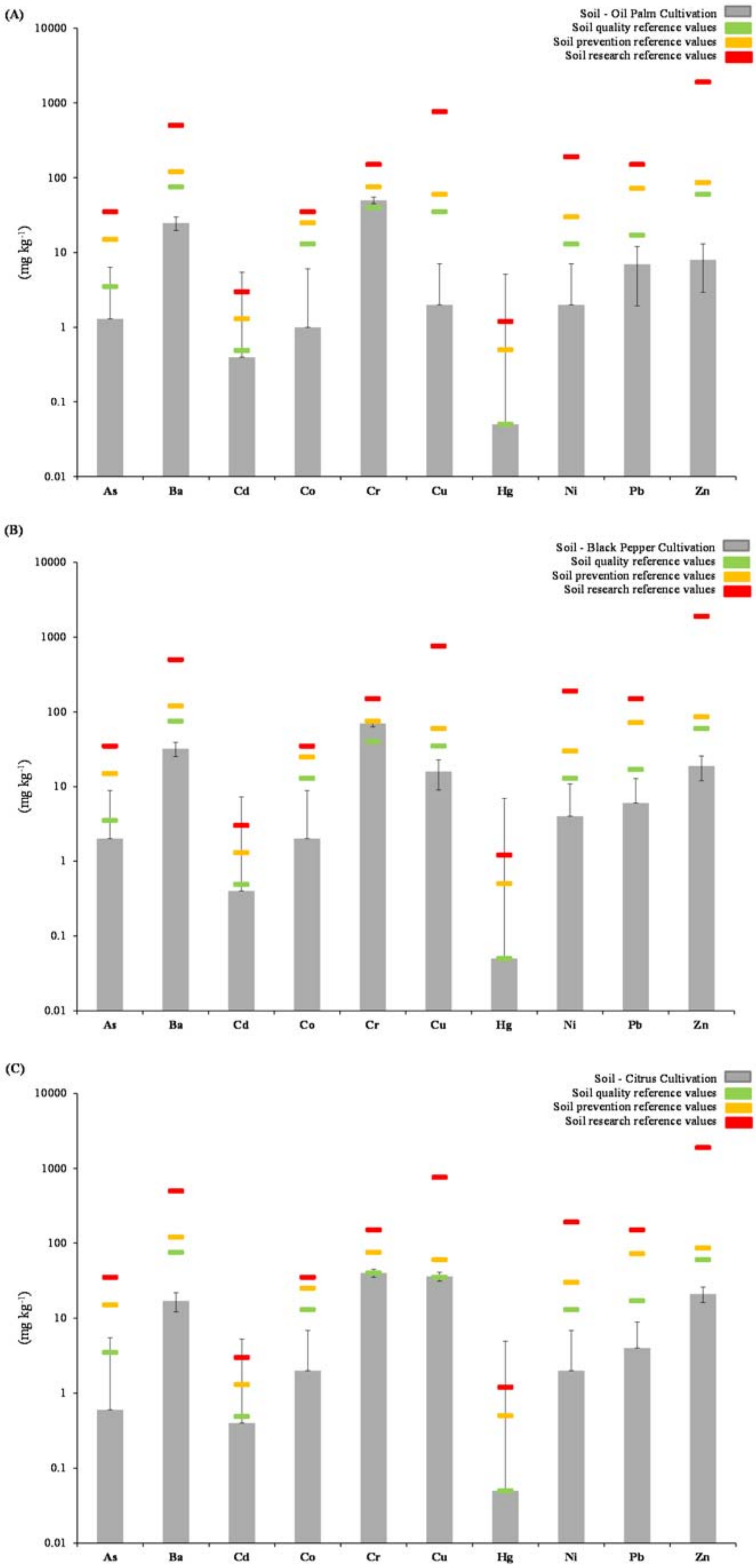


Figure 4. Relationship between PTEs contents in agricultural soils and environmental protection agency. (A): Oil Palm, (B): Black Pepper, (C): Citrus (orange).

5.4 DISCUSSION

5.4.1 Soil attributes

The soils of this study, except for the black pepper cultivation, even following the criteria and recommendations for the use of limestone and fertilizers, have high acidity (pH H_2O <5). In tropical regions, the climatic conditions further the loss of bases by leaching, increasing acidity, even in areas that have received liming. Study in the Eastern Amazon showed that Oxisols and Ultisols have high acidity (Birani et al. 2015; De Souza et al. 2018). In the Western Amazon, Moreira and Fageria (2009) studied 3340 soil samples collected in primary forest, secondary forest, native forest, fallow area, polyculture and monoculture areas, and observed that more than 94% have acidity values in ranges considered high to very high, according to the classification by Alvarez et al. (1999).

The total organic carbon (TOC) in soils with oil palm and orange were low, compared to black pepper cultivation, due to the longer time of implantation of these crops and the climatic conditions with intense rains and high temperatures that prevail in this part of the Amazon. These conditions contribute to the rapid decomposition of organic matter (De Souza et al. 2018). The organic carbon lower observed in soil cultivated with orange, may be related to the longer cultivation time of the soil. Bayer and Mielniczuk (1997) observed that the organic matter content in Ultisol was reduced from 31 g kg^{-1}, under natural conditions, to 18 g kg^{-1} as result of successive crops. Bowman et al. (1990) observed reductions of 55 to 63% in TOC of the soil (0-15 cm) in sixty years of cultivation. De Souza Braz et al. (2013) found decrease in organic carbon of soil Typic Hapludox from the Eastern Amazon, after 15 years of use of land with pasture.

The clay contents of the soils in this study were low, but within the range observed by Birani et al. (2015), in soils, Typic Hapludox (38 to 931 g kg^{-1}) and Typic Hapludult (53 to 719 g kg^{-1}), from the Eastern Amazon. The results obtained indicate the predominance of sand fraction, the characteristic observed in most of the soils in the Pará state (De Souza et al. 2018).

The soils cultivated with orange and oil palm showed low of the P, while in the black pepper cultivation the values were very high. Frazão et al. (2013) evaluated oil palm plantations in Amazon soils, with 4, 8 and 25 years of implantation, and observed P content in the soil of 4.3, 3.9 and 4.2 mg kg^{-1}, respectively. The higher P content of the soil in the area cultivated with black pepper may be related to the residual effect of fertilization with thermophosphate (Withers et al. 2018).

5.4.2 PTEs, EF and BAF in agricultural soils-plants

The average concentrations of PTEs, compared with the respective reference areas (control), were higher for As, Ba, Cr and Pb (oil palm cultivation); As, Ba, Cr, Cu, Ni, Pb and Zn (black pepper); Cu and Zn (orange). Due to the management and use of the mineral and organic fertilizers in the areas of this study, it may have contributed directly to increases PTEs in these areas, since agricultural inputs are carriers of several chemical elements (Table 2: Kabata-Pendias and Pendias 2001). The soils subjected to intensive cultivation for long period tend to have higher concentrations of EPTs (Ramalho et al. 1999).

However, in the soil with oil palm cultivation, Ni and Zn concentrations decreased from 6.0 to 2.0 (mg kg^{-1}) and 11 to 8.0 (mg kg^{-1}), respectively, being an indication of accumulation / exportation by the crop. The bioaccumulation of Zn by the oil palm obtained in the present study corroborates the results of Aini Azura et al. (2012), which obtained increasing values of Zn in oil palm leaves with different implantation ages (<10, > 15 and > 20 years), due to phosphate fertilizer applications.

The Cu enrichment in areas cultivated with black pepper and orange is associated with the use of fungicides, especially cupric, including Bordeaux mixture ($CuSO_4$ + Ca $(OH)_2$), which is commonly applied in these crops, resulting in increased concentrations of Cu in the soils (Lokesh and Gangadharappa 1995; Fan et al. 2011; Behlau et al. 2017). Increases in the Cu concentration were also observed in soils of the grapes cultivation, related to the application of fungicides (Mirlean et al. 2007; Komárek et al. 2010; Preston et al. 2016).

The average Cd concentration (0.4 mg kg^{-1}) in the studied soils was not altered by the cultivation and use of inputs, values below 1 mg kg^{-1} of Cd are expected in uncontaminated soils (Alloway 1995). Under natural conditions, according to Kabata-Pendias and Pendias (2001), 0.53 mg kg^{-1} of Cd is the average value in soils. Campos et al. (2003) observed average 0.66 mg kg^{-1} of Cd in Oxisols from Brazil.

The As (0.1 - 2.0 mg kg^{-1}) in this study was well below the average of 5.2 mg kg^{-1} (natural conditions) observed by Campos et al. (2007) for 17 Brazilian Oxisols. In the Oxisol from second largest Brazilian biome, the Cerrado, Marques (2000) obtained average 38 mg kg^{-1} of As. The average value 10 mg kg^{-1} of As is considered normal for uncontaminated soils (Fitz and Wenzel 2002; Smedley and Kinniburgh 2002). The World Health Organization considers the range from 1.0 to 40 mg kg^{-1} as natural for uncontaminated soils (WHO 2001).

The Co concentrations of 1.0 to 2.0 mg kg^{-1} in the soils with oil palm, orange and black pepper cultivation are below the background average (20.3 mg kg^{-1}) observed by Dos Santos and Alleoni (2013) in soils from the Southwest Amazon. The highest concentration of Zn (21 mg kg^{-1}) observed in soil with orange cultivation was less than the average of 22.52 mg kg^{-1}, obtained by Biondi et al. (2011) in soils from Northeast of the Brazil. The low concentrations of EPTs in the studied soils may be related to the sedimentary origin of Amazon soils (Do Nascimento et al. 2018; De Souza et al. 2018). Other processes may have been preponderant for the results found in the present study, such as the low adsorption capacity of the soils, increasing the potential for loss by leaching, followed of the absorption by plants (De Matos et al. 2001; Kellman 2002).

The soils sandy, like those in this study, have low adsorption capacity and allow greater leaching of EPTs (Fernandez et al. 2007). Tume et al. (2011) observed positive correlations of the clay fraction with the concentration and mobility of EPTs in soils. However, EF values show moderate enrichment of Ba, Pb and Zn (2 > FE < 5), and significant enrichment for As and Cu (5 > FE < 20), indicating anthropic origin.

The high BAF of Hg in orange cultivation may be related to the low organic carbon content of the soil. Yu et al. (2018), studying the accumulation of Hg in plants, observed an inverse relationship between the organic carbon of soil and the concentration of Hg in plant tissues, and the lower organic carbon of the soil, the greater the concentration of Hg in plants. In the plant tissues of black pepper, Duressa and Leta (2015) observed concentrations of As (0.43 to 0.81 mg kg^{-1}), Cd (0.87 to 1.45 mg kg^{-1}), Cr (0.55 to 2.25 mg kg^{-1}), Hg (0.29 to 0.77 mg kg^{-1}) and Pb (0.53 to 0.84 mg kg^{-1}). Sebastian and Godwin (2017), evaluated the concentrations of Cd, Cu, Pb and Zn in two species of orange and obtained the average values in *C. reticulata* (Cd - 0.45; Cu - 0.55; Pb - 1.34; Zn - 6.27 mg kg^{-1}), *C. sinensis* (Cd - 0.84; Cu - 1.14; Pb - 1.75; Zn - 4.41 mg kg^{-1}). In the present study, the bioaccumulation factors (BAF > 1) were: oil palm (Cu and Zn), orange (Ba, Hg and Ni), black pepper (Zn). The BAF > 1 suggests that the plant could be hyperaccumulator, which could be useful in phytoremediation of polluted environments (Oti 2015).

In this study, the PTEs under agricultural conditions, compared to the quality reference values (QRVs) established by the brazilian environmental protection agency CETESB (Cetesb 2005) were low, except so in the case of Cr for black pepper cultivation, indicating low risk of environmental contamination and hazard to human health. Corroborated by the results obtained by Fernandes et al. (2018) for soils in the eastern Amazon.

The PTEs in soils cultivated of eastern Amazon were low, also compared to the averages cited in the international scientific literature (Hawrami et al. 2019; ur Rehman et al. 2020; Mirzaei et al. 2020; Timofeev et al. 2020; Gruszecka-Kosowska et al. 2020). This is attributable to the lower capacity of most soils from eastern Amazon for retaining these elements, due to their natural acidity and to the constant rainfall in the Amazon region, which leads to the removal or weathering of basic elements (De Souza et al. 2018).

5.5 CONCLUSIONS

The results showed variation in the concentration of PTEs in soils cultivated with oil palm, black pepper and orange, with high values of the enrichment factor for As, Ba, Cu, Pb and Zn in these areas. The bioaccumulation factors (BAF > 1) of Ba, Cu, Hg, Ni and Zn were observed in the plant tissues studied, suggesting that these elements were mainly derived from anthropogenic sources. In addition, the BAF of Hg in orange, indicates the need for further research on the mechanisms of interaction of this species with this element, related to growth, productivity and possible contamination of fruits. The concentrations of PTEs in cultivated soils, except for Cr in the black pepper cultivation, remain within the Quality Reference Values (QRVs), according to the legislation of the environmental agency, indicating low levels of pollution.

Acknowledgements

The first author thank the Pro-Rectory of Research and Technological Development (PROPED/UFRA) for Support (Prodoutoral - 04/2017). The second author thank the CNPQ for the financial support (Grant 305015/2016-8).

Conflict of Interest

The authors declare that they have no conflict of interest.

CAPÍTULO 6 – CONSIDERAÇÕES FINAIS

A baixa capacidade na retenção de ETRs, U, Th e EPTs nos solos (Argissolos e Latossolo) pode ser explicada como consequência da lixiviação excessiva, associado às constantes chuvas da região amazônica e, principalmente neste estudo, com a textura arenosa dos solos. A textura arenosa atenuou e homogeneizou os possíveis efeitos do fator tempo sobre o fator de enriquecimento, contribuindo à baixa bioacumulação nos tecidos vegetais de laranja, dendê e pimenta-do-reino. Mas, de modo geral, as áreas com plantios de laranja, dendê e pimenta-do-reino apresentaram acúmulos de ETRs, U, Th e EPTs em relação às áreas com fragmentos florestais remanescentes. Por isso, em solos agrícolas com cultivos perenes que são fertilizados anualmente, o monitoramento por órgãos ambientais quanto ao acúmulo de elementos químicos que ofereçam riscos potenciais à saúde humana deve ser contínuo.

Em função dos resultados mais significativos do európio e sua relação com os processos fisiológicos das plantas, principalmente, relacionados a absorção de cálcio, recomenta-se para trabalhos futuros os experimentos em casa de vegetação com mudas cultivadas em solos enriquecidos com európio. E também, dadas as particularidades dos solos da Amazônia, como o horizonte superficial arenoso, recomenda-se para avaliar a mobilidade relativa e o potencial de contaminação do lençol freático, ensaios com colunas de percolação.

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

PARECER

Sobre a Defesa Pública da Tese de Doutorado de ANDERSON MARTINS DE SOUZA BRAZ

A banca examinadora da Tese de Doutorado de **ANDERSON MARTINS DE SOUZA BRAZ** orientando do Prof. Dr. Marcondes Lima da Costa (UFPA) e composta pelos professores doutores Edna Santos de Sousa (Membro externo-UNIFESSPA), Antonio Carlos de Azevedo (Membro externo-USP), Francisco de Assis Oliveira (Membro externo-UFRA), e Rômulo Simões Angélica (Membro interno-UFPA), após apresentação da sua tese intitulada **"ELEMENTOS TERRAS RARAS, U, Th E ELEMENTOS POTENCIALMENTE TÓXICOS EM AGROECOSSISTEMAS COM USO DE FERTILIZANTES NO NORDESTE DO PARÁ"**, emite o seguinte parecer:

O candidato realizou sua apresentação de forma clara, bem organizada e segura no tempo estipulado. Na arguição mostrou domínio da temática abordada e respondeu às perguntas formuladas pela banca. O trabalho escrito foi apresentado na forma de três artigos, sendo um já publicado, um submetido, ambos em periódicos internacionais, e o terceiro artigo ainda em elaboração. Consta em anexo um quarto artigo no qual o doutorando é coautor. O conjunto de artigos forma uma unidade coerente, compatível com uma tese de doutorado.

Finalmente, a banca examinadora decidiu por unanimidade aprovar a tese de doutorado.

Belém, 30 de novembro de 2020.

Prof. Dr. Marcondes Lima da Costa (Orientador – UFPA)

Edna Santos de Souza

Prof. Dra. Edna Santos de Sousa (Membro externo-UNIFESSPA)

Prof. Dr. Antonio Carlos de Azevedo (Membro externo-USP)

Prof. Dr. Francisco de Assis Oliveira (Membro externo-UFRA)

Prof. Dr. Rômulo Simões Angélica (Membro interno UFPA)