



FÁBIO HENRIQUE ALVES BISPO

**RARE EARTH ELEMENTS IN BRAZILIAN
BIOME-DIFFERENTIATED SOILS**

LAVRAS - MG

2018

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

Orientador

Luiz Roberto Guimarães Guilherme, PhD

Coorientadora

Dra. Michele Duarte de Menezes

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*“Nunca considere seus estudos como uma obrigação,
mas como uma invejável oportunidade de aprender
a conhecer a influência libertadora da beleza do espírito,
para a sua própria alegria pessoal e para o
proveito da comunidade a que pertencerá
o trabalho posterior de vocês.”*

Albert Einstein

RESUMO

Pretendeu-se com essa pesquisa gerar informações acerca da ocorrência e do comportamento dos elementos maiores, traço e terras raras em solos de referência dos biomas brasileiros, a fim de entender a distribuição e quantificar as concentrações naturais ou antropogênicas desses elementos em biomas. Além disso, os teores naturais dos elementos-traço e maiores foram determinados juntamente com o estabelecimento de valores de referência de qualidade para os elementos terras raras em cada bioma, visto que o bioma expressa as particularidades dos ambientes. Para isso, foram selecionadas amostras de solos de referência de um banco de solos brasileiros, de maneira que as amostras representassem a diversidade geológica, geomorfológica, pedológica, climática e edáfica das regiões estudadas. A determinação dos teores semitotais de elementos terras raras nas amostras de solos foi realizado através do procedimento de digestão ácida nítrica assistida por micro-ondas, com posterior quantificação por espectrometria de massa por plasma acoplado indutivamente. Por outro lado, a quantificação dos teores totais dos elementos-traço e maiores foi verificada utilizando a técnica de espectrometria de fluorescência de raios-X por reflexão total. Todos os procedimentos analíticos seguiram um rigoroso protocolo de controle e garantia de qualidade, incluindo a utilização de materiais de referência certificados para validação das metodologias. Os resultados obtidos evidenciam uma alta variabilidade nas concentrações dos elementos maiores, traço e terras raras em solos, influenciados principalmente por materiais de origem referente à crosta terrestre e processos pedogenéticos, tendo o clima um papel de destaque. Esses fatores promoveram uma remoção diferencial dos elementos maiores, traço e terras raras em alguns biomas (Floresta Amazônica, Cerrado, Mata Atlântica e Pantanal) e menor remoção em outros (Caatinga). Particularmente, a aplicação de fosfógeno e fertilizantes fosfatados portadores de elementos terras raras em áreas agrícolas aumentou involuntariamente o conteúdo desses elementos em solos. Por fim, as concentrações naturais dos elementos maiores e traço, além dos valores de referência de qualidade de solos propostos para os elementos terras raras podem servir para auxiliar no diagnóstico ambiental e fundamentar cientificamente futuras políticas públicas e regulamentações ambientais.

Palavras-chave: Lantanídeos. Solos de referência. Valores orientadores.

ABSTRACT

The aim of this research was to generate data on the occurrence and behaviour of major, trace, and rare earth elements in benchmark soils of Brazilian biomes, in order to understand their distribution and quantify their natural or anthropogenic concentrations in biomes. In addition, the natural contents of the major and trace elements were determined together with the establishment of quality reference values for rare earth elements for each biome, since the biome expresses the particularities of the environments. For this purpose, samples of benchmark soils from a Brazilian soils databank were selected in order to represent the geological, geomorphological, pedological, climatic, and edaphic diversity of the studied regions. Determination of the semi total contents of rare earth elements in soil samples was performed through a microwaved-assisted nitric-acid digestion procedure, followed by quantification with inductively coupled plasma mass spectrometry. On the other hand, the quantification of the total contents of the major and trace elements was performed using the technique of total reflection X-ray fluorescence spectrometry. The analytical procedures followed a rigorous quality assurance/quality control protocol, including the use of certified reference materials in order to validate the methodologies. The results showed high variability in the concentrations of major, trace, and rare earth elements in soils, which were mainly influenced by parent material referring to terrestrial crust and pedogenetic processes, having the climate a prominent role. These factors promoted a differential removal of the major, trace, and rare earth elements in some biomes (Amazon Forest, Cerrado, Atlantic Forest, and Pantanal) and smaller removal in others (Caatinga). Particularly, the application of phosphogypsum and phosphate fertilizers carrying rare earth elements in agricultural areas has involuntary increased the content of these elements in soils. Finally, the natural contents of the major and trace elements and the proposed quality reference values for rare earth elements can give support to environmental survey while also providing important science-based information for future public policies and environmental regulations.

Keywords: Lanthanides. Benchmark soils. Guiding values.

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PRIMEIRA PARTE

1 INTRODUÇÃO

O comportamento dos elementos químicos nos solos brasileiros pode estar intimamente relacionado à diversidade de condições edafoclimáticas, processos pedogenéticos e fatores de formação do solo, frente à ampla variedade de pedoambientes evidenciado pelos biomas. Diante disso, o conhecimento das concentrações dos elementos maiores, traço e terras raras, é importante para desvendar os processos geoquímicos e a distribuição desses elementos em solos, os quais, ao mesmo tempo, são progressivamente influenciados pelas atividades antropogênicas e materiais de origem.

Nesse contexto, embora tenham sido muito estudados de maneira regionalizada, os solos brasileiros carecem de pesquisas sobre a composição geoquímica em escala nacional que auxiliem na gestão de políticas públicas, fornecendo informações básicas para legislação futura e regulando os níveis de limitação numa ampla gama de solos. Portanto, conhecer as concentrações naturais pode ajudar na compreensão da influência das atividades antrópicas, agrícolas, industriais e urbanísticas nos solos. Essas concentrações naturais vêm sendo cada vez mais estudadas para elementos-traço (também denominados metais pesados) nas condições de solos brasileiros. Contudo, há uma falta de estudos no hemisfério sul sobre o montante de elementos terras raras em solos, especialmente quando comparados aos dados disponíveis para muitos elementos-traço de interesse ambiental (MATSCHULLAT et al., 2012).

Desse modo, o conteúdo dos elementos maiores em solos reflete os processos pedogenéticos ocorridos durante longo período de tempo. Em contraste, alguns elementos-traço por serem considerados elementos potencialmente tóxicos podem ter alta toxicidade para animais e/ou plantas, necessitando de mais estudos

sobre sua dinâmica em solos. Assim, dentre os elementos-traço estão presentes um grupo de elementos com propriedades físicas e químicas peculiares denominado de elementos terras raras.

Esses elementos terras raras (ETRs) são cruciais para muitas indústrias modernas e têm sido cada vez mais utilizados em nossa sociedade. Em geral, a agricultura brasileira requer quantidades significativas de fertilizantes fosfatados portadores de ETRs fornecidos pelo uso intensificado de insumos agrícolas (HU et al., 2006; RAMOS et al., 2016a; TYLER, 2004; VOLOKH et al., 1990) que, conseqüentemente, aumentam involuntariamente os níveis de ETRs em vários compartimentos ambientais, incluindo solos. Nesse contexto, a intensa atividade agrícola brasileira e a crescente necessidade dos insumos demandam um conhecimento das concentrações e dos valores de referência de qualidade abrangendo uma diversidade de biomas brasileiros (PAYE et al., 2016; PÉREZ et al., 1997).

Portanto, esta pesquisa pretende fornecer informações sobre o conteúdo de elementos terras raras em solos de referência dos principais biomas brasileiros distinguindo ambientes naturais e agrícolas, visando ainda estabelecer valores de referência de qualidade para os biomas e avaliar a influência do uso agrícola nos teores desses elementos. Por fim, procedeu-se a determinação dos teores naturais de elementos-traço e maiores nos solos dos biomas brasileiros, avaliando-se a influência dos atributos dos solos na diferenciação geoquímica.

2 REFERENCIAL TEÓRICO

2.1 Elementos-traço e maiores

Os elementos-traço (também denominados de metais pesados) compreendem os metais catiônicos e aniônicos presentes em baixas concentrações usualmente inferiores a 0,1% (ESSINGTON, 2004; GUILHERME et al., 2005). Alguns desses elementos são considerados potencialmente tóxicos aos animais e/ou plantas (e.g., As, Hg, Cd, Pb, V e Cr), e outros são essenciais para as funções vitais (e.g., B, Co, Cu, Fe, Mn, Mo, Ni e Zn). Entretanto, é necessário que esses elementos estejam prontamente biodisponíveis no ambiente para que possam causar algum risco ambiental e à saúde humana. Assim, o conhecimento dos teores naturais dos elementos-traço é fundamental para uma avaliação do risco ambiental causado pelo aumento nas concentrações dos elementos nos ecossistemas terrestres e aquáticos.

As principais fontes naturais de elementos-traço no ambiente são a liberação pelo intemperismo da crosta terrestre ou dos minerais primários, juntamente com o incremento dos elementos nos solos pelas fontes biogênicas ou deposições atmosféricas provenientes das atividades vulcânicas e queimadas de florestas (CALLENDER, 2014). Por outro lado, as fontes antropogênicas estão associadas às atividades de mineração, aplicação de fertilizantes e insumos em solos agrícolas, queima de combustíveis fósseis, descarte de efluentes domésticos e industriais, águas residuárias, dentre outros (ALLEONI; BORBA; CAMARGO, 2005; KABATA-PENDIAS, 2011), podendo causar poluição de ecossistemas terrestres e aquáticos.

Os elementos maiores são aqueles presentes em altas concentrações acima de 0,1% (e.g., Si, Al, Ti, K, Ca, Mg e Na); e na geoquímica dos solos, são usualmente expressos como óxidos devido a composição mineral dos solos ser

normalmente de silicatos. Contudo, os elementos maiores são principalmente originados de rochas de composição granítica e basáltica que predominam na crosta terrestre (especialmente rochas ígneas e metamórficas) (PARKER, 1967), sendo posteriormente liberados através do intemperismo para a fração mineral dos solos.

2.2 Elementos terras raras

Em 1794, foram descobertos os primeiros elementos terras raras pelo químico finlandês Johan Gadolin, na Suécia (WILLIAMS-JONES; MIGDISOV; SAMSON, 2012). Essa denominação “terras” foi designada em função da aparência terrosa de seus óxidos e “raras” refere-se à dificuldade de quantificação por meio de métodos convencionais, pois a maioria dos ETRs são abundantes na crosta terrestre (RUDNICK; GAO, 2014), representando cerca de 0,01% dos elementos (HU et al., 2006). Nas últimas décadas, esses elementos foram utilizados como traçadores muito úteis em estudos geoquímicos (TAYLOR; McLENNAN, 1995; WANG et al., 2011) devido aos métodos avançados terem superado as questões de quantificação por meio de melhorias técnicas (LAVEUF; CORNU, 2009) e o grupo desses elementos terem estruturas químicas peculiares.

Os lantanídeos compreendem a maioria dos elementos terras raras, juntamente com o escândio (Sc) e o ítrio (Y) (IUPAC, 2005). Esse grupo é composto pelos seguintes elementos: Escândio (Sc), Ítrio (Y), Lantânio (La), Cério (Ce), Praseodímio (Pr), Neodímio (Nd), Promécio (Pm), Samário (Sm), Európio (Eu), Gadolínio (Gd), Térbio (Tb), Disprósio (Dy), Hólmio (Ho), Érbio (Er), Túlio (Tm), Itérbio (Yb) e Lutécio (Lu). Entretanto, esses elementos não são nem essenciais à vida e nem fortemente tóxicos ao meio ambiente (ŠMUC et al., 2012).

Embora apresentem características químicas semelhantes, são comumente divididos em leves (pesos atômicos menores: La, Ce, Pr, Nd, Pm, Sm e Eu) e pesados (pesos atômicos maiores: Gd, Tb, Dy, Ho, Er, Tm, Yb e Lu) baseado nas propriedades físico-químicas e em função dos raios iônicos (DOLEGOWSKA; MIGASZEWSKI, 2013; RAMOS et al., 2016a; SADEGHI et al., 2013; TYLER, 2004). Em particular, o Y é frequentemente agrupado como pesado pelas suas propriedades químicas (SAMSON; WOOD; FINUCANE, 2004) e o Sc não se inclui nessa classificação (GUPTA; KRISHNAMURTHY, 1992; JORDENS; CHENG; WATERS, 2013).

A China possui aproximadamente 80% das reservas mundiais (WEN et al., 2001; XU et al., 2002; XU; WANG, 2001) e cerca de 97% desse mercado, detendo o monopólio dos elementos terras raras e das técnicas de exploração desde a década de 50 (KANAZAWA; KAMITANI, 2006; SERRA, 2011). Entretanto, outros países como Brasil, Estados Unidos, Austrália, Canadá e África do Sul também possuem reservas desses elementos (KANAZAWA; KAMITANI, 2006).

Tais elementos são usados principalmente como componentes de supercondutores, telas LCD, smartphones, tablets, indústria bélica, baterias de carros híbridos, materiais luminescentes de dispositivos optoeletrônicos, geradores eólicos e fibras ópticas, além de vários equipamentos de alta tecnologia (SERRA, 2011). Podem, também, ser utilizados na formulação de catalisadores de Ce e La para processamento do petróleo, pois o Ce é oxidante de monóxido de carbono e hidrocarbonetos e, ainda, redutor de óxidos de nitrogênio, reduzindo as emissões atmosféricas de gases (MAESTRO; HUGUENIN, 1995).

2.3 Geoquímica dos elementos terras raras

Esse grupo de elementos químicos geralmente apresenta forma trivalente (estado de oxidação +3), raio iônico grande e eletronegatividade inferior à dos elementos de transição da tabela periódica (LAVEUF; CORNU, 2009). São encontrados na crosta terrestre como litófilos, mostrando afinidade pelos silicatos, minerais e rochas (GOLDSCHMIDT, 1937), e formando, preferencialmente, ligações iônicas (HENDERSON, 1984). Contudo, apresenta uma gradual diminuição do raio atômico à medida que aumenta o número atômico, sendo esta uma característica conhecida como contração dos lantanídeos (SADEGHI et al., 2013).

O Cério (valência +3 e +4) e o Európio (valência +2 e +3) são encontrados em dois estados de oxidação nas condições da superfície terrestre (HENDERSON, 1984), enquanto o Promécio não ocorre naturalmente na Terra devido à rápida desintegração dos isótopos (FIGUEIREDO, 1985). Os ETRs possuem raios iônicos muito semelhantes aos do Ca, Na, Th e U, substituindo-os, conseqüentemente, na estrutura mineral (KANAZAWA; KAMITANI, 2006). Conforme a regra de Oddo-Harkins (NIKANOROV, 2009), os elementos químicos que têm pesos atômicos pares tendem a ser mais comuns na natureza do que seus vizinhos ímpares, pois os isótopos são mais estáveis permitindo uma maior abundância na natureza.

A distribuição e o fracionamento dos ETRs na solução do solo são afetados pela estabilidade e natureza dos minerais primários/secundários através do intemperismo (LING et al., 2015; TYLER, 2004). Desse modo, os ETRs pesados são preferencialmente transportados em solução, enquanto que os ETRs leves podem ser facilmente adsorvidos pelos óxidos/hidróxidos ou coloides da fase sólida (LING et al., 2015).

A mobilidade e a solubilidade dos minerais primários portadores de ETRs controlam as concentrações desses elementos na solução do solo e, dependendo do estágio de intemperismo, pode ocorrer a migração dos mesmos através do perfil do solo (LING et al., 2015; ÖHLANDER et al., 1996; PANAHI; YOUNG; RAINBIRD, 2000; YUSOFF; NGWENYA; PARSONS, 2013). Portanto, no topo do perfil, os teores de ETRs são menores do que na parte inferior, embora o horizonte superficial possa ser enriquecido numa eventual reprecipitação (BRAUN et al., 1993) ou através de fontes antropogênicas.

Os lantanídeos dissolvidos na solução do solo têm a capacidade de serem adsorvidos pelos minerais da fração argila (BAO; ZHAO, 2008) ou incorporados nos minerais secundários, principalmente nos óxidos de ferro e manganês, carbonatos (LAVEUF; CORNU, 2009; ÖHLANDER et al., 1996) ou na matéria orgânica do solo (TYLER, 2004). KABATA-PENDIAS (2011) também relata associação entre o conteúdo de argila e os elementos-traço, incluindo os elementos terras raras.

Eventualmente, a adsorção de ETRs pode ser controlada pela natureza dos minerais de argila, pH, matéria orgânica e força iônica da solução (COPPIN et al., 2002; LAUFER, 1984; WAN; LIU, 2005). Assim, os ETRs podem substituir facilmente os metais alcalinos/alcalinos terrosos devido seu estado trivalente favorecer uma adsorção mais forte (COPPIN et al., 2002). Em pH ácido e baixa força iônica, a adsorção de ETRs ocorre como complexos de esfera externa em superfícies basais (carga estrutural permanente), enquanto que em pH alcalino esses elementos ficam adsorvidos como complexos de esfera interna nas bordas das partículas (forte quimissorção, cargas variáveis dependentes de pH). Via de regra, o aumento do pH favorece o processo de adsorção dos ETRs pelos colóides do solo (COPPIN et al., 2002).

Nesse sentido, os argilominerais são portadores de ETRs no solo (GNANDI; TOBSCHALL, 2003; HENDERSON, 1984; LI et al., 2006;

ÖHLANDER, 1996; PAPOULIS, 2004), sendo que suas concentrações dependem do grau de intemperismo dos silicatos primários. Similarmente, os óxidos de ferro e manganês também podem conter os elementos terras raras em sua composição (PALUMBO et al., 2001), sendo que a sua presença e concentração são influenciados por mecanismos de adsorção, coprecipitação, troca iônica e formação de complexos superficiais (CAO, 2001).

As concentrações de ETRs são normalmente mais elevadas em óxidos de ferro e manganês amorfos do que nos cristalinos (COMPTON; WHITE; SMITH, 2003), mostrando a influência dos elementos-traço incluindo ETRs no processo de cristalização desses óxidos (CORNELL, 1987). Sabe-se que os óxidos de Fe (hematita, goethita e lepidocrocita) apresentam ponto de carga zero (PCZ) em torno de 5,3 a 6,5, a ferridrita em torno de 5,3 a 8,8 e os óxidos de Mn (birnessita ou vernadita) em torno de 2 (APPEL, 2003; GOLDBERG; FORSTER; GODFREY, 1996). Isso explica porque os óxidos de Mn são mais eficientes como portadores de ETRs em solos, pois o processo de sorção em condições de pH ácido do solo é mais rápido e eficiente nos óxidos de Mn do que nos óxidos de Fe (ELDERFIELD; GREAVES, 1981).

Nos minerais primários com Ti (anatásio, ilmenita, titanita, rutilo) e Zr, os ETRs pesados concentram-se como “impurezas” (AIDE; PAVICH, 2002; AUBERT; STILLE, PROBST, 2001; BRAUN et al., 1990; KANAZAWA; KAMITANI, 2006; TAKAHASHI, 2003) e são pouco mobilizados para a solução do solo, já que esses minerais pesados são muito estáveis frente ao intemperismo (NICKEL, 1973). Alguns minerais como o quartzo não contêm ETRs (COMPTON; WHITE; SMITH, 2003), enquanto outros como feldspatos geralmente contêm quantidades insignificantes, exceto Eu (PANAHI; YOUNG; RAINBIRD, 2000), onde ocorre a substituição do Eu por Ca, Sr ou Na (NAGASAWA, 1971). Nas apatitas, as concentrações de ETRs chegam a 20%

(DUTRA; FORMOSO, 1995) e as micas podem exibir anomalias positivas ou negativas de Eu (CHASE; WINCHESTER; CORYELL, 1963).

Vale destacar que os compostos orgânicos do solo têm grande capacidade de adsorção, complexação e quelatação dos elementos terras raras devido as grandes quantidades de cargas negativas (POURRET et al., 2007; TYLER, 2004). Dessa forma, os complexos orgânicos com ETRs pesados são mais estáveis do que com os leves e, por isso, a matéria orgânica do solo é mais rica em ETRs pesados (AUBERT; PROBST; STILLE; 2004; HENDERSON, 1984).

Geralmente os ETRs estão hospedados ou associados a rochas ígneas alcalinas e carbonatos (SADEGHI et al., 2013). Entretanto, os minerais economicamente importantes portadores de ETRs são do grupo da bastnasita (Ce, La), monazita (Ce, La), xenotímio (Y), loparita (Nb) e argilas iônicas portadoras de terras raras. Os ETRs pesados, que ocorrem em óxidos como titanatos, niobatos e tantalatos, são menos comuns do que os leves, que são ricos em carbonatos e fosfatos (KANAZAWA; KAMITANI, 2006).

Por fim, cada mineral contém teores de ETRs dependente basicamente da valência e raio iônico, sendo que os leves ocupam sítios com maiores números de coordenação enquanto os pesados ocupam sítios de menor coordenação. Conforme ÖHLANDER et al. (1996), o que determina as concentrações dos ETRs no solo é a liberação pela dissolução dos silicatos (epídoto, feldspato, mica hornblenda), fosfatos (apatita) dentre outros minerais primários (monazita e albanita). Além disso, os minerais secundários da fração argila podem conter ETRs, como a clorita, que contém teores significativos, além de esmectita, vermiculita e illita, que também são enriquecidos em ETRs leves (COPPIN et al., 2002), e os aluminossilicatos (caulinita, illita e esmectita), que podem adsorver ETRs.

2.4 Fontes antropogênicas

O conteúdo de ETRs em solos pode ser adicionado através de fertilizantes, irrigação, esgotos, águas pluviais e partículas atmosféricas (AUBERT et al., 2002; LIJUN et al., 2004) além de resíduos provenientes de áreas industriais. Entretanto, os fertilizantes fosfatados e fosfogesso são as fontes antrópicas mais relevantes para o aumento dos níveis de ETRs em solos (DIATLOFF; ASHER; SMITH, 1996; RAMOS et al., 2016b; TURRA et al., 2011; VOLOKH et al., 1990), devido à alta afinidade dos ETRs pelos compostos fosfatados (TYLER, 2004) intensamente usados na agricultura brasileira. Por outro lado, em áreas nativas ou solos agrícolas pouco alterados, os teores de ETRs provêm dos materiais de origem ricos nesses elementos (LIJUN et al., 2004).

Em contraste, as deposições atmosféricas são fontes insignificativas de ETRs em solos (LIJUN et al., 2004), ocorrendo baixos teores quando são provenientes de emissão de partículas (secas) ou teores significativos quando provêm de deposições por chuva e neve (úmidas). Depreende-se, pois, que os teores de ETRs são também influenciados pela natureza da deposição (AUBERT et al., 2002).

A produtividade e o crescimento das plantas têm sido o foco da utilização de fertilizantes fosfatados portadores de ETRs (CHALLARAJ EMMANUEL et al., 2010; TURRA et al., 2011; XU et al., 2002), principalmente em solos de regiões tropicais. Assim, o uso intensificado desses elementos pode acarretar na bioacumulação em ambientes agrícolas e a transferência através da cadeia alimentar para o corpo humano (WEN et al., 2001; XU et al., 2002), com potenciais efeitos prejudiciais ao meio ambiente (ZHANG; YAMASAKI; KIMURA, 2001) apesar de haver poucas informações sobre os efeitos dos elementos terra raras nas plantas e nos humanos (RAMOS et al., 2016b; LI et al.,

2010; SHI; HUANG; CHEN, 2006; TURRA et al., 2011; TYLER, 2004; XU; WANG, 2001).

Na composição dos fertilizantes, via de regra, apenas os conteúdos dos nutrientes são controlados pela legislação, podendo ocorrer também situações onde os elementos-traço contaminantes possam ser regulamentados (e.g., Brasil, Canadá e Estados Unidos). Embora alguns países tenham estabelecido limites de tolerância para vários elementos, por outro lado, não há recomendação para teores de ETRs - considerados como “poluentes emergentes” - aos insumos agrícolas (OTERO et al., 2005; TURRA et al., 2011). Portanto, os ETRs adicionados via fertilizantes devem ser motivo de preocupação devido à carência de estudos sobre eventuais benefícios e, ou, riscos toxicológicos e ambientais.

Os principais consumidores de fertilizantes no mundo são China, Índia, Estados Unidos e o Brasil (IFA, 2018). Entretanto, o Brasil necessita de fontes de fósforo (P) para composição dos fertilizantes, necessitando importar de países como Marrocos, Argélia, Israel, Togo e Tunísia. Essa dependência de fontes externas de P é importante para se avaliar a adição involuntária de ETRs em solos, devido às diversas fontes de P serem determinantes nos teores de ETRs dos fertilizantes a serem utilizados na agricultura brasileira (RAMOS et al., 2016a; TURRA et al., 2011; TYLER, 2004).

2.5 Valores de referência de qualidade e teores naturais do solo

Os valores de referência de qualidade (VRQs) dos elementos representam as concentrações naturais dos solos em áreas pristinas ou que sofreram mínimas atividades antropogênicas (KABATA-PENDIAS, 2011; PRESTON et al., 2014). Entretanto, MATSCHULLAT et al. (2000) relatam que é uma medida relativa utilizada para distinguir as concentrações naturais daquelas adicionadas através de fontes antropogênicas. Particularmente, o conhecimento das concentrações

naturais (*background concentration*) dos elementos é importante para o entendimento da dinâmica e da composição geoquímica dos solos, refletindo os processos de formação e as condições ambientais em que esses solos foram desenvolvidos.

Nesse sentido é importante que as áreas analisadas apresentem uma gama de variação geológica, geomorfológica, pedológica e edafoclimática. É particularmente com foco nesse contexto que a legislação brasileira enfatiza a necessidade de se estabelecerem diretrizes e normas referentes aos teores naturais dos elementos em solos para cada estado brasileiro (CONAMA, 2009), visto que a intensidade do crescimento industrial e agrícola pode afetar os níveis dos poluentes emergentes nos solos.

Sabe-se que o solo é um compartimento ambiental que exerce diversas funções ecológicas, ambientais e agrícolas e que possui a capacidade de acumular diversas substâncias, como resíduos líquidos e sólidos (que podem conter diversos elementos-traço e terras raras). O acúmulo dessas substâncias precisa ser avaliado, pois, dependendo de sua intensidade, pode causar perdas da funcionalidade dos solos, problemas ambientais e de saúde humana (AMARAL SOBRINHO; BARRA; LÃ, 2009).

A legislação brasileira (CONAMA, 2009) classifica os valores orientadores de qualidade do solo quanto à presença de substâncias químicas em: i) valor de referência de qualidade (VRQ), que é a “concentração de determinada substância que define a qualidade natural do solo, sendo determinado com base em interpretação estatística de características físico e químicas de amostras de diversos tipos de solos”; ii) valor de prevenção (VP), que é a “concentração de valor limite de determinada substância no solo, tal que ele seja capaz de sustentar as suas principais funções”; e iii) valor de investigação (VI), que é a “concentração de determinada substância no solo ou na água subterrânea acima da qual existem riscos potenciais, diretos ou indiretos, à saúde humana, considerando um cenário

de exposição padronizado”. Nessa resolução, o critério para o estabelecimento dos valores de referência de qualidade é o limite superior da faixa de concentração natural dos elementos (DUDKA; PONCE-HERNANDEZ; HUTCHINSON, 1995) obtidos a partir da interpretação estatística dos resultados analíticos de áreas naturais (CONAMA, 2009).

Diversos países (e.g., Alemanha, Áustria, China, Holanda, Inglaterra, Itália e Polônia) já definiram seus valores orientadores de qualidade para solos. No Brasil, os VRQs já foram estabelecidos para alguns elementos-traço, mas ainda falta uma clara definição para os elementos terras raras. Portanto, o estabelecimento desses valores poderá auxiliar no gerenciamento ambiental e monitoramento de áreas contaminadas principalmente por elementos decorrentes das atividades antrópicas.

Embora ainda não exista uma regulamentação específica envolvendo VRQs para ETRs no Brasil, alguns estudos em diversos estados brasileiros propuseram VRQs para determinados elementos-traço ou terras raras, a saber: Minas Gerais (COPAM, 2010; De SOUZA et al., 2015), São Paulo (CETESB, 2016), Mato Grosso e Rondônia (Dos SANTOS; ALLEONI, 2013), Pernambuco (BIONDI et al., 2011; SILVA et al., 2016), Espírito Santo (PAYE et al., 2010), Rio Grande do Norte (PRESTON et al., 2014), Paraíba (ALMEIDA JUNIOR et al., 2016), Paraná (LICHT et al., 2006; MELO et al., 2017), Piauí (De PAULA FILHO et al., 2015), Rio Grande do Sul (FEPAM, 2014) dentre outros. Esses estudos foram feitos de maneira independente e não tiveram como foco a determinação de VRQs para solos de biomas específicos.

3 CONSIDERAÇÕES FINAIS

Este trabalho procura agregar informação inédita e incremental visando minimizar a carência de informações sobre a composição geoquímica dos solos brasileiros, enfatizando principalmente a diferenciação por biomas. Essas informações são especialmente relevantes para os elementos terras raras, já que as pesquisas sobre elementos terras raras nesses solos mencionados ainda são escassas. Dessa forma, nesse estudo são apresentadas as concentrações parciais de elementos terras raras além de serem propostos os valores de referência de qualidade para cada bioma.

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SEGUNDA PARTE

ARTIGO 1 - Rare Earth Elements (REE): geochemistry, distribution, and quality reference values in benchmark soils of Brazilian biomes

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Rare Earth Elements (REE): geochemistry, distribution, and quality reference values in benchmark soils of Brazilian biomes

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Highlights

- The distribution of rare earth elements contents in agricultural and native areas from Brazilian biomes was assessed
- The influence of the agricultural activities in rare earth elements contents in benchmark soils was evaluated
- Establishment of baseline values to support future legislation concerning geochemical backgrounds is proposed

Abstract

Rare Earth Elements (REE) have been increasingly used in our modern society, including their application in agroecosystems. Yet, our understanding of REE contents/fate in soils is still incipient. Thus, a comprehensive overview of REE occurrence/distribution in soils is necessary, especially in agricultural areas, to assess the effect of anthropogenic uses on soil REE contents, as well as in reference areas for proposing soil REE guideline values. This study quantified REE contents in agricultural and native areas of selected Brazilian biomes, aiming to: i) propose quality reference values that can be used for regulatory purposes; ii) analyze the influence of agricultural uses on REE contents in Brazilian soils; and, iii) understand chemical/physical soil properties that influence REE contents in soils. Benchmark soil samples selected from a databank representing different Brazilian biomes were analyzed for their REE contents by inductively coupled plasma mass spectrometry, after nitric-acid digestion. Baseline REE contents were established based on their frequency distribution analyzed in topsoil samples collected in reference areas. The analytical procedures followed a rigorous QA/QC protocol, which included the use of certified reference material for validation of the extraction methodology and the reliability of the contents found. The REE contents (ΣREE in topsoils of agricultural/reference areas in mg kg^{-1}) for each biome decreased as follows: Caatinga (186.6/257.4) > Atlantic Forest (138.1/63.4) > Pantanal (137.4/61.6) > Cerrado (135.1/54.3) > Amazon Rainforest (64.3/35.6). The Caatinga biome presented the highest background concentrations for all REEs, whereas the Amazon Rainforest exhibited the lowest ones. Our findings suggests that REE contents in

Brazilian soils are affected by past climatic conditions, especially precipitation and temperature, which in turn influenced the intensity of weathering-leaching, and promoted differential removal of elements in some biomes - Amazon Rainforest, Cerrado, Atlantic Forest, and Pantanal - and smaller removal in others - Caatinga. The obtained results also demonstrated that the anthropic use affected soil REE contents in most biomes, except for the Caatinga, which may be related to the unintentional addition of REE via application of phosphate fertilizers and phosphogypsum in agricultural soils.

Keywords: lanthanides, analytical geochemistry, soils of the tropics, agricultural soil, baseline values.

1. Introduction

Rare Earth Elements (REE) have been increasingly employed in our society due to their multiple applications, which include their uses in many modern industries as well as in agriculture (Long et al., 2010; Mazzilli et al., 2011; Ramos et al., 2016b; Turra et al., 2011; Tyler, 2004; Volokh et al., 1990). In addition, as geochemical tracers, their importance has risen in pedological and physiological studies (Laveuf et al., 2012; Laveuf and Cornu, 2009; Tyler, 2004; Wang et al., 2011; Yang et al., 2010).

The lanthanides are home of most REE, a group of elements that comprises also scandium (Sc) and yttrium (Y) (Dołęgowska and Migaszewski, 2013). Although they present similar chemical

characteristics, as electronegativity and ionization potential, they are commonly divided into light (LREE - La, Ce, Pr, Nd, Sm and Eu) and heavy (HREE - Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) ones, based on their physical and chemical properties (Tyler, 2004). Their electronegativity is similar to those of Ca, Na, and Sr and lower than those of the transition elements. They usually are found in trivalent form with large ionic radius and electronic configuration with six shells (Laveuf and Cornu, 2009; Ramos et al., 2016a; Sadeghi et al., 2013a). The small but gradual decrease of atomic radii while increasing the atomic number is a characteristic of REE, known as lanthanides contraction (Sadeghi et al., 2013a). Additionally, they form mostly ionic bonds instead of covalent ones (Henderson, 1984).

As they present affinity for silica, they are found on Earth's crust and are lithophile (Goldschmidt, 1937). Through weathering, REE are distributed in soils according to the stability and nature of their bearing minerals (Ling et al., 2015; Tyler, 2004). Most REE are actually not very rare in Earth's crust (Haxel et al., 2002). In fact, the term "rare" stands for the difficulty of quantification by means of conventional methods. Although advanced methods have overcome most quantification issues by

means of technical improvements (Laveuf and Cornu, 2009), the literature dealing with REE contents in soils is still very scarce when compared with available data for many trace elements of environmental interest, especially for the southern hemisphere (Matschullat et al., 2012; Ramos et al., 2016a; Schucknecht, 2012).

It is well known that humid areas have higher soil weathering and leaching rates, which in turn renders the concentrations of most elements - REE included - lower in the soil matrix than in the parent material (Kabata-Pendias, 2011; Tyler, 2004). However, considering that Brazil has a continental geographical expression, the climate varies considerably especially from the tropical North (crossed by the Equator) to the temperate zones of the South (below the Tropic of Capricorn 23°26' S latitude), along with other several climatic zones, as tropical wetlands in the Midwest and semi-arid areas in the Northeast (Alvares et al., 2013). Taking into consideration other soil forming factors (Jenny, 1941), it is noteworthy the large variability of parent materials, influenced by a huge geologic background (acid and basic igneous rocks, metamorphic rocks, sedimentary rocks) and the presence of unconsolidated sediments (de Alkmim, 2015), as well as relief or landform variations (Vieira et al., 2015).

Such soil forming factors affecting also the occurrence and abundance of living organisms that make up the natural boundaries of Brazilian biomes. The pedogenesis processes are linked to time, which in turn, depends basically of erosion rates in tropical environment (Resende et al., 2014). Thanks to that, the Brazilian territory may be divided into six continental biomes: Amazon Rainforest, Caatinga, Cerrado, Atlantic Forest, Pantanal, and Pampa (IBGE, 2015).

The variability observed in different biomes for climate and vegetation occurs also in soil geochemical data (Licht et al., 2006; Reimann et al., 2009; Schucknecht, 2012). Thus, a representative database concerning geochemical records is necessary for a better understanding of elemental distribution and occurrence - including data for REE - in Brazilian biomes, in order to properly assist soil management strategies as well as public policies (e.g., establishing soil quality reference values). Moreover, the determination of REE contents in soils can assist to predict if anthropogenic actions - agricultural, industrial, and urbanization - can lead to REE enrichment in different environments.

Involuntary entrance of REE in soils by addition of phosphate fertilizers and phosphogypsum, which may contain high REE contents (Hu

et al., 2006a; Ramos et al., 2016a, 2016b; Volokh et al., 1990), is a fact in many Brazilian agroecosystems, as vast areas of native vegetation in all biomes have been converted into farmlands (Lapola et al., 2014). Such intense agricultural activity and the need for agricultural inputs that contain high contents of REE require the knowledge of soil REE contents in the Brazilian biomes, with special focus on studies that distinguish concentrations in natural environments (i.e., soil reference values) from anthropogenic ones (de Sá Paye et al., 2016). Lastly, addressing REE inputs, occurrence, and fate in different biomes is strategic as there is still very limited knowledge about the biological role of REE (Ramos et al., 2016a; Skovran and Martinez-Gomez, 2015), which highlights the importance of establishing soil quality reference values in face of the agriculture frontiers increase.

This study quantified REE contents in benchmark topsoils covering different Brazilian biomes, encompassing native and agricultural ecosystems, aiming to: i) establish/suggest soil quality reference values (QRVs) to provide basis for formulating policies and future legislation concerning background concentration (pristine) as well as soil screening contents for REE in Brazil; ii) analyze the impacts of agricultural use on

REE contents in Brazilian soils; and iii) understand the most relevant chemical and physical soil properties affecting their REE contents.

2. Materials and method

2.1. Soil databank

A total of 175 benchmark topsoil (0-20 cm) samples was selected from a databank from the Soil Science Division of the Brazilian Agricultural Research Corporation, seeking for the representativeness of different Brazilian biomes and climates (based on Köppen's climate classification - Alvares et al., 2013) (Figure 1). Such biomes contain a wide variety of soil classes, consisting of: Ferralsols (30.9%); Acrisols (19.4%); Cambisols (17.7%); Plinthosols (5.7%); Nitisols (5.1%); Fluvisols, Leptosols, Arenosols, and Regosols (4.7%); Gleysols (4.6%); Podzols (3.4%); Planosols (3.4%); Vertisols (2.3%), Histosols (1.7%); and, Luvisols (1.1%), classified according to WRB/FAO (IUSS Working Group WRB, 2014). From the total number of samples, 131 were taken from agricultural areas (here called anthropic areas) and 44 were taken from reference (non-agricultural) areas. The database was organized and thus,

land use, chemical, and physical analyses were determined for all soil samples.

Köppen's climate classes for the Brazilian territory include: Af (Tropical without dry season), Am (Tropical monsoon), As (Tropical with dry summer), Aw (Tropical with dry winter), BSh (Dry semi-arid low latitude and altitude), Cfa (Humid subtropical oceanic climate, without dry season with hot summer), Cfb (Humid subtropical oceanic climate, without dry season with temperate summer), Csa (Humid subtropical with dry summer and hot), Csb (Humid subtropical with dry summer and temperate summer), Cwa (Humid subtropical with dry winter and hot summer), Cwb (Humid subtropical with dry winter and temperate summer), and Cwc (Humid subtropical with dry winter and short and cool summer) (Alvares et al., 2013).

2.2. General characterization of biomes

Except for the Pampa, our soil databank included samples from all Brazilian biomes, i.e.: 1) Amazon Rainforest (equatorial rainforest); 2) Caatinga (white forest); 3) Cerrado (neotropical savanna); 4) Atlantic Forest (tropical forest); and 5) Pantanal (wetland). The Amazon Rainforest

is the world's largest region of continuous forest in an ancient geologically stable area – the Amazon craton - dominated by varied sediments, formed under tropical conditions. In general, it is characterized by high annual rainfall (about 2,100 mm) and high mean temperature (about 26°C), along with high soil water availability (Schaefer et al., 2017). The main soils of the Amazon Rainforest are Ferralsols (41% of the area); Acrisols (33%); Plinthosols (9%); Gleysols (6%); Arenosols (5%); Leptosols (3%); Podzols (2%), and other soils (1%) (Rodrigues, 1996).

The Cerrado biome consists of a neotropical savanna presenting annual rainfall between 600 to 2,200 mm with two well-defined seasons (dry and rainy with short periods of drought) and mean annual temperatures of 22-27°C (IBGE, 2015). The warm climate, along with very low content of easily weatherable primary minerals, on flat geomorphic surfaces conducive to leaching, where soil organisms were very active, form mostly highly weathered tropical soils in much, but not all, of the Cerrado (Motta et al., 2002a; 2002b). The main soils of Cerrado are Ferralsols (37% of the area); Acrisols (28%); Arenosols (12%); Plinthosols (12%); Cambisols (5%); Leptosols (5%), and other soils (1%) (Oliveira et al., 2017).

The exclusive Brazilian biome of the Caatinga presents a characteristic deciduous vegetation (Lima, 1966). It is located in a region of great water deficit in the northeast of Brazil: annual rainfall range from 400 to 800 mm and the dry period extends over 8 months, with a very hot and semi-arid climate (Arruda et al., 2017). It causes severe water deficiency, which reflects on soil formation with predominance of Leptosols, Arenosols, Regosols, and Fluvisols (35% of the area); Ferralsols (21%); Acrisols (15%); Luvisols (13%); Planosols (10%); Cambisols (4%); Vertisols (1.3%), and other soils (0.7%) (Araújo Filho et al., 2017).

The Atlantic Forest is a tropical forest that stretches along the Brazilian coast, being the terrestrial biome with the greater biodiversity of the planet (Myers et al., 2000). It is characterized by high rainfall, with biogeochemical nutrient cycling allowing larger biomass formation (Coelho et al., 2017; Rossatto et al., 2015). In general, the landforms are quite dissected, with predominance of Ferralsols (36% of the area); Acrisols (30%); Cambisols (15%); Leptosols, Arenosols, Regosols, and Fluvisols (6%); Nitisols (5%); Planosols (1%), and other soils (7%) which are mainly dystrophic, and it is soils expressing the water regime of this biome (Coelho et al., 2017).

The Pantanal is a large quaternary sedimentation basin, characterized as fluvial and lacustrine depositional systems in a seasonal floodplain (Assine and Silva, 2009; Nascimento et al., 2013). This biome does not present a single vegetation type. But there are large areas with savanna-type vegetation (Couto et al., 2017) and the main soils of Pantanal are Planosols (35% of the area); Podzols (21%); Plinthosols (21%); Gleysols (10%); Acrisols (5%); Vertisols (4.8%); Leptosols, Arenosols, Regosols, and Fluvisols (2.5%); and other soils (0.7%) (Couto et al., 2017). The climate is humid tropical/subtropical, with mean annual rainfall of 1,200 mm and monthly temperatures between 22-32°C (Nascimento et al., 2013).

2.3. Analytical procedures

REE contents were determined by inductively coupled plasma mass spectrometry (ICP-MS) after acid digestion. Soil samples and certified reference materials (CRMs) were digested into a programmable microwave digester CEM-Mars 6 (Mars Xpress, CEM Corporation, Matthews, NC, U.S.A), using Teflon Xpress vessels (USEPA 3051A method – USEPA,

2007). The conditions within each vessel were monitored and controlled by means of an infrared sensor.

After acid digestion, the extracts from soil samples and CRMs were taken into centrifuge tubes and diluted with ultrapure water to 20 mL. The solutions were further diluted to obtain REE contents suitable for analysis. Indium (In) was added ($1 \mu\text{g g}^{-1}$) in the final dilution as an internal standard (Spex Certiprep, USA) to minimize equipment fluctuations and matrix effects. The determination was made by means of external calibration, and the analytical curve was constructed with 0.1, 0.5, 2, 10, and $20 \mu\text{g kg}^{-1}$, in 2% nitric acid solution, from Spex standard solutions, containing $1000 \mu\text{g kg}^{-1}$ (Spex CertiPrep, USA) of individual REE: ^{89}Y , ^{139}La , ^{140}Ce , ^{141}Pr , ^{142}Nd , ^{152}Sm , ^{153}Eu , ^{158}Gd , ^{159}Tb , ^{164}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{174}Yb , and ^{175}Lu .

The methodology validation was carried out by means of certified reference materials, CRM (Calcareous Soil ERM-CC690®, Institute for Reference Materials and Measurements - IRMM, Geel, Belgium) in quadruplicate. The quantification limits (QL) were obtained according to INMETRO (2003) standards, after analyses of pentaplicate blank samples added to the analytical procedure.

The USEPA 3051A method is considered a “partial” digestion technique (semi-total), as it might not dissolve refractory matrices (silicates and titanium oxides), which are particularly relevant for HREE. However, it is considered a standard method for the purpose of the Brazilian legislation (CONAMA, 2009) as well as by ISO 11466 – ISO (2016). Thus, the results presented can be considered as semi-total or “environmentally available” REE contents. The operating conditions of the ICP-MS apparatus and the measurement parameters are presented in Table 1.

The analytical REE contents were compared with the World Soil Average - WSA (Kabata-Pendias, 2011). Such comparisons aimed to serve as a guide concerning enrichment or depletion of REE contents. In this study, the median values are the main parameter used to compare the geochemical data, since data distortion could affect the arithmetic mean values that do not adequately represent the natural contents of soils elements (Reimann et al., 2012; Yamasaki et al., 2001).

In order to characterize biomes and better understand soil properties that might influence REE contents, soil chemical analyses were carried out following standard procedures for Brazilian soils (Teixeira et al., 2017): the pH was determined in water (potentiometer) using a soil:solution ratio

of 1:2.5 after shaking and 1-h rest. Organic Carbon (OC) was obtained by wet oxidation with K-dichromate in sulfuric acid medium. The concentrations of exchangeable Al^{3+} , Ca^{2+} , and Mg^{2+} were extracted with a 1 mol L^{-1} KCl solution and determined by atomic absorption spectrometer. Available K^{+} and P were extracted by a Mehlich-I solution ($0.0125 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.05 \text{ mol L}^{-1} \text{ HCl}$), with K being determined by flame photometer and P by colorimetry. Cation exchange capacity, base saturation, and Al saturation were calculated from aforementioned results.

Particle size distribution was analyzed by the pipette method (Day, 1965). Briefly, the sand fraction was separated using a 0.05-mm sieve. Silt and clay fractions were separated after the silt sedimentation, by pipetting a volume of the solution containing only the clay fraction, followed by oven-drying the solution and weighting the remaining clay fraction. The silt quantification was obtained by subtracting the weights of sand and clay fractions from the total weight of the soil.

2.4. Quality Reference Values (QRVs)

The background concentrations or reference contents represent natural element values in soil, without any anthropogenic interference

(Nogueira et al., 2018). Thus, the natural REE contents were established in reference areas (non-agricultural soil) based on frequency distribution, more specifically on the 75th percentile (top quartile) of its semi-total REE contents, according to Resolution No. 420/2009 of the Brazilian Environmental Council (CONAMA, 2009). As the extreme values represent the natural contents found in soils and their removal did not affect significantly the QRVs, it was preferred to keep them in the statistics approach.

2.5. Statistical analysis

The analytical results were submitted to descriptive statistical analysis. Box plot analyses were also performed to demonstrate REE contents in soils as well as extreme values, in order to establish quality reference values (QRVs). Pearson correlation analysis (significance levels at $p < 0.05$) was performed to better understand the relationships between REE contents and the soil chemical and physical attributes. A priori logarithmic transformation was applied to the analytical data to describe the mean contents values and minimize the distorting effects of high values

(Dudka et al., 1995), since there was no linearity of the data according to the Shapiro-Wilk test performed.

3. Results and discussion

3.1. Analytical quality control

The quality control of REE determination is presented in Table 2. Since REE values were obtained by acid digestion (partial contents - determined), we applied a correction factor on the partial analytical results (corrected) obtained by the USEPA 3051A method in order to represent the total REE contents (recovery). The recovery method of CRM ranged from 57% (Tm) to 99.7% (Nd). The highest recoveries were obtained for La, Nd, Sm, and Dy, while Ce, Gd, Tb, Tm, and Yb yielded the lowest recoveries. Results for quantification limits (QL) were ($\mu\text{g kg}^{-1}$): Y (0.69), La (0.72), Ce (0.72), Pr (0.79), Nd (0.80), Sm (0.83), Eu (0.87), Gd (0.89), Tb (0.91), Dy (0.91), Ho (0.94), Er (0.91), Tm (0.82), Yb (0.91), and Lu (0.93).

3.2. Chemical and physical characterization of biomes soils (reference areas)

In order to better characterize the biomes in their natural context, Table 3 depicts the general physical and chemical characterization of benchmark soils from each Brazilian biome, considering reference areas solely.

The Amazon Rainforest biome presented the lowest values for natural soil pH, base saturation, CEC, $\text{Ca}^{2+} + \text{Mg}^{2+}$, and K^+ . In addition, higher exchangeable Al^{3+} as well as Al saturation ($m = 67 \pm 26.5\%$) were observed. Such soil chemical characteristics resulted from higher temperature and rainfall, which leads to intense and long weathering-leaching processes, forming mainly well-drained soils with relatively low OC (Fernandes et al., 2018; Schaefer et al., 2017) among all biomes analyzed. Along with considerable higher sand fraction (Mendonça et al., 2014; Schaefer et al., 2008), there is high depletion of mobile soil nutrients affected by one of the world's most severe weather conditions (Arafa et al., 2015; Minuzzi et al., 2008; Souza et al., 2018; Wang et al., 2017).

In the Caatinga biome, the potential evapotranspiration can reach twice the rainfall, which makes this environment conservative of soil bases (Araújo Filho et al., 2017). Thus, the soils sampled are moderately alkaline (pH around 6.5), with high base saturation (eutrophic) and CEC, and low

Al saturation. This fact, along with the highest silt fraction, evidences that such biome presents the lesser weathered-leached soils among all biomes analyzed.

The Cerrado soils presented variable texture (from loam to clay), with the lowest sand fraction. Because they are highly weathered-leached, the soils tend to be infertile (low values of K^+ , $Ca^{2+} + Mg^{2+}$, CEC, and dystrophic) and present high Al saturation. When base cations are removed from negative sites, they are first replaced by H^+ , which turns the soils more acidic. In addition, such biome has also high P-fixing soils (Lopes and Guilherme, 2016).

The Atlantic Forest soils were developed mostly in dissected geomorphic surfaces, mainly over Pre-Cambrian acid rocks. Thus, the moist climate along with relatively stable surfaces tends to form well developed soils (lowest silt fraction), characterized by high acidity, low CEC, low content of bases (Coelho et al., 2017), with variable soil texture (from loam do clay texture).

According to Couto et al. (2017), pedogenetic processes in the Pantanal biome are closely related to seasonal flooding events. In this sense, although ions could be leached, another possibility is ion

concentration. High base saturation, CEC, and $\text{Ca}^{2+} + \text{Mg}^{2+}$, with lower Al^{3+} contents and alkaline reaction, denotes high soil natural fertility. Such properties might be explained by the following reasons: a) flooding processes have caused the deposition of easily weatherable primary minerals (plagioclase and K-feldspar from crystalline basement); b) there is a trend of evapotranspiration being higher than precipitation (Couto et al., 2017), which turned this environment favorable for conserving soil bases mainly in the southern part of the Pantanal, where most samples were taken. The lowest organic matter contents among biomes (values around 9.2 g kg^{-1}) was found for the Pantanal, which might be related to water removal after mineralization during the dry season (Nogueira et al., 2002). Preterit climatic conditions, which in turn govern water regimes, have driven the nature of the sedimentation process. In this case, coarser deposits (higher sand content and the lower clay content) seem to be predominant.

In summary, and based on soil properties analyzed, Caatinga and Pantanal presented soils pedogenically less developed, with the opposite trend observed for Amazon Rainforest, Cerrado, and Atlantic Forest. Such contrast is mostly related to water availability. Water is the main

weathering agent promoting conservation/removal of soil elements, well as the temperature is high in all biomes.

3.3. *Quality reference values (QRVs)*

Figure 2 presents REE contents of reference areas plotted in box plots, representing the range of values, the mean, median, minimum, maximum, 1st and 3rd quartiles, and the interquartile range of the data set. QRVs (75th percentile of the frequency distribution) for each Brazilian biome was performed with samples collected under native vegetation or under minimal anthropogenic influence. Thus, they reflect pedological, geological, geomorphological, and climatic diversity of each environment as suggested by CONAMA (2009). Considering that the background concentrations may change from biome to biome (Reimann and Garrett, 2005), the reference values are prepared could guide policies in a more realistic manner.

QRVs are presented in Table 4, with values from the Pantanal being absent due to the small amount of samples. The Caatinga biome presented the highest values for all REE, followed by intermediate values of Cerrado and Atlantic Forest samples. The Amazon Rainforest biome presented the

lowest values. Such trend might be related to different weathering-leaching conditions, being the Caatinga more conservative of REE. The differences in the QRVs verified in each biome are due to the diversity of parent materials and pedogenetic processes influenced mainly by tropical climatic conditions (Melo et al., 2017; Nogueira et al., 2018).

These QRVs may be the basis for the implementation of public policies and for further of natural contents of REE in Brazilian soils. Considering we evaluated benchmark soils in each biome, to the best of our knowledge, this is the first study that depicts soil REE contents focusing on different Brazilian climatic conditions and establishing QRVs for each biome. Considering the REE reference values obtained in more detailed-scale already published in Brazil, most of them are located in the northeastern region, where there is a predominance of Caatinga, with small proportion of Atlantic Forest in the Coast Plain areas. Therefore, QRVs can be used as a tool for prevention, control and monitoring of soil pollution and anthropogenic activities.

Comparing the values found by Silva et al. (2016) in Brazilian benchmark soils, only the Amazon Rainforest presented lower values of QRVs. In a study with a wide variation of parent materials, de Sá Paye et

al. (2016) reported slightly higher REE contents than those found in the Caatinga biome by our study. Conversely, Licht et al. (2006), working with samples from the Atlantic Forest biome, found smaller values than those established in this study. Finally, a comparison of Ce (43 mg kg^{-1}) and La (19 mg kg^{-1}) values reported for Caatinga soils by Matschullat et al. (2012) revealed also contents smaller than those showed in this study.

The wide variation in the results compared to others must have been influenced by different analytical methodologies for quantification (Alfaro et al., 2015; Melo et al., 2017; Paye et al., 2010). In the Atlantic Forest biome, particularly may be due to the wide range territorial coverage, high environmental variability and geological diversity such as those verified by Arruda et al. (2017), Melo et al. (2017), and Paye et al. (2010). dos Santos and Alleoni (2013) suggest a standardized analytical methodology and regional studies for the establishment of QRVs for soils.

3.4. REE contents in Brazilian biomes (agricultural and reference areas)

The overall contents of REE for each biome in agricultural and reference areas are presented in box plots (Figure 3). Through visual analysis, the differences among groups are clear. The Amazon Rainforest

has comparatively short range variation, with lower contents of REE among biomes. On the other hand, the Caatinga box plot is higher than others, which means that most of the data set has consistently higher REE contents, increasing the median as a consequence. However, the extremely high REE values (higher maximum values or outliers) were found in the Cerrado and the Atlantic Forest (the highest upper whisker), because of the large territorial coverage and, consequently, climatic variation, which in turn showed quite similar median values with variable data. The Cerrado covers the entire central region of Brazil between the equatorial line and the tropic of Capricorn and Atlantic Forest covers a large part of the Brazilian Coast, encompassing tropical, equatorial, and temperate climates (Coelho et al., 2017). Lastly, the Pantanal showed a median slightly higher than that of the Caatinga, but with more elongation of upper and lower box plots, due to a wider range of REE contents.

The median and standard deviation of REE contents in different Brazilian biomes are presented in Table 5. In addition, mean values of the WSA were used in order to verify the possible enrichment of REE in soils. Enrichment ratios for REE contents relative to soils worldwide were

obtained by the ratio of median values/WSA (with values above the unit expressing enrichments), as showed in the Table 5.

From Table 5, and according to median values, contents of REE followed the descending order in agricultural and reference areas (Σ REE in mg kg^{-1}), respectively: Caatinga (186.6/257.4) > Atlantic Forest (138.1/63.4) > Pantanal (137.4/61.6) > Cerrado (135.1/54.3) > Amazon Rainforest (64.3/35.6). Thus, the REE contents in reference areas were higher than the agricultural areas only in the Caatinga biome, because the soils were derived from the parent materials REE-rich, along with the low weathering. Besides, the main REE reserves in Brazil occur in association with alkali-carbonatitic complexes (Antoniassi et al., 2015) that are common in the Caatinga biome. In reference areas, REE contents are inherited from the easily parent materials bearing these elements (Lijun et al., 2004), and maintained in the soils systems.

The relationships between REE contents in agricultural/reference areas from each biome, decreased in order: Cerrado (2.5) > Atlantic Forest e Pantanal (2.2) > Amazon Rainforest (1.8) > Caatinga (0.7). It demonstrates that in agricultural areas of the all biomes (except for the Caatinga), there was an increase in REE contents possibly influenced by

the intensified application of phosphate fertilizers or phosphogypsum, both carriers of REE (Diatloff et al., 1996; Hu et al., 2006a; Ramos et al., 2016a; Turra et al., 2011; Tyler, 2004; Volokh et al., 1990). Besides, the highest ratio was verified in the Cerrado biome (2.5), probably because this one is the main Brazilian agricultural frontier, with a well-known high demand of P inputs (Fink et al., 2016).

According to Kabata-Pendias (2011), all lanthanides are slightly mobile in soils, although the light ones behave quite different from the heavy ones, as discussed further. In this sense, REE contents were likely driven by the preterit climatic conditions (especially rainfall and temperature), which in turn influenced the intensity of weathering-leaching, and promoted differential removal of elements in some biomes (Amazon Rainforest, Cerrado, Atlantic Forest, and Pantanal) and smaller removal in others (Caatinga).

As already mentioned, due to the positive balance of evapotranspiration over precipitation, the Caatinga biome is a more conservative environment due to the semi-arid climate (Arruda et al., 2017), having relative REE enrichment ratios (agricultural areas: 1.2 and reference areas: 1.6) as a consequence. On the other hand, considering the

other biomes, REE bearing minerals are especially weathered-leached from topsoil and tend to accumulated, partially or totally, in the lower parts of the soil profile as they are incorporated into secondary minerals (Cidu et al., 2013; Harlavan et al., 2009; Ramos et al., 2016b; Sadeghi et al., 2013a; Tyler, 2004). In addition, the Amazon Rainforest, as well as the Cerrado and the Atlantic Forest soils, presented acid pH (Table 3), which may lead to lower values of REE, once lanthanides are removed from soluble hydroxides or organic compounds complexes (Cao et al., 2001; Diatloff et al., 1996; Kabata-Pendias, 2011; Tang and Johannesson, 2003).

Regarding LREE and HREE, the light ones were the most abundant for all biomes when compared with the heavy ones, in accordance with results found in other Brazilian soils (de Sá Paye et al., 2016; Licht et al., 2006; Silva et al., 2016) and worldwide (Kanazawa and Kamitani, 2006; Laveuf and Cornu, 2009; Liu et al., 2015; Sadeghi et al., 2013a, 2013b), mainly associated with silicate minerals (Laveuf and Cornu, 2009; Tyler, 2004). In agricultural areas, the LREE values ranged from 83.4% for the Pantanal (the least contribution) to 89.2% for the Atlantic Forest (the highest contribution), with the smallest contribution (79.7%) found for reference areas for Caatinga and Cerrado. The LREE are more easily

adsorbed by organic or oxides/hydroxides soil particles than HREE (Coppin et al., 2002; Ling et al., 2015). In contrast, HREE are preferably transported through solution and leached from the soil system (Ling et al., 2015; Smedley, 1991; Tyler, 2004; Wood, 1990).

In general, the REE contents followed the order Ce > Nd > La > Y > Pr > Sm > Dy > Gd > Yb > Er > Eu > Tb > Ho > Tm > Lu, which is the same sequence found in the earth's crust, as described by Rudnick and Gao (2014). Ce is the most abundant REE due to its incorporation into clay minerals structure, due to its oxidized form (Ce IV) and smaller ionic radius (Cao et al., 2001; Laveuf and Cornu, 2009; Sanematsu et al., 2013). In this study, an exception occurred in the Amazon Rainforest, whose soils presented, respectively for agricultural and reference areas, low contents of La (14.33 and 8.07 mg kg⁻¹) and Ce (20.29 and 14.23 mg kg⁻¹), again, as a result of intense weathering-leaching conditions (Souza et al., 2018). Minuzzi et al. (2008) also verified REE and Y depleted in Amazon Rainforest biome soils. In accordance with Sadeghi et al. (2013b), the highest REE contents (especially Ce, La, and Y) are found in alkaline soils similar to the Caatinga biome with higher pH values (6.5), since pH

increases REE adsorption process by soil particles, causing their low mobility in soils (Coppin et al., 2002; Tyler and Olsson, 2001).

Except for the Caatinga (Σ REE contents: 257.4 mg kg⁻¹ in reference areas and 186.6 mg kg⁻¹ in agricultural areas), relative REE depletions were found in soils from all biomes when compared with the WSA (see enrichment ratio in Table 5). Soil processes in tropical/subtropical climates normally cause greater depletion of REE, which result in lower contents per unit soil weight, especially in topsoils (Braun et al., 1993; Kabata-Pendias, 2011; Tyler, 2004). On the other hand, when compared with the WSA, soils from the Caatinga presented an enrichment mainly for LREE (La, Ce, Pr, and Nd). Part of this behavior could be explained by the fact that, in agricultural areas, the application of phosphate fertilizers and phosphogypsum can significantly increase LREE concentrations in soils (Turra et al., 2011; Volokh et al., 1990) (Table 5). Except for the Amazon Rainforest, Nd was the only REE that presented enrichment for all biomes in agricultural areas. Nd enrichment may be related to the fact that this is the only REE that can occur with pentavalent valence (Kabata-Pendias, 2011) in highly oxidized environments, as in tropical soils conditions.

3.5. Enrichment ratio of rare earth elements with agricultural use

Table 6 depicts the enrichment ratio of REE contents for each Brazilian biome, in order to verify the effects of agricultural inputs. When the ratio of REE contents in agricultural/reference areas is higher than the unit (1), there is enrichment (Holmgren et al., 1993). Thus, based on the knowledge of the history of use of these areas, this is mainly due to agriculture uses.

REE contents in agricultural areas were higher than in the reference areas, except for the Caatinga biome, which presented enrichment ratios below the unit, as previously discussed. Caatinga reference areas belong to geological formations rich in REE, especially carbonatitic sedimentary rocks (Antoniassi et al., 2015; Kanazawa and Kamitani, 2006; Tyler, 2004), shales and calcareous (Hu et al., 2006b; Tyler, 2004). Soils originated from sedimentary and alkaline igneous rocks present the highest REE contents (de Sá Paye et al., 2016), maximized under semi-arid conditions. In Brazil, phosphate products present a wide variety of REE contents depending on the raw materials used or rock processing operations as demonstrated by Ramos et al. (2016a, 2016b). Thus, what happened in these agricultural areas (Caatinga) might have been the application of phosphate fertilizers

poor in REE and/or a smaller rate of application of P fertilizers in such agricultural areas (FAO, 2004).

Countries as Australia, China, Japan, Korea, Switzerland, and Philippines have consistently used fertilizers bearing REE (Hu et al., 2006a; Wang et al., 2008), yet the effects of REE in increasing agricultural productivity have not been confirmed so far (Skovran and Martinez-Gomez, 2015; Thomas et al., 2014). In Brazil, REE have been unintentionally added to soils through the application of phosphate fertilizers and phosphogypsum (Otero et al., 2005; Turra et al., 2011; Tyler, 2004; Volokh et al., 1990; Waheed et al., 2011). Therefore, intensively cultivated agricultural areas, industrial/urban areas, sites with parent materials rich in REE are the most likely conditions to find high contents of REE (Smidt et al., 2011).

The geochemical composition of anthropogenic soils may have been significantly affected by P-fertilizers and phosphogypsum, among other inputs (Aubert et al., 2002; Lijun et al., 2004; Tyler, 2004; Volokh et al., 1990), increasing mainly the LREE contents adsorbed by organic or oxidic particles, the latter being abundant in tropical soils (Ling et al., 2015).

According to Tyler (2004), the main significant sources of REE in agricultural inputs are phosphate fertilizers (phosphogypsum, single superphosphate and triple superphosphate) due to the high affinity of REE for P-compounds, which may explain the REE enrichment in cultivated areas. Since Brazilian agriculture demands large quantities of these supplies, such inputs can significantly increase the REE contents in soils (Turra et al., 2011).

3.6. Relationships between soil attributes and REE contents

According to de Sá Paye et al. (2016), individual REE contents depends on soil characteristics (mainly texture and physical-chemical characteristics), which in turn are influenced by pedogenic processes. In this sense, Table 7 summarizes the Pearson's correlation coefficients (r) between REE, LREE, HREE and some soil properties.

In general, REE presented significant statistical correlation ($p < 0.05$) with sand, silt, pH, OC, CEC, $\text{Ca}^{2+} + \text{Mg}^{2+}$, and K^{+} (Table 7). Even though one could expect a significant correlation between REE and clay content (de Sá Paye et al., 2016; Hu et al., 2006b; Tyler, 2004), this was not found in our study ($p < 0.05$), which may be explained by the distinct

soils mineralogy (Resende et al., 2011). In addition, the clay fraction ($r = 0.17$) in our samples had little influence in CEC, when compared with OC ($r = 0.81$).

Although important for REE complexation processes (Picard et al., 2002; Pourret et al., 2007a), organic matter in tropical countries usually presents less stability, being easily degraded (Souza et al., 2018). Yet, REE can be adsorbed by soil organic matter due to its negative charges (Pourret et al., 2007b; Tyler, 2004). Under these circumstances, LREE are easily adsorbed by organic complexes and soil oxides (Ling et al., 2015), whereas HREE are preferentially leached during weathering.

REE adsorption is favored by high pH and CEC (Coppin et al., 2002). Unlike acidic soils (Amazon Rainforest, Cerrado, and Atlantic Forest), which adsorb REE mostly as outer-sphere complexes in basal surfaces, in more alkaline soils (Caatinga and Pantanal), the adsorption as inner-sphere complexes may occur at the edges of the particles (Cao et al., 2001; Coppin et al., 2002). Finally, REE retention is also increased by the higher CEC of soils, as reported elsewhere (de Sá Paye et al., 2016; Laveuf and Cornu, 2009; Tyler, 2004).

Higher and significant correlations between REE and $\text{Ca}^{2+} + \text{Mg}^{2+}$ ($r = 0.30$) and K^+ ($r = 0.39$) were found due to the similar electronegativity of REE and Ca (Laveuf and Cornu, 2009), favoring Ca substitution into the minerals structure by REE (Kanazawa and Kamitani, 2006). In addition, REE easily replace alkaline (K) and alkaline earth metals (Ca and Mg) in colloidal, because their trivalent state favors adsorption (Coppin et al., 2002). These results demonstrated that these chemical attributes in topsoils, especially Ca^{2+} , Mg^{2+} , and K^+ , explained part of the variation found between the soil properties and REE contents.

Most of the samples were taken from agricultural areas (131 samples) that probably had application of soil acidity amendments (e.g., lime and phosphogypsum), which contain Ca and Mg. Some of those agricultural inputs may contain also high REE contents, which may be explain the positive and stronger correlations found between REE, Ca and Mg.

4. Conclusion

The soil weathering-leaching intensity, as well as water availability, in Brazilian biomes played an important role in REE distribution and

fractionation processes in benchmark soils from agricultural and reference areas. It promoted differential removal of elements in soils of some biomes as Amazon Rainforest, Cerrado, Atlantic Forest and Pantanal; and smaller removal in others as Caatinga.

REE contents found in natural ecosystems can be used in the determination of soil quality reference values, being a base for regulation of REE limits in soils and for studies concerning soil contamination prevention.

Among the physical-chemical properties of benchmark topsoils, the ones that had higher correlations with REE were CEC, Ca^{2+} , Mg^{2+} , and K^{+} .

Anthropogenic activities had a fundamental relevance in REE enrichment contents in topsoils of agricultural areas.

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Figures and Tables

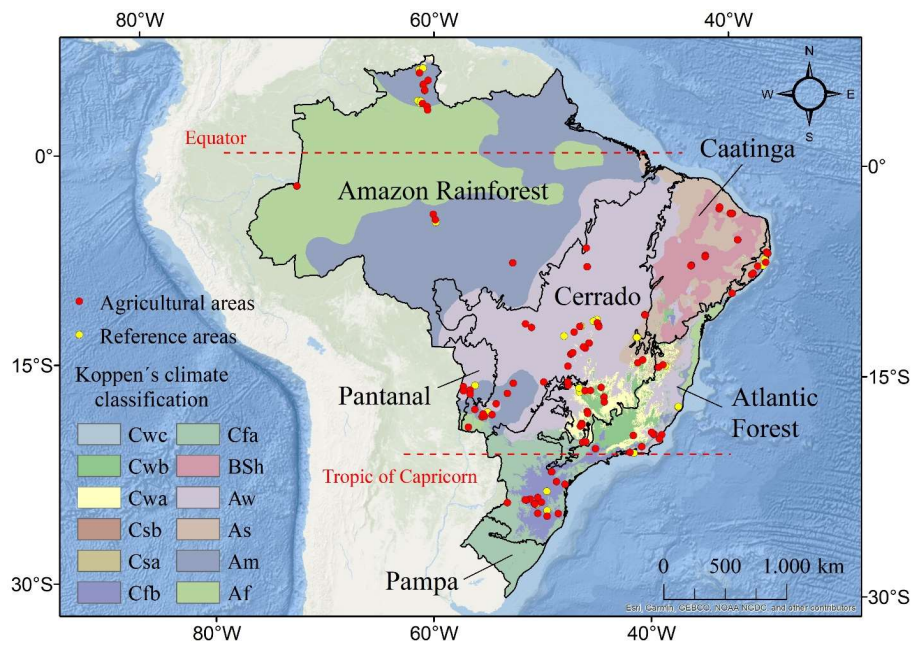


Figure 1. Spatial distribution of benchmark soil samples for main Brazilian biomes.

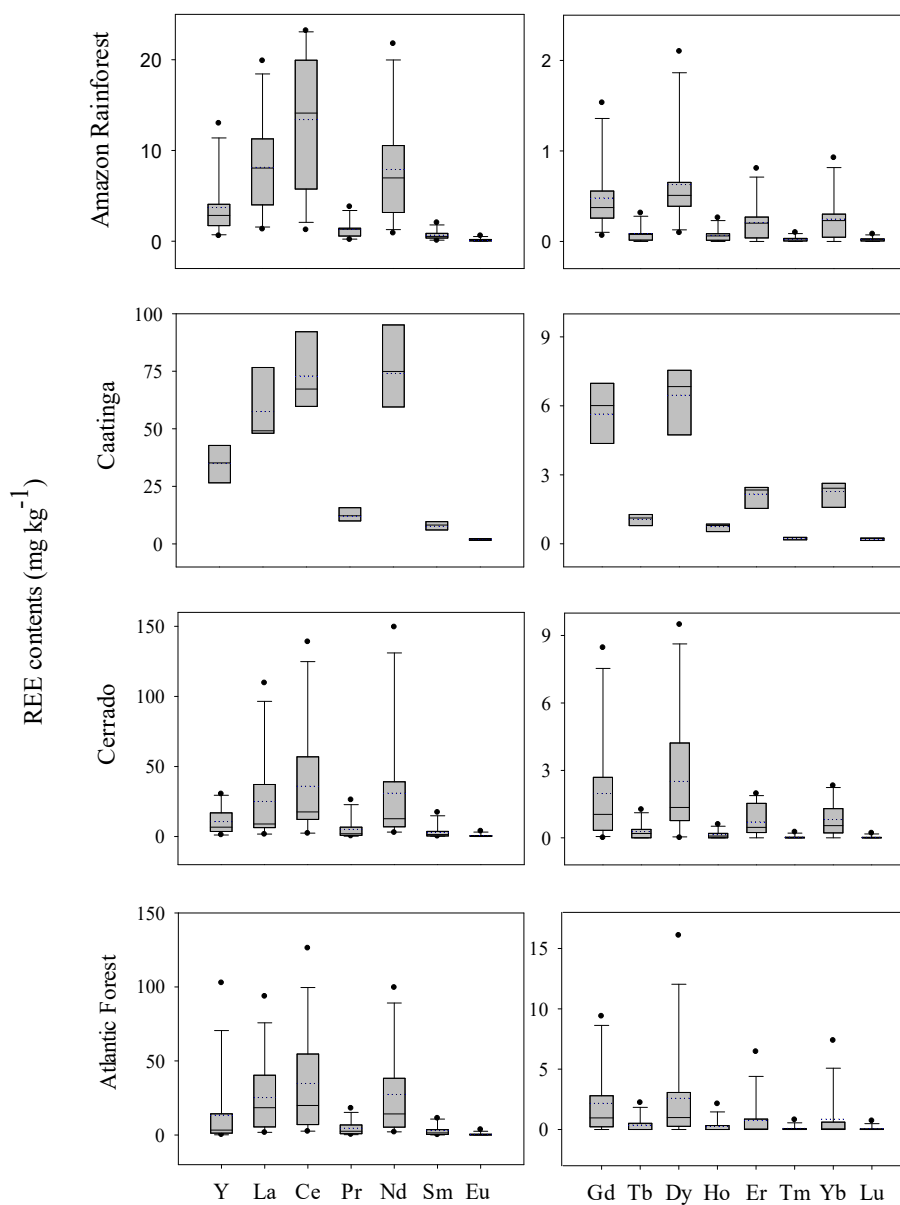


Figure 2. Box plots of Rare Earth Element (REE) contents in benchmark soils of native areas (dotted lines - mean; black lines – median) including Amazon Rainforest, Caatinga, Cerrado and Atlantic Forest in Brazil.

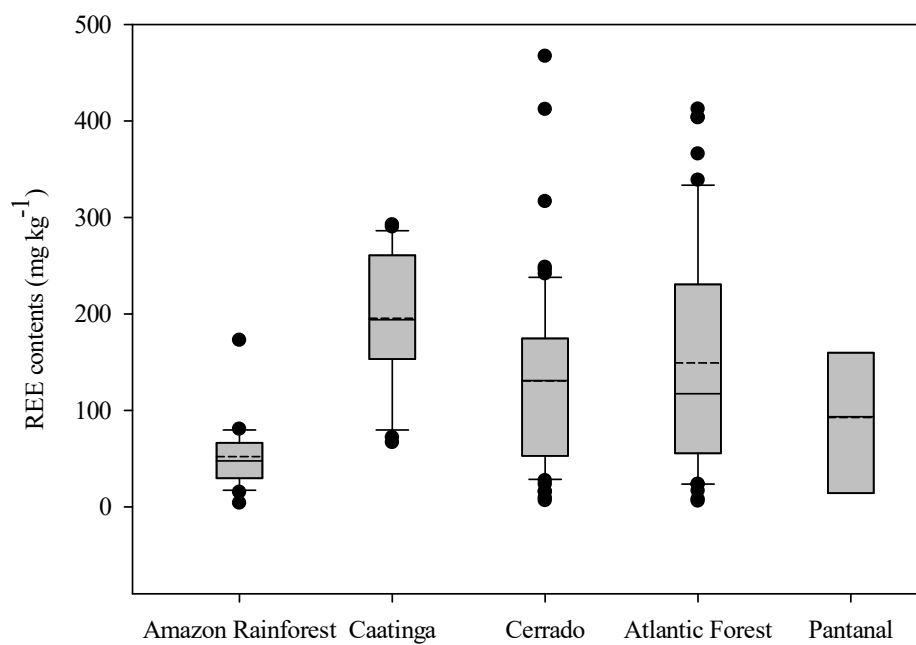


Figure 3. Box plot showing Rare Earth Elements (REE) contents in benchmark soils of Brazilian biomes (mean values: dotted lines, median: black lines).

Table 1. Equipment operating conditions and measurement parameters of ICP-MS.

Equipment	Perkin Elmer NexIon 300D
RF Power	1600 W
Nebulizer gas flow	1.12 l min ⁻¹
Auxiliary gas flow	1.375 l min ⁻¹
Plasma gas flow	18 l min ⁻¹
Sampler cone	Nickel - 1mm
Skimmer cone	Nickel - 0.7 mm
Integration mode	Peak jump
Rinse time between standards or samples	60 s (with 2 % v/v HNO ₃)
Number of replicates	15
Internal Standard	¹¹⁵ In

Table 2. Rare Earth Element (REE) quality control recovered for certified reference material.

REE	Certified (mg kg ⁻¹)	Determined (mg kg ⁻¹)	Corrected (mg kg ⁻¹)	Recovery (%)
La	24.4 ± 1.7	16.60	21.90	90
Ce	49.1 ± 2.5	20.18	32.07	65.3
Nd	19.1 ± 2.2	18.14	19.05	99.7
Sm	3.5 ± 0.4	1.92	2.79	80
Gd	3.2 ± 0.4	1.48	2.28	71
Tb	0.5 ± 0.07	0.19	0.31	62
Dy	2.9 ± 0.28	2.04	2.65	91
Tm	0.232 ± 0.026	0.08	0.13	57
Yb	1.57 ± 0.19	0.77	1.16	74

Certified values ± standard deviation, Determined = mean values, Recovery (%) = (corrected/certified values) x 100.

Table 3. Physical-chemical median and standard deviation (range in brackets) values in benchmark soils of reference areas of Brazilian biomes.

Soil propertie	Amazon Rainforest (n = 11)	Caatinga (n = 7)	Cerrado (n = 11)	Atlantic Forest (n = 13)	Pantanal (n = 2)
Sand (g kg ⁻¹)	620 ± 295 (67-958)	431 ± 251 (49-895)	435 ± 285 (0-880)	563 ± 332 (20-940)	750 ± 257 (568-932)
Silt (g kg ⁻¹)	179 ± 198 (22-532)	235 ± 84 (45-292)	166 ± 153 (0-505)	100 ± 115 (25-401)	105 ± 109 (28-182)
Clay (g kg ⁻¹)	201 ± 184 (20-540)	376 ± 175 (60-659)	305 ± 269 (0-758)	283 ± 262 (20-870)	145 ± 148 (40-250)
OC (g kg ⁻¹)	9.9 ± 16.6 (3.3-53.8)	15.9 ± 6.4 (1.7-24.0)	15.0 ± 50.2 (7.0-180.6)	13.5 ± 10.3 (2.9-37.5)	9.2 ± 4.7 (5.8-12.5)
pH (soil/water)	4.7 ± 0.7 (3.7-6.3)	6.5 ± 0.6 (5.1-6.7)	5.0 ± 0.8 (4.0-6.4)	4.9 ± 0.9 (3.7-7.1)	7.1 ± 1.1 (6.3-7.9)
V (%)	10.0 ± 20.5 (4.0-76.0)	80.5 ± 20.2 (37.0-88.0)	22.0 ± 33.3 (3.0-92.0)	24.0 ± 31.7 (2.0-90.0)	82.0 ± 25.5 (64.0-100.0)
m (%)	67.0 ± 26.5 (0.0-87.0)	0.0 ± 5.8 (0.0-13.0)	33.0 ± 30.9 (0.0-77.0)	27.0 ± 39.0 (0.0-94.0)	0.0-0.0 (0.0-0.0)
CEC (cmol _c kg ⁻¹)	3.9 ± 7.6 (1.8-23.3)	13.6 ± 5.1 (1.7-19.0)	12.5 ± 17.3 (2.8-63.6)	8.2 ± 8.7 (3.7-32.0)	15.5 ± 15.9 (4.2-26.7)
Al ³⁺ (cmol _c kg ⁻¹)	0.6 ± 2.3 (0.0-6.3)	0.0 ± 0.2 (0.0-0.5)	0.5 ± 1.8 (0.0-6.2)	0.7 ± 3.1 (0.0-11.2)	0.0-0.0 (0.0-0.0)
Ca ²⁺ + Mg ²⁺ (cmol _c kg ⁻¹)	0.4 ± 0.8 (0.0-2.8)	9.9 ± 4.8 (0.6-15.2)	0.9 ± 7.6 (0.2-21.1)	1.8 ± 6.8 (0.2-25.8)	14.4 ± 16.8 (2.5-26.3)
K ⁺ (cmol _c kg ⁻¹)	0.1 ± 0.1 (0.0-0.3)	0.3 ± 0.2 (0.1-0.8)	0.1 ± 0.2 (0.1-0.5)	0.1 ± 0.2 (0.0-0.6)	0.2 ± 0.1 (0.2-0.3)
P (mg kg ⁻¹)	2.0 ± 1.4 (0.0-5.0)	3.0 ± 4.3 (1.0-14.0)	1.0 ± 4.8 (1.0-17.0)	1.0 ± 18.4 (1.0-68.0)	25.0 ± 14.1 (15.0-35.0)

n: number of samples for each biome, median ± standard deviation ranged in brackets, OC: organic carbon, pH: hydrogen ion concentration in water, V: base saturation, m: aluminum saturation, CEC: cation exchange capacity, Al³⁺, Ca²⁺ and Mg²⁺ in exchangeable forms and K⁺ and P in available forms.

Table 4. Quality reference values (QRVs) of Rare Earth Elements (REE) for benchmark soils of Brazilian biomes.

	Amazon Rainforest (n = 11)	Caatinga (n = 7)	Cerrado (n = 11)	Atlantic Forest (n = 13)
mg kg ⁻¹			
Y	4.08	42.79	16.96	14.36
La	11.28	76.66	37.14	40.36
Ce	19.94	92.20	56.89	54.68
Pr	1.44	15.72	6.74	6.81
Nd	10.54	95.12	39.06	38.32
Sm	0.87	9.66	3.71	3.63
Eu	0.19	2.31	0.71	0.57
Gd	0.56	6.98	2.69	2.80
Tb	0.09	1.28	0.38	0.52
Dy	0.65	7.54	4.22	3.07
Ho	0.09	0.86	0.20	0.33
Er	0.27	2.45	1.54	0.86
Tm	0.03	0.28	0.03	0.07
Yb	0.30	2.63	1.30	0.61
Lu	0.03	0.25	0.02	0.05
LREE	44.26	291.66	144.25	144.36
HREE	6.09	65.06	27.33	22.65
ΣREE	50.36	356.73	171.58	167.01

n: number of reference areas for biomes, 75th percentile is considered as reference values in this study.

Table 5. Median and standard deviation of Rare Earth Elements (REE) contents of Brazilian benchmark soils related to the enrichment ratio (in brackets) relative to World Soil Average¹.

REE	Amazon Rainforest		Caatinga		Cerrado		Atlantic Forest		Pantanal	
	A (n = 13)	R (n = 11)	A (n = 17)	R (n = 7)	A (n = 52)	R (n = 11)	A (n = 45)	R (n = 13)	A (n = 4)	R (n = 2)
mg kg ⁻¹									
Y	4.62 ± 5.8 (0.2)	2.84 ± 3.3 (0.1)	17.23 ± 8.9 (0.7)	33.52 ± 14.7 (1.5)	10.58 ± 13.9 (0.5)	6.74 ± 10.0 (0.3)	8.24 ± 9.5 (0.4)	3.36 ± 27.8 (0.1)	15.30 ± 10.9 (0.7)	6.41 ± 6.2 (0.3)
La	14.33 ± 8.1 (0.5)	8.07 ± 5.3 (0.3)	42.23 ± 18.7 (1.6)	49.08 ± 24.0 (1.8)	23.32 ± 17.1 (0.9)	8.98 ± 31.8 (0.3)	31.15 ± 28.9 (1.2)	18.42 ± 26.1 (0.7)	29.21 ± 18.7 (1.1)	13.29 ± 13.0 (0.5)
Ce	20.29 ± 12.9 (0.4)	14.13 ± 7.6 (0.2)	58.37 ± 28.7 (1.0)	66.70 ± 30.5 (1.2)	53.02 ± 31.5 (0.9)	17.58 ± 40.3 (0.3)	44.88 ± 45.9 (0.8)	19.92 ± 35.2 (0.4)	40.79 ± 28.5 (0.7)	19.19 ± 17.9 (0.3)
Pr	2.61 ± 1.6 (0.4)	1.31 ± 1.0 (0.2)	7.86 ± 3.6 (1.1)	11.31 ± 5.0 (1.6)	5.06 ± 4.4 (0.7)	2.05 ± 7.6 (0.3)	5.61 ± 5.7 (0.8)	2.50 ± 5.2 (0.4)	5.53 ± 3.8 (0.8)	2.40 ± 2.4 (0.3)
Nd	17.19 ± 8.9 (0.7)	6.98 ± 5.7 (0.3)	47.27 ± 26.7 (1.8)	68.94 ± 30.6 (2.7)	31.06 ± 30.3 (1.2)	12.79 ± 43.1 (0.5)	37.85 ± 42.5 (1.5)	14.26 ± 29.8 (0.5)	35.50 ± 24.2 (1.4)	15.59 ± 14.9 (0.6)
Sm	1.63 ± 1.0 (0.4)	0.53 ± 0.5 (0.1)	4.24 ± 2.1 (0.9)	7.43 ± 3.2 (1.6)	3.46 ± 3.4 (0.8)	1.43 ± 4.9 (0.3)	3.23 ± 3.3 (0.7)	1.39 ± 3.7 (0.3)	3.20 ± 2.3 (0.7)	1.27 ± 1.2 (0.3)
Eu	0.26 ± 0.3 (0.2)	0.19 ± 0.2 (0.1)	0.64 ± 0.6 (0.5)	1.78 ± 0.8 (1.3)	0.73 ± 1.0 (0.5)	0.43 ± 1.0 (0.3)	0.52 ± 0.9 (0.4)	0.26 ± 0.9 (0.2)	0.37 ± 0.3 (0.3)	0.18 ± 0.1 (0.1)

Gd	0.98 ± 0.8 (0.3)	0.37 ± 0.4 (0.1)	3.18 ± 1.5 (0.8)	5.46 ± 2.3 (1.4)	2.28 ± 2.1 (0.6)	1.04 ± 2.5 (0.3)	2.34 ± 2.3 (0.6)	0.96 ± 2.9 (0.2)	2.21 ± 1.5 (0.6)	0.82 ± 0.8 (0.2)
Tb	0.24 ± 0.2 (0.4)	0.09 ± 0.1 (0.1)	0.27 ± 0.3 (0.4)	1.03 ± 0.4 (1.6)	0.24 ± 0.3 (0.4)	0.24 ± 0.3 (0.4)	0.24 ± 0.3 (0.4)	0.24 ± 0.6 (0.4)	0.24 ± 0.1 (0.4)	0.24 ± 0.1 (0.4)
Dy	1.06 ± 1.1 (0.3)	0.51 ± 0.5 (0.1)	3.16 ± 1.6 (0.9)	6.35 ± 2.7 (1.8)	2.79 ± 2.8 (0.8)	1.35 ± 2.8 (0.4)	2.28 ± 2.5 (0.6)	0.99 ± 4.4 (0.3)	2.98 ± 2.2 (0.8)	1.13 ± 1.1 (0.3)
Ho	0.24 ± 0.1 (0.3)	0.07 ± 0.1 (0.1)	0.24 ± 0.2 (0.3)	0.75 ± 0.3 (1.0)	0.24 ± 0.2 (0.3)	0.20 ± 0.1 (0.3)	0.24 ± 0.2 (0.3)	0.24 ± 0.5 (0.3)	0.24 ± 0.1 (0.3)	0.24 ± 0.1 (0.3)
Er	0.27 ± 0.4 (0.1)	0.21 ± 0.2 (0.1)	0.85 ± 0.6 (0.4)	2.23 ± 0.9 (1.0)	0.84 ± 0.9 (0.4)	0.47 ± 0.6 (0.2)	0.61 ± 0.7 (0.3)	0.23 ± 1.7 (0.1)	0.65 ± 0.6 (0.3)	0.18 ± 0.2 (0.1)
Tm	0.17 ± 0.1 (0.4)	0.03 ± 0.1 (0.1)	0.21 ± 0.1 (0.6)	0.26 ± 0.1 (0.7)	0.21 ± 0.1 (0.6)	0.21 ± 0.1 (0.6)	0.21 ± 0.1 (0.6)	0.21 ± 0.2 (0.6)	0.21 ± 0.1 (0.6)	0.21 ± 0.1 (0.6)
Yb	0.25 ± 0.5 (0.1)	0.23 ± 0.2 (0.1)	0.68 ± 0.7 (0.3)	2.31 ± 1.0 (0.9)	1.00 ± 1.1 (0.4)	0.55 ± 0.7 (0.2)	0.45 ± 0.8 (0.2)	0.23 ± 2.0 (0.1)	0.74 ± 0.7 (0.3)	0.23 ± 0.3 (0.1)
Lu	0.14 ± 0.1 (0.4)	0.03 ± 0.1 (0.1)	0.19 ± 0.1 (0.5)	0.22 ± 0.1 (0.6)	0.24 ± 0.1 (0.6)	0.24 ± 0.1 (0.6)	0.24 ± 0.1 (0.6)	0.24 ± 0.2 (0.6)	0.24 ± 0.1 (0.6)	0.24 ± 0.1 (0.6)
LREE	56.3 ± 31.9 (0.5)	31.2 ± 18.7 (0.3)	160.6 ± 65.0 (1.3)	205.3 ± 88.8 (1.7)	116.6 ± 74.4 (1.0)	43.3 ± 128.1 (0.4)	123.2 ± 108.3 (1.0)	56.7 ± 98.8 (0.5)	114.6 ± 77.8 (0.9)	51.9 ± 49.5 (0.4)

	8.0 ± 8.9 (0.2)	4.4 ± 4.9 (0.1)	26.0 ± 13.4 (0.7)	52.1 ± 22.4 (1.4)	18.4 ± 21.0 (0.5)	11.0 ± 16.1 (0.3)	14.9 ± 15.8 (0.4)	6.7 ± 40.1 (0.2)	22.8 ± 16.3 (0.6)	9.7 ± 8.7 (0.3)
HREE										
	64.3 ± 39.0 (0.4)	35.6 ± 22.5 (0.2)	186.6 ± 76.6 (1.2)	257.4 ± 110.4 (1.6)	135.1 ± 88.9 (0.8)	54.3 ± 140.9 (0.3)	138.1 ± 120.4 (0.9)	63.4 ± 125.7 (0.4)	137.4 ± 94.1 (0.9)	61.6 ± 58.2 (0.4)
ΣREE										

n: number of samples for biomes; median ± standard deviation (enrichment ratio in brackets); ¹source: Kabata-Pendias (2011); LREE – Light Rare Earth Elements (La - Eu); HREE – Heavy Rare Earth Elements (Gd - Lu) + Y; A: anthropic areas and R: reference areas.

Table 6. Enrichment ratio of Rare Earth Elements (REE) content in Brazilian biomes for benchmark topsoils.

	Amazon Rainforest	Caatinga	Cerrado	Atlantic Forest	Pantanal
Y	1.6	0.5	1.6	2.5	2.4
La	1.8	0.9	2.6	1.7	2.2
Ce	1.4	0.9	3.0	2.3	2.1
Pr	2.0	0.7	2.5	2.2	2.3
Nd	2.5	0.7	2.4	2.7	2.3
Sm	3.0	0.6	2.4	2.3	2.5
Eu	1.4	0.4	1.7	2.0	2.1
Gd	2.6	0.6	2.2	2.4	2.7
Tb	2.7	0.3	1.0	1.0	1.0
Dy	2.1	0.5	2.1	2.3	2.6
Ho	3.6	0.3	1.2	1.0	1.0
Er	1.3	0.4	1.8	2.6	3.6
Tm	6.0	0.8	1.0	1.0	1.0
Yb	1.1	0.3	1.8	2.0	3.2
Lu	5.1	0.9	1.0	1.0	1.0
LREE	1.8	0.8	2.7	2.2	2.2
HREE	1.8	0.5	1.7	2.2	2.4
Σ REE	1.8	0.7	2.5	2.2	2.2

Enrichment ratio = agricultural/reference areas.

Table 7. Correlation coefficients (r) between Rare Earth Elements (REE) and benchmark soil chemical and physical properties ($p < 0.05$).

	Sand	Silt	Clay	pH	OC	CEC	Ca ²⁺ + Mg ²⁺	K ⁺
Y	-0.20*	0.24*	0.01 ^{n.s}	0.25*	0.12 ^{n.s}	0.31*	0.42*	0.44*
La	-0.19*	0.17*	-0.03 ^{n.s}	0.19*	0.18*	0.31*	0.30*	0.39*
Ce	-0.36*	0.21*	0.21*	-0.07 ^{n.s}	0.18*	0.21*	0.06 ^{n.s}	0.17*
Pr	-0.22*	0.19*	0.01 ^{n.s}	0.20*	0.18*	0.30*	0.30*	0.39*
Nd	-0.22*	0.18*	0.03 ^{n.s}	0.22*	0.17*	0.30*	0.31*	0.40*
Sm	-0.23*	0.21*	0.05 ^{n.s}	0.19*	0.16*	0.29*	0.30*	0.37*
Eu	-0.19*	0.11 ^{n.s}	0.04 ^{n.s}	0.22*	0.16*	0.27*	0.30*	0.33*
Gd	-0.20*	0.18*	0.02 ^{n.s}	0.24*	0.14 ^{n.s}	0.28*	0.34*	0.40*
Tb	-0.10 ^{n.s}	0.02 ^{n.s}	0.02 ^{n.s}	0.12 ^{n.s}	0.08 ^{n.s}	0.06 ^{n.s}	0.05 ^{n.s}	0.17*
Dy	-0.23*	0.21*	0.04 ^{n.s}	0.21*	0.16*	0.32*	0.37*	0.40*
Ho	-0.04 ^{n.s}	0.13 ^{n.s}	0.08 ^{n.s}	0.16*	-0.23*	-0.13 ^{n.s}	0.11 ^{n.s}	0.22*
Er	-0.21*	0.17*	0.05 ^{n.s}	0.21*	0.14 ^{n.s}	0.30*	0.38*	0.39*
Tm	-0.26*	0.16*	0.18*	0.05	0.11 ^{n.s}	0.22*	0.16*	0.19*
Yb	-0.20*	0.14 ^{n.s}	0.07 ^{n.s}	0.19*	0.12 ^{n.s}	0.27*	0.38*	0.35*
Lu	-0.29*	0.15 ^{n.s}	0.21*	0.06 ^{n.s}	0.14 ^{n.s}	0.27*	0.24*	0.17*
LREE	-0.28*	0.19*	0.09 ^{n.s}	0.16*	0.19*	0.30*	0.27*	0.38*
HREE	-0.21*	0.23*	0.02 ^{n.s}	0.23*	0.13 ^{n.s}	0.30*	0.39*	0.42*
REE	-0.28*	0.20*	0.09 ^{n.s}	0.17*	0.18*	0.31*	0.30*	0.39*
CEC	-0.54*	0.15 ^{n.s}	0.17*	-0.09 ^{n.s}	0.81*	1.00*	0.50*	0.44*

* Significant at 0.05; n.s.: not significant.

APPENDIX A: Total contents of the Rare Earth Elements in Brazilian biomes.

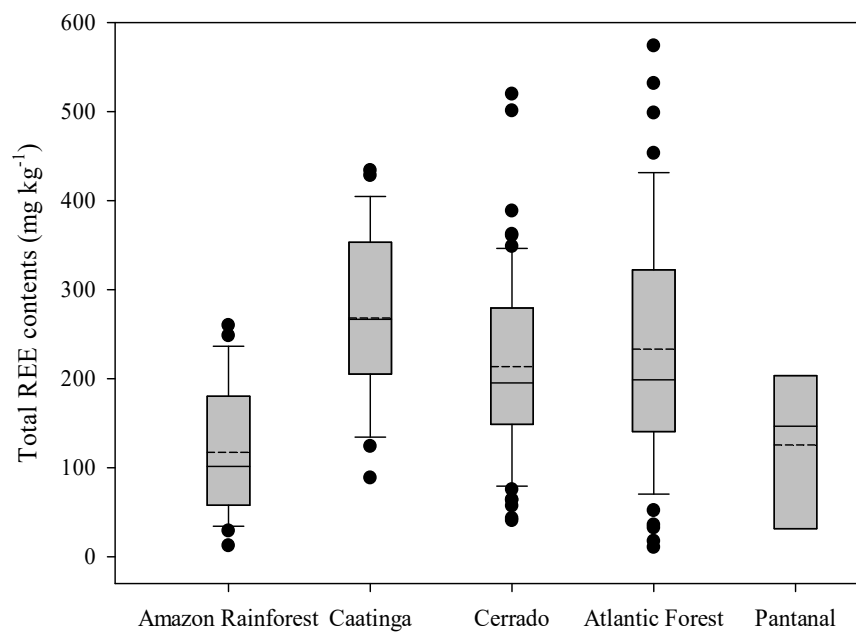


Figure 1A. Box plot showing total contents of the Rare Earth Elements (REE) in benchmark soils of Brazilian biomes (mean values: dotted lines, median: black lines).

APPENDIX B: Comparison of methods of extracting Rare Earth Element contents.

Table 1A. Comparison of methods of extracting Rare Earth Element contents in benchmark soils of Brazilian biomes.

	USEPA 3051A		Multi-acid digestion	
	Mean	Median	Mean	Median
mg kg ⁻¹			
Sc	-	-	12.7	11.1
Y	13.1	7.6	20.2	19.1
La	30.2	22.5	37.6	33.5
Ce	46.6	42.3	84.9	73.8
Pr	5.9	4.3	8.1	6.5
Nd	38.9	28.5	30.7	26
Sm	3.6	2.9	5.7	4.8
Eu	0.9	0.7	1.2	1.0
Gd	2.6	2.2	5.3	4.6
Tb	0.5	0.4	0.8	0.7
Dy	3.02	2.3	4.5	4.1
Ho	0.3	0.2	0.8	0.7
Er	0.9	0.8	2.4	2.2
Tm	0.1	0.08	0.3	0.3
Yb	1.1	0.8	2.4	2.3
Lu	0.1	0.07	0.4	0.3
LREE	101.2	126	168.2	145.7
HREE	14.5	21.7	37.1	34.4
ΣREE	115.7	147.8	218	191.3

USEPA 3051A (n = 175 samples) and HF-HNO₃-HClO₄ acid digestion (n = 176 samples).

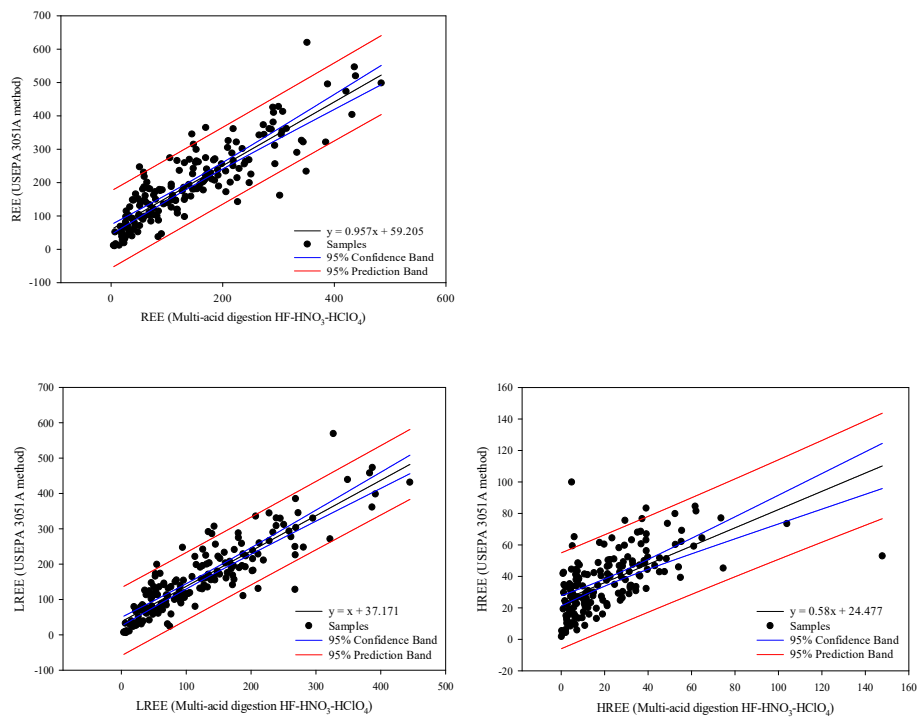
APPENDIX C: Linear regression of the extracting methods.

Figure 2A. Linear regression of the extracting methods (USEPA 3051A and HF-HNO₃-HClO₄ acid digestion).

APPENDIX D: Pearson's correlations between Rare Earth Element contents and soil attributes.

Table 2A. Pearson's correlations between Rare Earth Elements (REEs) contents and soil attributes from Brazilian soils ($n = 176$ samples, $p < 0.05$).

	Clay	CEC	OC	Ca ²⁺ + Mg ²⁺	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	K ₂ O	MnO
Sc	0.81**	0.37**	0.45**	0.11 ^{n.s}	0.35**	0.76**	0.72**	-0.12 ^{n.s}	0.36**
Y	0.34**	0.15 ^{n.s}	0.16 ^{n.s}	0.09 ^{n.s}	0.11 ^{n.s}	0.29**	0.26**	0.33**	0.16 ^{n.s}
La	0.31**	0.19**	0.02 ^{n.s}	0.19**	0.05 ^{n.s}	0.32**	0.26**	0.51**	0.16**
Ce	0.39**	0.16**	0.06 ^{n.s}	0.13 ^{n.s}	0.11 ^{n.s}	0.45**	0.39**	0.41**	0.16**
Pr	0.32**	0.20**	0.01 ^{n.s}	0.20**	0.06 ^{n.s}	0.35**	0.29**	0.50**	0.19**
Nd	0.33**	0.20**	0.02 ^{n.s}	0.22**	0.06 ^{n.s}	0.39**	0.30**	0.51**	0.25**
Sm	0.33**	0.22**	0.03 ^{n.s}	0.24**	0.06 ^{n.s}	0.37**	0.28**	0.53**	0.28**
Eu	0.45**	0.29**	0.11 ^{n.s}	0.28**	0.11 ^{n.s}	0.50**	0.36**	0.45**	0.40**
Gd	0.38**	0.25**	0.08 ^{n.s}	0.25**	0.06 ^{n.s}	0.42**	0.34**	0.46**	0.29**
Tb	0.43**	0.28**	0.15 ^{n.s}	0.24**	0.09 ^{n.s}	0.44**	0.38**	0.43**	0.30**
Dy	0.47**	0.30**	0.19**	0.23**	0.11 ^{n.s}	0.45**	0.40**	0.39**	0.28**
Ho	0.48**	0.32**	0.23**	0.22**	0.10 ^{n.s}	0.42**	0.41**	0.33**	0.28**
Er	0.48**	0.32**	0.25**	0.19**	0.10 ^{n.s}	0.38**	0.40**	0.28**	0.25**
Tm	0.44**	0.30**	0.24**	0.17**	0.07 ^{n.s}	0.33**	0.38**	0.23**	0.20**
Yb	0.43**	0.27**	0.25**	0.13 ^{n.s}	0.07 ^{n.s}	0.29**	0.36**	0.20**	0.16**
Lu	0.38**	0.24**	0.22**	0.10 ^{n.s}	0.03 ^{n.s}	0.23**	0.32**	0.18**	0.13 ^{n.s}
LREE	0.38**	0.18**	0.04 ^{n.s}	0.17**	0.08 ^{n.s}	0.43**	0.36**	0.47**	0.19**
HREE	0.44**	0.29**	0.19**	0.23**	0.09 ^{n.s}	0.39**	0.36**	0.40**	0.27**
ΣREE	0.47**	0.23**	0.12 ^{n.s}	0.18**	0.14 ^{n.s}	0.50**	0.41**	0.44**	0.25**

** Significant at 0.05; n.s.: not significant

ARTIGO 2 - Soil geochemical screening contents for Brazil using total reflection X-ray fluorescence spectrometry

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**Soil geochemical screening contents for Brazil using total reflection
X-ray fluorescence spectrometry**

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Abstract

A comprehensive overview of major and trace elements distribution in Brazilian soils is necessary for better knowledge of background concentrations in natural compartments. This information in soils of Brazilian biomes is still scarce and there is a need for studies concerning geochemical composition to assist in regulations and evaluation of contamination by anthropogenic sources. This work aimed to evaluate

background concentration of major and trace elements and their relationship with soil physical-chemical attributes in representative soils of major Brazilian biomes (Amazon Rainforest, Caatinga, Cerrado, and Atlantic Forest). For this purpose, benchmark soils were sampled at 37 locations in native or minimally disturbed areas. Total reflection X-ray fluorescence spectrometry (TXRF) was used to quantify total major and trace elements in all soil samples, following a rigid QA/QC protocol. Principal component analysis was used to identify which elements/soil attributes were better correlated among the different biomes studied. The TXRF technique was able to provide accurate data for total soil contents. The highest natural contents of major and trace elements was found in the Caatinga soils, since there were less depleted under semi-arid climate influence (less weathered-leached). On the other hand, the Amazon Rainforest, Cerrado, and Atlantic forest soils were more depleted. Soil attributes did not help in grouping biomes, which may reflect the diversity of parent materials and climates in pedoenvironments.

Keywords: benchmark soil, soil attributes, Brazilian biomes, analytical geochemistry.

Highlights

- Major and trace elements distribution in Brazilian biomes were assessed with TXRF

- Total major and trace elements contents from native areas were determined
- Background concentration for soils of major Brazilian biomes are obtained

1. Introduction

Knowledge of the geochemical composition in natural compartments is essential for environmental risk assessment, soil contamination studies, and human health protection. Thus, screening contents information of benchmark soils serves to provide basis for environmental regulations and policies. However, there is common wide variability in the natural contents of major and trace elements in soils, mainly influenced by soil formation factors (Hao et al., 2014; Jenny, 1941; Reimann et al., 2015, 2009).

The Brazilian territory is covered by a wide range of climates (Alvares et al., 2013), parent materials (acid and basic igneous rocks, metamorphic rocks, sedimentary rocks and unconsolidated sediments) (de Alkmim, 2015), as well as topography or landforms (Vieira et al., 2015), creating on a great diversity of environments. Given this great

environmental diversity, the Brazilian territory was divided, for a number of practical and legal purposes, into six continental biomes: Amazon Rainforest, Caatinga, Cerrado, Atlantic Forest, Pantanal, and Pampa (IBGE, 2015). In general, tropical/subtropical regions typically present higher nutrient depletion (Price, 1995; Richter and Babbar, 1991; Schucknecht et al., 2012), influencing the formation of highly weathered soils, and consequently influencing the dynamics of major and trace elements. For this reason, the soil geochemical data variability was verified in different biomes (Licht et al., 2006; Marques et al., 2004a; Matschullat et al., 2012; Reimann et al., 2009; Schucknecht et al., 2012) requiring a better understanding of the background concentration.

Several studies have reported incipient understanding about the distribution and behavior of major and trace elements in tropical soils (Campos et al., 2003; Davies, 1997; de Alcântara and de Camargo, 2004; Herpin et al., 2002; Marques et al., 2004a, 2004b; Reeves, 2003; Rieuwerts, 2007). In this context, the TXRF technique has been very promising when dealing with environmental studies (Dhara and Misra, 2011; Herpin et al., 2002; Marguí et al., 2010; Pierangeli et al., 2015; Stosnach, 2005; Towett et al., 2015, 2013), mainly focused on soil contamination and pollution.

Therefore, this technique is used to perform a quick and simultaneous determination of several elements in many matrices (Knoth et al., 1989; Pierangeli et al., 2015; Stosnach, 2005), eliminating the generation of pollutants to the environment, since acid digestion is not required. Thus, the present study is pioneer in the determination of background concentrations in benchmark soils of Brazilian biomes, encompassing spatial distribution and climatic conditions.

In the present study, we aimed to: i) investigate and analyze the soil geochemical screening contents using total reflection X-ray fluorescence spectrometry in benchmark soil samples collected in native areas of the main Brazilian biomes; ii) determine the background concentrations for soils in Brazil; and, iii) explore the natural variation of soil properties and relationship with composition elemental in different biomes in surface and subsurface samples.

2. Materials and methods

2.1. Soil databank

Benchmark soil samples were collected from surface samples (0 to 0.2 m) of topsoil (hereafter called TOP), and subsurface samples (0.3 to 0.5

m) of bottom soil layers (hereafter called BOT) of 37 pristine areas. These samples were selected from a database provided by the Brazilian Agricultural Research Corporation (Soil Science Division/Embrapa Solos), seeking the representativeness of different biomes. The following Brazilian biomes were studied: Amazon Rainforest (equatorial rainforest), Caatinga (white forest), Cerrado (neotropical savanna), and Atlantic Forest (tropical forest). The Pantanal (wetland) and Pampa biome were excluded due to the limited number of representative samples.

The Amazon Rainforest is an extensive equatorial rainforest with higher rainfall and temperatures rates combined with high water availability (Arruda et al., 2017; Schaefer et al., 2017) and intense soil weathering-leaching (Price, 1995; Schucknecht et al., 2012). The Caatinga is characterized by a dry season and a pronounced water deficit (dry semi-arid climate), as well as low rainfall and high temperatures rates throughout the year (Arruda et al., 2017). The Cerrado is located in the central region of Brazil with high rainfall rates, presenting two well-defined seasons (dry and rainy with short periods of drought) and high temperature rates (IBGE, 2015). Finally, the Atlantic Forest is a tropical forest stretching along almost the entire Brazilian coast, and represents the highest rainfall rate and

biogeochemical cycling of nutrients among the studied biomes (Matschullat et al., 2012; Rossatto et al., 2015).

Such biomes contain a wide variety of soils classes composed by Ferralsols (22.1%), Cambisols (16.7%), Acrisols (13.9%), Podzols (13.9%), Plinthosols (11%), Gleysols (5.6%), Fluvisols, Leptosols, Arenosols and Regosols (5.6%), Nitisols (2.8%), Histosols (2.8%), Planosols (2.8%), and Vertisols (2.8%), classified according to WRB/FAO (IUSS Working Group WRB, 2014).

2.2. Analytical methods

Soil samples (fraction < 2 mm) were previously air-dried, ground and sieved in a 0.05 mm nylon mesh sieve, and subsequently prepared in soil suspension as a thin film on a quartz disk using the obtained 10 μ L aliquot from the solution. The solution was prepared using 0.5 g of soil sample mixed with 2.5 mL of Triton X-100 as a dispersing agent (5% volume). As an internal standard 0.5 mL of a gallium solution (Ga: 1,000 mg kg⁻¹) was used and added to the quartz disk.

The accuracy of the measurements was verified by using three international reference materials (2709 San Joaquin Soil, 2710 Montana I

Soil, highly elevated trace element concentrations, and 2711 Montana II Soil, moderately elevated trace element concentrations), certified by the National Institute of Standards and Technology (NIST, 2002). The CRMs were prepared in triplicate following a rigorous QA/QC protocol and adding blank samples (control) in the analytical procedures. Interpretation of the spectra and data were performed using the software Spectra 6.3, and each sample was read in duplicate after a 60-fold dilution. Technical specifications and the measurement parameters of the apparatus are shown in **Table 1**.

Table 1. Technical specification of the TXRF Picofox.

Instrument	S2 Picofox TM High Efficiency
X-ray tube	0.602 mA, Mo Anode
Element range	Na to U
Optics	Multilayer monochromator, 17.5 keV
Detector	Silicon drift detector (SDD)
Carrier	Quartz, 30 mm diameter
Control	PC, data transfer via serial interface
Power	17.5 kV
Voltage	20 kV
Manufacturer	Bruker GmbH – Germany

Total contents of major (Al, Fe, Ti, Ca, K, P, and Mn) and trace (V, Cr, Ni, Cu, Zn, As, Rb, Sr, Ba, Hf, and U) elements were determined by

Total Reflection X-Ray Fluorescence Spectroscopy (TXRF S2 Picofox™ High Efficiency), according to a procedure proposed by Towett et al. (2013), with modifications.

The pipette method was used for particle size analysis (Day, 1965). Soil samples were air-dried and passed through a sieve with a 2 mm mesh. Briefly, the sand fraction was firstly separated using a 0.05-mm sieve. Silt and clay fractions were separated after the silt sedimentation, by pipetting a volume of the solution containing only the clay fraction, followed by oven-drying the solution and weighting the remaining clay fraction. The values of silt were obtained by subtracting the weights of sand and clay fractions from the total weight of the soil.

In order to characterize the biomes and better understand soil properties that might influence major and trace elements contents, soil chemical analyses were carried out following standard procedures for Brazilian soils (Teixeira et al., 2017). Soil pH was determined in water using a soil:solution ratio of 1:2.5 after shaking and 1-hour rest. Organic Carbon (OC) was obtained by wet oxidation with K-dichromate in sulfuric acid medium. The contents of exchangeable Al^{3+} , Ca^{2+} , and Mg^{2+} were extracted with a 1 mol L^{-1} KCl solution and determined by atomic

absorption spectrometer. Available K^+ was extracted by a Mehlich-1 solution ($0.0125 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.05 \text{ mol L}^{-1} \text{ HCl}$) being determined by flame photometer. Cation exchange capacity (CEC), base saturation (V), and Al saturation (m) were calculated from aforementioned results.

2.3. Statistical analysis

In this study, the analytical results were submitted to descriptive statistical analysis and median values were used to analyze the data, since it is the measure of the central tendency and has been recognized as suitable for analyzing geochemical results (Reimann et al., 2012). Thus, background concentrations were calculated based on median values of the major and trace element contents.

Major elements contents were compared with the values reported in the Upper Continental Crust (UCC) (Rudnick and Gao, 2014), and European Geochemical Mapping of Agricultural Soils (GEMAS) project (Reimann and de Caritat, 2012). Similarly, trace elements contents were compared to those reported by the World Soil Average (WSA) (Kabata-Pendias, 2011), Upper continental crust (UCC) (Rudnick and Gao, 2014), and other studies conducted in Brazil (Cetesb, 2016; Kronberg et al., 1979;

Licht et al., 2006; Marques et al., 2004a, 2004b; Matschullat et al., 2012; Melo et al., 2017; Paye et al., 2010; Souza et al., 2018).

A principal component analysis (PCA) was applied to the entire data for TOP and BOT horizons separately. The PCA was a biplot of sites and variables performed in order to better understand the relationship among soil physical-chemical attributes from different biomes, and identify possible groups of variables with similar patterns of distribution. The data was first scaled, and then the PCA was performed using the function `princomp` and the graphic was plotted using the package `ggbiplot` in the software R 3.4.4 (R development core team, 2018).

3. Results and discussion

3.1. Analytical quality control

The quality control of the elements analyzed is presented in **Table 2**. Although several chemical elements were analyzed by the TXRF, we chose to report only those elements that presented satisfactory accuracy according to Towett et al. (2013). The limit of detection (DL, in mg kg^{-1}) was calculated as: Al_2O_3 (12.5), Fe_2O_3 (0.05), Ti_2O (0.14), CaO (0.19), K_2O (0.23), P_2O_5 (3.6), MnO (0.06), V (0.08), Cr (0.06), Ni (0.02), Cu (0.02),

Zn (0.02), As (0.01), Rb (0.01), Sr (0.01), Ba (0.17), Hf (0.02), and U (0.02).

The recovery rates reported for the CRMs varied from 20 to 116% for the NIST 2709 San Joaquin Soil, from 14 to 97% for the NIST 2710 Montana I Soil, and from 14 to 120% for the NIST 2711 Montana II Soil for all the elements quantified, with most of them presenting satisfactory results according to the range recommended by the USEPA (1996). A correction factor (1.86) was used to represent the total Al_2O_3 contents in soils due to the low recovery rates obtained (14 to 20%) for this element.

Some technical limitations were found in the analytical procedure, such as the difficulty in quantifying elements at low concentrations (close to the limit of detection) and at high concentrations, due to overlaps when two X-ray photons reach the detector of the apparatus at the same time. Thus, there were interferences in the lines among the elements Na, La, Nd, W and, Bi and for Zr due to the use of Mo tubes in the X-ray equipment (Towett et al., 2013). In addition, Si was not determined due to the use of quartz disk sample carriers.

Table 2. Analytical quality control parameters using certified reference materials.

Certified.....		Obtained.....		Recovery.....		
	2709 San Joaquin Soil	2710 Montana I Soil	2711 Montana II Soil	2709 San Joaquin Soil	2710 Montana I Soil	2711 Montana II Soil	2709	2710	2711
weight %.....					%.....		
Al	7.37 ± 0.16	5.95 ± 0.05	6.72 ± 0.06	1.44 ± 0.14	0.85 ± 0.06	0.94 ± 0.36	20	14	14
Fe	3.36 ± 0.07	4.32 ± 0.08	2.82 ± 0.04	2.57 ± 0.16	2.84 ± 0.26	2.49 ± 0.13	76	66	88
Ti	0.336 ± 0.07	0.311 ± 0.007	0.317 ± 0.01	0.20 ± 0.02	0.14 ± 0.02	0.22 ± 0.02	60	45	69
Ca	1.91 ± 0.09	0.964 ± 0.045	2.42 ± 0.06	1.36 ± 0.06	0.35 ± 0.04	1.58 ± 0.12	71	36	65
K	2.11 ± 0.06	2.17 ± 0.13	2.53 ± 0.10	0.79 ± 0.07	0.90 ± 0.10	1.34 ± 0.13	37	41	53
P	0.069 ± 0.001	0.105 ± 0.004	0.084 ± 0.001	0.08 ± 0.02	0.02 ± 0.01	0.05 ± 0.01	116	19	55
Mn	0.053 ± 0.002	0.214 ± 0.006	0.067 ± 0.002	0.05 ± 0.01	0.16 ± 0.01	0.06 ± 0.01	95	75	95
mg kg ⁻¹								
V	110 ± 11	*82 ± 9	80.7 ± 5.7	96.8 ± 22.6	32.3 ± 5.4	55.5 ± 2.6	88	39	69
Cr	130 ± 9	*23 ± 6	52.3 ± 2.9	79.5 ± 10	22.3 ± 6.3	51.9 ± 2.5	61	97	99
Ni	*85 ± 2	n.d.	21.7 ± 0.7	56.6 ± 2.6	n.d.	16.6 ± 0.6	67	n.d.	76
Cu	*33.9 ± 0.5	3420 ± 50	140 ± 2	24.8 ± 2.9	3000 ± 128	139 ± 18	73	88	99
Zn	*103 ± 4	4180 ± 150	414 ± 11	101 ± 3.2	3020 ± 136	498 ± 73	98	72	120
As	*10.5 ± 0.3	1540 ± 100	107 ± 5	6.2 ± 2.4	1312 ± 98	103 ± 1.7	59	85	97
Rb	*99 ± 3	*117 ± 3	*120 ± 3	55.2 ± 5.1	68.4 ± 10	118 ± 7.8	56	58	98
Sr	239 ± 6	255 ± 7	242 ± 10	124.4 ± 3.7	100 ± 17	165 ± 25	52	39	68
Ba	979 ± 28	792 ± 36	730 ± 15	616.9 ± 7.1	429 ± 37.5	628 ± 72	63	54	86

Certified: CRM values; obtained: mean values; recovery (%) = (obtained/certified values).100; n.d.: no data; * reference values.

3.2. Chemical and physical soil properties in Brazilian biomes

Table 3 shows the fundamental physicochemical characterization of soils sampled from each Brazilian biome, in order to better characterize the biomes studied, considering native areas only.

Table 3. Chemical and physical (median \pm standard deviation) soil attributes in topsoil (TOP) and bottom (BOT) of native areas from Brazilian biomes.

Soil attribute	Hor.	Amazon Rainforest (n = 11)	Caatinga (n = 5)	Cerrado (n = 9)	Atlantic Forest (n = 12)
Sand (g kg ⁻¹)	TOP	620 \pm 295	346 \pm 253	449 \pm 232	572 \pm 340
	BOT	515 \pm 312	438 \pm 215	435 \pm 252	490 \pm 288
Silt (g kg ⁻¹)	TOP	179 \pm 198	258 \pm 70	172 \pm 151	105 \pm 119
	BOT	77 \pm 192	172 \pm 54	162 \pm 143	164 \pm 103
Clay (g kg ⁻¹)	TOP	201 \pm 184	397 \pm 189	338 \pm 262	274 \pm 262
	BOT	282 \pm 215	365 \pm 167	324 \pm 260	344 \pm 280
OC (g kg ⁻¹)	TOP	9.9 \pm 16.6	15.1 \pm 1.6	15.0 \pm 55.2	13 \pm 10.5
	BOT	2.5 \pm 3.2	1.8 \pm 0.8	5.8 \pm 3.4	6.2 \pm 5.5
pH (soil/water)	TOP	4.7 \pm 0.7	6.5 \pm 0.3	5.0 \pm 0.8	5.0 \pm 0.9
	BOT	4.8 \pm 0.9	6.0 \pm 0.6	5.8 \pm 0.5	4.9 \pm 0.4
Al ³⁺ (cmol _c kg ⁻¹)	TOP	0.6 \pm 2.3	0.0 \pm 0.1	0.5 \pm 2.0	0.6 \pm 3.3
	BOT	0.4 \pm 3.1	0.0 \pm 0.1	0.2 \pm 0.4	0.9 \pm 3.1
Ca ²⁺ + Mg ²⁺ (cmol _c kg ⁻¹)	TOP	0.4 \pm 0.8	9.9 \pm 3.3	0.8 \pm 6.2	1.4 \pm 7.1
	BOT	0.1 \pm 0.6	6.2 \pm 1.8	0.7 \pm 5.0	0.4 \pm 13.6
K ⁺ (cmol _c kg ⁻¹)	TOP	0.1 \pm 0.1	0.3 \pm 0.1	0.1 \pm 0.2	0.1 \pm 0.2
	BOT	0.0 \pm 0.1	0.1 \pm 0.5	0.0 \pm 0.0	0.0 \pm 0.1
CEC (cmol _c kg ⁻¹)	TOP	3.9 \pm 7.6	13.6 \pm 4.0	12.5 \pm 18.6	6.9 \pm 9.0
	BOT	2.2 \pm 4.7	8.2 \pm 2.3	3.0 \pm 4.6	5.1 \pm 13.9
V (%)	TOP	10.0 \pm 20.5	80.5 \pm 4.8	12 \pm 31.9	24.0 \pm 31.7
	BOT	6.0 \pm 28.6	80.0 \pm 9.7	23 \pm 33.5	20.5 \pm 27.6
m (%)	TOP	67.0 \pm 26.5	0.0 \pm 0.0	40.0 \pm 32.4	27 \pm 32.7
	BOT	80.0 \pm 36.1	0.0 \pm 0.9	7.0 \pm 41.0	44 \pm 35.9

n: number of samples, median \pm standard deviation, particle size distribution (sand, silt and clay fraction), OC: organic carbon, pH: hydrogen-ion concentration in water, Al³⁺, Ca²⁺, Mg²⁺ and K⁺ exchangeable, CEC: cation exchange capacity, V: base saturation, and m: Al saturation.

Soil textures presented a wide variation among the biomes studied and were predominantly composed by the sand fraction in relation to clay and silt fractions in both horizons for all biomes, except in for the Caatinga. The TOP of the biome Caatinga presented the highest silt contents, which demonstrates a low development of soils (Araújo et al., 2018; Arruda et al., 2017; Gloaguen and Passe, 2017) than in other biomes where the soils are more weathered.

The Amazon Rainforest biome is located under tropical climate, where soils were developed under higher temperature and rainfall rates, leading to the formation of highly weathered, dystrophic, and well-drained soils as can be noticed by the higher values of sand and low silt contents (Arruda et al., 2017; Schaefer et al., 2017). Such climatic conditions are considered one of the most severe in the world for weathering (Arafa et al., 2015; Minuzzi et al., 2008; Souza et al., 2018; Wang et al., 2017), with a great capacity to promote loss of mobile soil elements (Mendonça et al., 2014; Schaefer et al., 2017) and high organic carbon decomposition rates (Fernandes et al., 2018; Schaefer et al., 2008). Therefore, the lowest pH values, CEC, OC, base saturation, basic cations (Ca^{2+} , Mg^{2+} and K^{+}) were observed under these circumstances.

The Caatinga biome has soil for less weathered, due to lower rainfall, that can be as low as half of the potential evapotranspiration (Araújo Filho et al., 2017; Arruda et al., 2017), preventing elements from leaching. These conditions are reflected on higher base saturation (eutrophic) and CEC, moderately alkaline soils (pH around 6.0 to 6.5) and low Al saturation. Thus, it is evident that the high silt contents had a relevant contribution in the soil geochemical inheritance of the Caatinga biome, as mentioned before.

The Cerrado biome is an intensely weathered environment as reflected on the variable texture (from sandy to clayey with low silt contents) of the soils sampled. These conditions led to the leaching of basic cations (Ca^{2+} , Mg^{2+} , and K^{+}) and to the formation of dystrophic soils, rich in exchangeable Al^{3+} , low CEC, and predominance of low-activity clays. When basic cations are removed from negative sites, they are first replaced by H^{+} , which makes the soils more acidic, but later, acid Al-compounds replace the H^{+} ions.

The soils sampled from the Atlantic Forest biome expressed the climate in which they were developed promoting weathering (Coelho et al., 2017). Thus, the soils presented low silt content, high acidity, low CEC,

and base saturation. The soil attributes show that the Caatinga biome present less developed soils and lower depletion of elements during the weathering as compared to the biomes Amazon Rainforest, Cerrado, and Atlantic Forest, where these processes are more intense in the long-term.

3.3. Background concentrations in Brazilian biomes

Respectively, **Tables 4** and **5** show background concentrations of the major elements (oxides: Al, Fe, Ti, Ca, K, P, and Mn) and trace elements (V, Cr, Ni, Cu, Zn, As, Rb, Sr, Ba, Hf, and U) in each biome. There is a great variability in the analytical data, which was reflected by the high standard deviations, as verified in other geochemical studies in Brazilian soils (Fernandes et al., 2018; Licht et al., 2006; Marques et al., 2004a; Matschullat et al., 2012; Reimann et al., 2009; Schucknecht et al., 2012).

3.3.1 Major elements

Major element contents were expressed as a percentage of the weight of oxides, because most minerals present in different soils of the Brazilian biomes are silicates. The background concentrations obtained for

the major elements in the present study were generally lower than those reported for the Amazon Rainforest (Souza et al., 2018), Cerrado (Marques et al., 2004b) and the Atlantic Forest (Kronberg et al., 1979; Licht et al., 2006), in all horizons. On the other hand, the Caatinga biome presented the highest background concentrations and higher values than those observed by Matschullat et al. (2012). For all Brazilian biomes studied, the natural background concentrations were less than those reported by UCC (Rudnick and Gao, 2014) and GEMAS (Reimann and de Caritat, 2012).

The highest background concentrations of oxides observed in the Caatinga biome may be due to the water deficit in the northeastern region of Brazil (Arruda et al., 2017). In fact, the high background concentrations of CaO, K₂O, and MnO were observed because the potential evaporation often reach twice the values of the rainfall, making this environment less chemically depleted, conserving the bases (Araújo Filho et al., 2017).

Table 4. Background concentrations (median \pm standard deviation) of major elements in topsoil (TOP) and bottom (BOT) of the Brazilian biomes.

		Amazon Rainforest (n = 11)	Caatinga (n = 5)	Cerrado (n = 9)	Atlantic Forest (n = 12)	AR ¹	CA ²	CE ³	AF ⁴	AF ⁵	UCC ⁶	GEMAS ⁷
.....weight %.....												
Al ₂ O ₃	TOP	4.4 \pm 4.1	4.3 \pm 1.3	6.5 \pm 7.1	4.2 \pm 2.6	15.6	9.49	23.45	23.03	16.6	15.4	10.5
	BOT	4.9 \pm 4.6	4.2 \pm 1.9	6.7 \pm 5.9	6.3 \pm 4.6							
Fe ₂ O ₃	TOP	1.7 \pm 2.5	5.4 \pm 1.8	3.0 \pm 4.4	2.7 \pm 3.0	5.31	2.09	9.52	16.87	6.94	5.6	3.6
	BOT	2.5 \pm 2.4	4.8 \pm 0.9	2.8 \pm 4.8	4.9 \pm 3.5							
TiO ₂	TOP	0.4 \pm 0.3	0.8 \pm 0.3	0.7 \pm 0.7	0.5 \pm 0.3	1.00	0.55	2.17	2.77	0.73	0.64	0.62
	BOT	0.8 \pm 0.5	0.7 \pm 0.1	0.6 \pm 0.3	0.6 \pm 0.3							
CaO	TOP	0.03 \pm 0.03	0.3 \pm 0.1	0.02 \pm 0.2	0.02 \pm 0.1	0.06	0.03	0.03	0.12	0.26	3.59	1.2
	BOT	0.03 \pm 0.02	0.2 \pm 0.04	0.01 \pm 0.1	0.02 \pm 0.2							
K ₂ O	TOP	0.03 \pm 0.5	0.5 \pm 0.6	0.05 \pm 0.7	0.1 \pm 0.5	0.81	0.16	0.04	0.22	0.11	2.8	1.9
	BOT	0.02 \pm 0.4	0.4 \pm 0.2	0.03 \pm 0.5	0.1 \pm 0.4							
P ₂ O ₅	TOP	0.03 \pm 0.02	0.09 \pm 0.03	0.04 \pm 0.03	0.04 \pm 0.03	0.05	0.02	0.05	0.13	0.10	0.15	0.18
	BOT	0.02 \pm 0.02	0.03 \pm 0.03	0.03 \pm 0.02	0.04 \pm 0.02							
MnO	TOP	0.01 \pm 0.10	0.1 \pm 0.08	0.01 \pm 0.10	0.01 \pm 0.10	0.02	0.01	0.06	0.07	0.10	0.1	0.08
	BOT	0.01 \pm 0.10	0.04 \pm 0.04	0.02 \pm 0.10	0.01 \pm 0.10							

n: number reference areas; median values will be considered as background concentrations this study; ¹ AR = Amazon Rainforest, topsoil (median) (Souza et al., 2018; n = 62); ² CA = Caatinga, A and B–transect bottom soil (median) (Matschullat et al., 2012; n = 101); ³ CE = Cerrado (Marques et al., 2004a; n = 90); ⁴ AF = Atlantic Forest, B-horizon soils (median) (Licht et al., 2006; n = 307); ⁵ AF = Atlantic Forest (Bahia state) (Kronberg et al., 1979; n = 17); ⁶ UCC = Upper continental crust (Rudnick and Gao, 2014); ⁷ GEMAS = European Geochemical Mapping of Agricultural Soils (Reimann and de Caritat., 2012, Ap = 0-20 cm, n = 2211).

The highest Al oxides contents and low cations (Ca^{2+} , Mn^{2+} , and K^+) verified in the Cerrado biome indicate higher weathering conditions (Rieuwerts, 2007). As a result, the soils tend to present low fertility: low values of Ca^{2+} , Mg^{2+} , K^+ , and CEC, being dystrophic and rich in Al oxides contents. Similarly, Marques et al. (2004a) observed in the Brazilian Cerrado that the acidic conditions of the soil are related to the depletion of mobile elements.

Generally, major elements are mobilized during intense weathering conditions in soils from tropical/subtropical climate regions (Braun et al., 2005; Cornu et al., 1999; Rieuwerts, 2007), exactly to what we may expect for the Amazon Rainforest, Cerrado, and Atlantic Forest biomes. The intense weathering conditions are evidenced in the soils sampled by the acid condition and low base saturation (dystrophic), which allowed the increase of mobility and subsequent loss of Al, Fe, Ca, K, P, and Mn by weathering. Souza et al. (2018) and Fernandes et al. (2018) observed that soils from the Amazon Rainforest are chemically poor mainly because of the tropical climatic conditions having caused an intense weathering and therefore the nutrients biogeochemical cycling could not replace the elements lost by leaching at the same rate and speed.

3.3.2 Trace elements

Comparing the trace element contents obtained in this study with others performed in several Brazilian regions (Souza et al., 2018; Matschullat et al., 2012; Marques et al., 2004a; Melo et al., 2017; Paye et al., 2010), most of the values obtained from the soils of the Amazon Rainforest biome were lower than those reported by Souza et al. (2018) and Fernandes et al. (2018). However, the background concentration obtained for the Caatinga biome were higher than the values reported by Matschullat et al. (2012). Besides, comparing our data with those reported in Marques et al. (2004a), lower contents were observed in the Cerrado biome. Finally, the values for the Atlantic Forest biome were similar to the values reported by Cetesb (2016), Melo et al. (2017) and Paye et al. (2010). In this sense, the Caatinga tends to present the highest natural contents for trace elements followed in descending order by the Cerrado, Atlantic Forest and Amazon Rainforest (**Table 5**).

Table 5. Background concentration (median \pm standard deviation) of trace elements in topsoil (TOP) and bottom (BOT) of the Brazilian biomes.

	Amazon Rainforest (n = 11)	Caatinga (n = 5)	Cerrado (n = 9)	Atlantic Forest (n = 12)	AR ¹	CA ²	CE ³	AF ⁴	AF ⁵	AF ⁶	UCC	WSA
 mg kg ⁻¹											
V	7.4 \pm 43	46.3 \pm 29	46.2 \pm 90	16.7 \pm 63	130	49	257	275	60.2	-	97	129
	14.9 \pm 49	45.5 \pm 9	39.6 \pm 106	30.4 \pm 46								
Cr	12.1 \pm 62	72.9 \pm 41	55 \pm 575	43.3 \pm 47	141	40	112	40	48.7	-	92	59.2
	20.7 \pm 52	62.4 \pm 7	72.4 \pm 758	51.1 \pm 55								
Ni	2.8 \pm 6	31.2 \pm 14	11.1 \pm 122	7.6 \pm 18	19.6	-	14	13	17.2	54.1	47	29
	2.8 \pm 7	22.6 \pm 7	11 \pm 151	8.1 \pm 21								
Cu	5.3 \pm 11	40.4 \pm 13	15.9 \pm 53	8.1 \pm 29	-	13	33	35	17.8	9.2	28	38.9
	6.3 \pm 12	20.1 \pm 7	15.4 \pm 60	13.9 \pm 51								
Zn	27.2 \pm 15	84.2 \pm 31	41.6 \pm 18	37 \pm 27	103	11	38	60	52.5	5.9	67	70
	29.5 \pm 20	62.9 \pm 13	35.8 \pm 19	41.1 \pm 18								
As	0.1 \pm 3	18.8 \pm 12	1.4 \pm 9	1.6 \pm 9	-	-	-	3.5	4.78	29.8	4.8	6.8
	1.0 \pm 3	9.6 \pm 9	1.2 \pm 5	4.1 \pm 8								
Rb	7.4 \pm 27	112 \pm 61	18.7 \pm 46	16.6 \pm 100	-	16	14	-	-	-	84	68
	11.7 \pm 30	62.4 \pm 25	12.7 \pm 42	29 \pm 64								
Sr	3.8 \pm 18	9.0 \pm 18	10.8 \pm 16	9.8 \pm 20	83.0	25.5	9	-	-	-	320	175
	7.4 \pm 18	6.4 \pm 8	8.9 \pm 24	11 \pm 17								
Ba	28.7 \pm 356	216 \pm 267	122 \pm 272	73.2 \pm 151	-	67.5	67	75	111.4	-	628	460

	46.8 ± 282	174 ± 90	16.9 ± 242	97.2 ± 144									
Hf	6.4 ± 4.6	0.6 ± 2	3.0 ± 7	3.5 ± 6	-	-	-	-	-	-	5.3	6.4	
	3.8 ± 32	3.5 ± 2	5.7 ± 6	0.01 ± 4									
U	0.01 ± 1.5	0.01 ± 1	1.7 ± 6	0 ± 1	-	-	3	-	-	-	2.7	3	
	1.9 ± 11	2.1 ± 2	1.8 ± 3	0.01 ± 18									

n: number reference areas, median values will be considered as background concentration this study; note: - data not valuated; ¹ AR = Amazon Rainforest, topsoil (median) (Souza et al., 2018; n = 62); ² CA = Caatinga, A and B–transect bottom soil (median) (Matschullat et al., 2012; n = 101); ³ CE = Cerrado, arithmetic mean (Marques et al., 2004b; n = 90); ⁴ AF = Atlantic Forest (São Paulo state) (Cetesb, 2016); ⁵ AF = Atlantic Forest (Paraná state) (Melo et al., 2017; n = 63); ⁶ AF = Atlantic Forest (Espírito Santo state) (Paye et al., 2010; n = 56); ⁷ UCC = Upper Continental Crust (Rudnick and Gao, 2014); ⁸ WSA = World Soil Average (Kabata-Pendias, 2011).

The acidic conditions, low CEC, and OC content verified in the Amazon Rainforest, Cerrado, and Atlantic Forest biomes soils favored the high mobility and availability of trace elements (Fernandes et al., 2018; Rieuwerts, 2007; Yao et al., 2014). Thus, the high mobility of elements was caused by the fast organic matter decomposition and low CEC of soil, which prevents the adsorption/retention of trace elements (Marques et al., 2004a; Paye et al., 2010; Rieuwerts, 2007), especially in the most representative soils of the Cerrado biome (Ferralsols and Acrisols) and Atlantic Forest. In the same way, replacement of trace elements in acidic soils by the H^+ present in the solution occurred, leaving them in solution and allowing their mobility/removal by leaching (Kabata-Pendias, 2011).

A wide variation in the results was noticed when comparing to other studies in the literature because of the difference in the methods used to obtain the data (Alfaro et al., 2015; Fadigas et al., 2006; Melo et al., 2017; Paye et al., 2010). In the Atlantic Forest biome, this variation particularly may be due to the wide territorial coverage, high environmental variability, and parent material diversity such as those verified elsewhere (Arruda et al., 2017; Melo et al., 2017; Paye et al., 2010).

In summary, the major and trace elements distribution in the Amazon Rainforest, Caatinga, Cerrado, and Atlantic Forest biomes was mainly influenced by the parent material, which through pedogenetic and weathering-leaching processes altered the soil geochemical composition in the long-term. Through the comparison among the biomes, we can observe a great variation in the natural geochemical concentrations of major and trace elements in soils, which is related to the geological characteristics of the parent material, soil physical-chemical attributes and climates (Fernandes et al., 2018; Gloaguen and Passe, 2017; Hao et al., 2014; Melo et al., 2017; Nogueira et al., 2018; Schucknecht et al., 2012).

3.4. Principal component analysis

The principal component analyses (PCA) of physical-chemical attributes, major and trace elements are presented in **Figures 1** (TOP) and **2** (BOT). Therefore, PCA described satisfactorily the variance, with 32% of the total variance explained by PC1 and 17.2% by the PC2 (total of 49.2% of the variance explained by the model). As can be observed by the groups formed by the ellipse drawn into PCA, there was not a soil attribute that helped to aggregate the sites, since there is a wide variation of attribute

within the biomes (**Fig. 1**), probably influenced by the variation of soil formation factors.

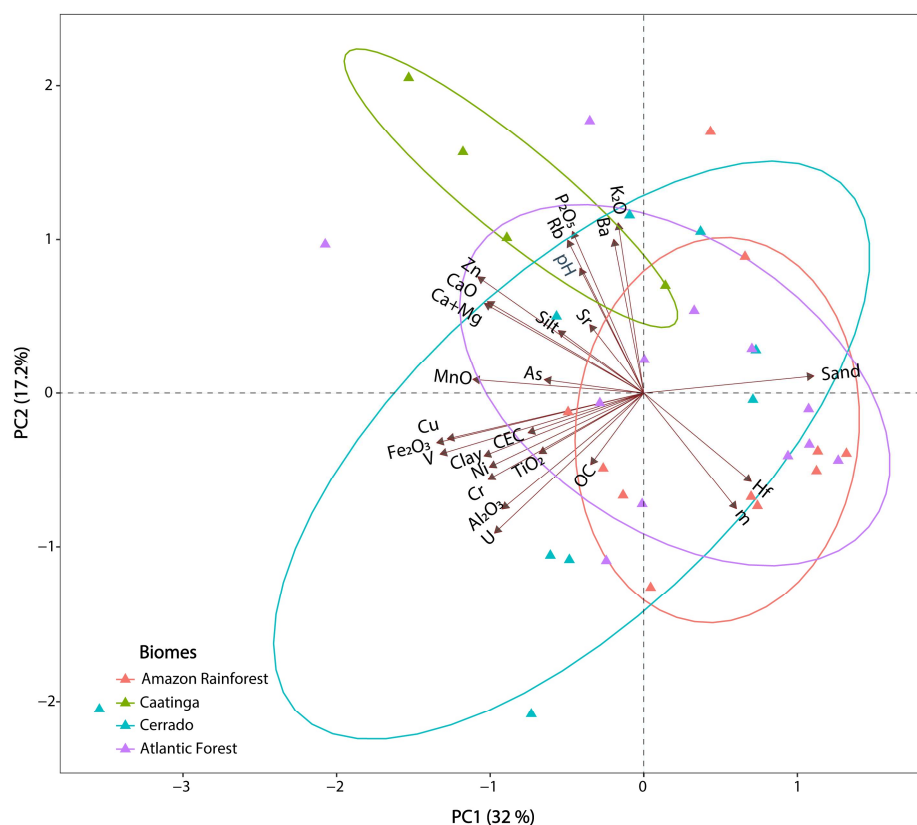


Fig. 1. Principal Component Analysis (PCA) of data for soil physical-chemical attributes in Brazilian biomes for topsoil samples.

CEC, OC, and clay were positively correlated with Al_2O_3 , Fe_2O_3 , TiO_2 , and trace elements (V, Cr, Cu, Ni and U) contents mainly for the soil samples from the Cerrado biome. This clearly reflects the composition of

the clay fraction in Cerrado soils, which is mostly composed by Al, Fe and Ti oxides (Fontes and Weed, 1991; Towett et al., 2015). Also, the OC have a strong influence in the CEC of the soil allowing the retention of these mentioned trace elements (Silveira et al., 2006).

On the other hand, pH and silt were positively correlated with oxides (CaO, K₂O, P₂O₅), and the cations Ca²⁺ + Mg²⁺, Ba, Rb, Zn. These attributes are relatively higher in soils of the Caatinga biome, as can be observed by the position of the sites and the group formed with the ellipse in the second quadrant of the PCA (**Fig. 1**). Since there are more basic cations in such soils, they are more alkaline, reflecting the low development of the soil as discussed previously. Another feature that evidently shows the low level of weathering is the high silt content in the topsoil.

The soil attribute with more contribution for PC1 was sand, and although there is not a well defined grouping for the biomes when considering this attribute, the Amazon Rainforest and Atlantic Forest biomes tend to present higher values (**Table 3**). Sand content was negatively correlated with CEC, clay, and most oxides (Al₂O₃, Fe₂O₃, TiO₂, and MnO). For all the other variables, there was no meaningful correlation. The lack of relationship between sand and the other trace elements might

be related to the composition of the sand fraction, which is comprised mostly by quartz (Burak et al., 2010). When soils have high sand content, the effect of any other soil attribute will be diluted.

For PC2, the variables with highest contribution were P_2O_5 , K_2O , Ba, and Zn, given the bigger size of the arrows in the second quadrant. On the other hand, pH and silt are soil attributes with a weak contribution to explain the data variance.

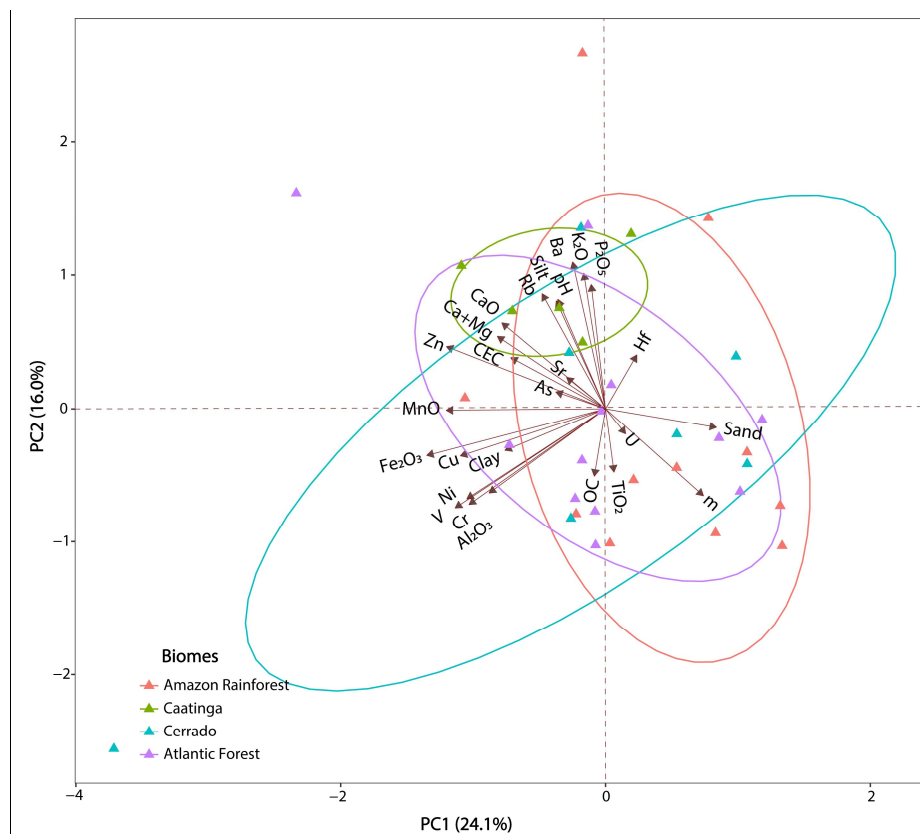


Fig. 2. Principal Component Analysis (PCA) of data for soil physical-chemical attributes in Brazilian biomes for samples of bottom soil layers.

The model performed for samples of bottom soil layers included two principal components that accounted for 40.1% of the total variance explained (24.1% for PC1 and 16% for PC2) (**Fig. 2**). The first (PC1) component is negatively dominated by all the soil attributes except sand, TiO_2 , Hf, U and m, whose greatest contribution was given by m (Al saturation) and sand. On the other hand, in the PC2 there are more attributes contributing positively, which are dominated by K_2O , P_2O_5 , and Ba, and negatively dominated by V, Cr, Ni and Al_2O_3 .

Similarly to what was observed for topsoil samples in **Fig. 1**, there was a positive correlation among the attributes pH, silt, Ba, Rb, K_2O , and P_2O_5 and a negative correlation between CEC and sand. So in terms of soil fertility, the biome Caatinga is more closely grouped in the second quadrant of the PCA, which is related to the fertility attributes.

In the third quadrant we can observe a relationship quite similar to the associations in the topsoil (**Fig. 1**), where we see the positive correlation among clay, Fe_2O_3 and Al_2O_3 . The close association among clay, Fe_2O_3 and Al_2O_3 means that when there are sites with higher values of clay, we

can infer that the composition of this material is predominantly Al and Fe oxides.

Comparing the PCA of TOP and BOT, it is possible to notice that the variables are more grouped in the bottom. PCA of BOT presented lower variability in terms of sites and variables studied than in the TOP, because the topsoil is more affected by biochemical factors in the soil and, therefore, presents more interaction with living organisms and the atmosphere.

4. Conclusions

The analytical results showed that the TXRF technique could be used as a reliable and fast quantification tool for the diagnosis of the total contents of the major and trace elements in soils.

The Caatinga biome presented the highest background concentrations for major and trace elements. On the other hand, Amazon Rainforest, Cerrado, Atlantic Forest biomes presented lowest values due removal of elements from soils.

The diversity of soil forming factors and pedogenetic process led to a heterogeneous geochemical composition of the soils, which

probably explain the fact that biomes were not well grouped, except for the Caatinga.

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The authors declare that they have no conflict of interest.

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