Geoderma 395 (2021) 115072

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Micronutrient availability in amazonian dark earths and adjacent soils

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ARTICLE INFO

Handling Editor: Ingrid Kögel-Knabner

Keywords:
Anthropic activity
ADE
Trace elements
Fertility
Terra Preta

ABSTRACT

Amazonian Dark Earths (ADEs) are highly fertile soils in areas with predominance of unfertile soils. However, the variation in nutrient availability between regions and the resilience of ADEs to modern agricultural use is still little known, particularly regarding micronutrient contents. Hence, the present study synthesized current information of ADE impacts on extractable micronutrient (Cu, Ni, Fe, Mn, Zn, B) contents at different soil depths and assessed in detail the role of both soil depth and land-use type on extractable Cu, Ni, Fe, Mn and Zn in nine ADEs and adjacent (ADJ) soils from different Amazonian regions. The land-use systems chosen were secondary old (OF) or young (YF) forests, and agricultural systems (AS) in Iranduba, Belterra and Porto Velho. Only eight studies compared extractable (Mehlich-1) micronutrient contents at 21 sites with ADEs and ADJ soils, but only four studies included depths greater than 30 cm, and B and Ni were evaluated in only one study. Higher Mn and Zn, but lower Fe contents were found in ADEs both from literature data and in the present study, especially in the first 30 cm depth. Increases in extractable Ni and Cu in ADEs varied according to the site and the land use considered. Micronutrient contents tended to decrease with depth, but varied depending on the element, site, soil type and land use. Sites with modern agriculture showed few differences in extractable micronutrient contents, except for a decrease in Fe in Belterra and Mn in Porto Velho. Considering the high amounts of some micro- and macronutrients in ADEs further work is warranted concerning soil management and nutrient balance in plants grown on these soils.

1. Introduction

The Amazon rainforest is the largest tropical rainforest in the world, being also an important source of biodiversity (Hoorn et al., 2010). In Brazil, the Amazon region covers around 5.1 million km^2, more than 60% of Brazil's territory (Fisch et al., 1998). The soils predominantly

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https://doi.org/10.1016/j.geoderma.2021.115072
Received 27 August 2020; Received in revised form 1 March 2021; Accepted 2 March 2021
Available online 30 March 2021
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found in the Brazilian Amazon upland areas ("*terra-firme*") are Acrisols, Ferralsols and Plinthosols (FAO classification), mostly with low natural fertility, so that nutrient cycling is the main factor responsible for the natural maintenance of soil fertility in the forests of this region (Moline and Coutinho, 2015; Moreira and Fageria, 2009; Vale Júnior et al., 2011). Deforestation and adoption of intensive agricultural land uses interrupt this process, quickly depleting nutrient reserves (Moline and Coutinho, 2015; Moreira and Fageria, 2009).

Slash-and-burn practices employed in Amazonia throughout millennia temporarily improve soil fertility, increasing nutrient availability over the short term (Moreira and Fageria, 2009; Moline and Coutinho, 2015). After some years, improper agricultural practices (e.g., low nutrient input and absence of soil conservation practices) reduce soil productivity and nutrient stock in these soils (Magalhães et al., 2013; Michelon et al., 2019). However, humans have been living in and cultivating Amazon rainforest soils for thousands of years, and in some cases, even creating anthropic soil horizons, such as the Amazonian Dark Earths (ADEs), also known in Brazil as the "*Terra Preta de Índio*" (Schmidt, 2013; Shepard et al., 2020). These soil horizons were formed on the main soil classes of the Amazon, and display high nutrients contents and a dark-colored surface horizon ranging between 10 and 200 cm in depth (Heckenberger et al., 2007; Falcão et al., 2009; Arroyo-Kalin, 2012; Glaser and Birk, 2012; Carson et al., 2014; Lins, 2015; Royo, 2015; Viana et al., 2016). The high soil fertility found in ADEs is due to the high nutrient contents, particularly of some macro- (Phosphorus, Calcium and Magnesium) and micro-nutrients (Manganese, Copper and Zinc), originating from the deposition, decomposition, and burning of plant and animal residues by pre-Columbian Amerindians (Kern and Kämpf, 1989; Moreira et al., 2009; Falcão et al., 2009; Silva et al., 2011; Schmidt et al., 2014; Royo, 2015). ADEs are frequently used for agricultural production due to their high nutrient contents (Glaser, 2007; Kawa and Oyuela-Caycedo, 2008), and many of the main characteristics of these soils are relatively well-known. However, the availability of micronutrients, elements essential for plant growth, and the effects of current agricultural use on micronutrient contents in these soils have been little studied.

Hence, the present study reviewed the differences in micronutrient (copper, iron, manganese, nickel, boron and zinc) contents in ADEs and adjacent (ADJ) soils in Amazonia using a meta-analysis, and evaluated in greater detail micronutrient (Cu, Fe, Ni, Zn, Mn) contents at various depths in different land-use systems (forests and agricultural systems) in ADEs and ADJ soils in three Amazonian regions. We hypothesized that ADEs have higher amounts of extractable micronutrients than ADJ soils, and that current agricultural use of ADEs would reduce micronutrient contents in these soils.

2. Material and methods

2.1. Field study sites

The field study was carried out in three Amazonian regions: Iranduba – AM, in Central Amazonia, Belterra – PA in the lower Amazon, and Porto Velho – RO in Southwestern Amazonia (Table 1). The main climates of the Brazilian Amazonian region, according to the Köppen classification, are tropical Am and Af, with an average annual temperature of 24 °C, and annual precipitation between 2000 and 2280 mm (Fisch et al., 1998; Quesada et al., 2010; Alvares et al., 2013). The formation of ADEs in Iranduba started between 950 and 1780 years ago (Neves et al., 2004; Macedo, 2014); in Belterra between 450 and 530 years (Maezumi et al., 2018), and in Porto Velho much earlier, approximately 6500 years ago (Watling et al., 2018).

Soil samples were collected in three land-use systems: secondary dense tropical moist broadleaf forest in intermediate/advanced (>20 years) regeneration stage defined as old forest (OF), or initial (<20 years) succession stage defined as young forest (YF), and agricultural systems (AS) with corn under conventional tillage in Iranduba, soybean under no-tillage in Belterra, and permanent pasture in Porto Velho (Table 1). Maize and soybean cropping began 4 and 8 years ago, respectively, and in both sites, lime was applied (before sowing), as well as inorganic (NPK) fertilizers and integrated pest management practices, according to recommendations for these regions (Demetrio, 2019). In Porto Velho, the Bahiagrass cv. Pensacola pasture (*Paspalum notatum*) on ADE was around 12 years old, while the *Urochloa* (*Brachiaria*) sp. pasture on ADJ soil was about 9 years old. Generally, ADEs and ADJ soils were very close to each other; distance ranged from a minimum of 150 m (soybean at Belterra) to a maximum of 1.3 km (pastures at Porto Velho).

2.2. Soil sampling, classification and chemical analysis

Soil samples (around 1–3 kg each) were collected within an area of approximately 1 ha of ADEs and ADJ soils within each municipality, at five depth intervals (0–10, 10–20, 20–30, 30–60 and 60–90 cm). Five samples per land use were collected until 30 cm depth, from soil monoliths 25 × 25 × 30 cm, dug for soil macrofauna sampling, following a standard method recommended by ISO (ISO, 2011). Samples from the 30–60 and 60–90 cm depths were collected using a Dutch auger at the bottom of the pit where each monolith was excavated. Soil sampling was done in April (Iranduba) and May (Belterra) of 2015 and in March of 2016 (Porto Velho). We obtained a total of 434 samples, since at some locations we were not able to sample the petro-plinthic horizons at certain depths.

Adjacent soils in Iranduba and Belterra were classified according to

Table 1
General information on the study sites (geographic coordinates, soil classification and current land use system).

County	State	Land use system	Acronyms	Soil	Soil classification	Coordinates
Iranduba	AM	Old forest	OF	ADJ	Xanthic Dystric Acrisol	3°14′49.00″S, 60°13′30.71″W
		Old forest		ADE	Pretic Clayic Anthrosol	3°15′11.05″S, 60°13′45.03″W
		Young forest	YF	ADJ	Xanthic Dystric Acrisol	3°13′34.47°S, 60°16′23.60″W
		Young forest		ADE	Pretic Clayic Anthrosol	3°13′49.23″S, 60°16′7.43″W
		Maize	AS	ADJ	Xanthic Dystric Acrisol	3°13′31.31″S, 60°16′29.18″W
		Maize		ADE	Pretic Clayic Anthrosol	3°13′46.13″S, 60°16′7.32″W
Belterra	PA	Old forest	OF	ADJ	Xanthic Dystric Ferralsol	2°47′4.59″S, 54°59′53.28″W
		Old forest		ADE	Pretic Clayic Anthrosol	2°47′3.25″S, 54°59′59.77″W
		Old forest	OF	ADJ	Xanthic Dystric Acrisol	2°41′13.90″S, 54°55′3.30″W
		Old forest		ADE	Pretic Clayic Anthrosol	2°41′7.18″S, 54°55′7.11″W
		Soybean	AS	ADJ	Xanthic Dystric Acrisol	2°41′3.56″S, 54°55′12.75″W
		Soybean		ADE	Pretic Clayic Anthrosol	2°41′3.79″S, 54°55′7.90″W
Porto Velho	RO	Young forest	YF	ADJ	Xanthic Dystric Plinthosol	8°52′11.50″S, 64°3′18.16″W
		Young forest		ADE	Pretic Clayic Anthrosol	8°51′51.92″S, 64°03′48.03″W
		Young forest	YF	ADJ	Xanthic Dystric Ferralsol	8°50′49.52″S, 64°3′59.20″W
		Young forest		ADE	Pretic Clayic Anthrosol	8°52′1.18″S, 64°4′3.07″W
		Pasture	AS	ADJ	Xanthic Dystric Ferralsol	8°52′35.30″S, 64°03′58.58″W
		Pasture		ADE	Pretic Clayic Anthrosol	8°51′56.53″S, 64°03′40.67″W

the FAO (IUSS WORKING GROUP/WRB, 2015) as Dystric Ferralsols and Acrisols, the two common-most soils in Amazonia (Gardi et al., 2015). In Porto Velho, both soils (ADE and ADJ) occurred over plinthic horizons, being the ADJ soil classified as Plinthosols. All ADEs were classified as Pretic Clayic Anthrosols (IUSS WORKING GROUP/WRB, 2015), with dark surface horizons and high content of organic matter and usually 20 cm or more in depth (Table 1). Soils in the Belterra and Iranduba region were formed over Cretacious deposits of the Alter-do-Chão Formation (sandstones, conglomerates and mudstones; Mendes et al., 2012), while at Porto Velho they were formed over the Porto Velho Depression area with a few granitic intrusions of the Mesoproterozoic Teotônio Intrusion (Herrera et al., 2016).

Large organic residues (e.g., leaves and roots) were removed from the soil samples which were subsequently oven-dried (45 °C), sieved at 2 mm and homogenized before chemical analyses. Micronutrients were extracted using the Mehlich-1 extractor according to standard Brazilian methods (Teixeira et al., 2017). This extractor was chosen since it has been used in various studies on soil fertility in Amazonia (especially for P and K extraction), and because it was shown to be the most efficient and recommended method for soil analysis in ADEs (Moreira et al., 2009). The contents of copper (Cu), nickel (Ni), manganese (Mn), zinc (Zn) and iron (Fe) in ADEs and ADJ soils were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) (VARIAN, 720-ES) after filtration of a solution of 10 g soil 100 ml $extractant^{-1}$. Further details on the soils of these sites, including basic routine chemical analysis results can be found in Segalla (2017) and Demetrio et al. (2019).

2.3. Data analysis

The data obtained from the chemical analysis were submitted to normality test (Shapiro-Wilk) and analysis of variance (ANOVA) considering the effects of soil type (ADE and ADJ) and the three land-use systems (OF, YF and AS) within each region (Iranduba, Belterra and Porto Velho). When we observed significant effects of ANOVA, means were further compared using Tukey tests ($p < 0.05$) with the software SISVAR 5.6 (Ferreira, 2014). Using the micronutrient data for each site and sample depth, we performed a principal component analysis (PCA) using the ADE-4 package (Dray and Dufour, 2007) in R software (R Core Team, 2015), to explore differences between sites and soil types, in terms of micronutrient contents.

2.4. Literature survey and micronutrient meta-analysis

Studies including peer-reviewed papers, dissertations and theses that evaluated extractable/exchangeable, pseudo-total, total and oxide micronutrient contents in ADEs and ADJ soils published between 1988 and 2020 were searched in online databases, including Science Direct, Web of Science, Google Scholar, Scielo, and the Brazilian Digital Library of Theses and Dissertations (Biblioteca Digital de Teses e Dissertação, BDTD). Extractable contents refer to those obtained with Mehlich-1 or resin, pseudo-total contents those including extraction using HNO_3 with or without HCl or H_2O_2, total contents any study involving HF with other extractors (Silva et al., 2014; Melo et al., 2016), and oxide contents those involving sodium dithionite-citrate-bicarbonate or X-ray fluorescence (semi-quantitative method). Besides the present study, we found 20 other studies that fitted our selection criteria for this review: i.e., the studies must have measured micronutrient contents in comparable depth increments and soil types in both ADEs and ADJ soils nearby or next to the ADE, and the values reported must have been greater than 0, in order to permit calculation of the "ADE-effect" (see below). However, only seven of these besides the current study reported extractable micronutrient contents measured with the standard extractor Mehlich-1 (Table 2), while the other 13 studies reported total, pseudo-total or "oxide" contents, or measured extractable micronutrients using different methods (Supplementary Table 1). Data extracted from these publications included four soil variables (horizon, sample depth, soil type and micronutrient concentrations), four biogeographic variables (vegetation cover/land use, location, county and state) and two methodological variables, i.e., micronutrients analyzed and extraction method. When the data was presented in figures, values were estimated manually.

For the meta-analysis the data on six extractable essential micronutrients, i.e., B, Cu, Fe, Mn, Ni and Zn were grouped according to depth, separated into three layers of approximately 0–30, 30–60 and >60 cm, in order to compare the literature data with that obtained in the present field study. Some studies did not evaluate all the micronutrients proposed, so there was variation in the number of observations for each.

To calculate the main ADE-effect on soil micronutrients, we used the following equations:

$$ADEResponseRatio(ln) = ln\left(\frac{ADE}{ADJ}\right) \quad (1)$$

$$ADEeffecttimes = 1 + (e^{ADEResponseRatio(ln)} \times 100 - 100)/100 \quad (2)$$

Table 2
Meta-data on the studies used for the meta-analysis of ADE effects on micronutrient availability in Amazonian soils. AS = agricultural system, F = forest (all broadleaf evergreen), AR = archaeological dig .

Reference	Sites (County, state)	Vegetation, Land use	Soil types (FAO equivalent)	Depth intervals evaluated (cm)	No. sites	No. comp.*	Micronutrients analyzed
Albuquerque (2017)	Santarém, PA	F	Ferralsols, Acrisols	0–10, 10–20, 20–30, 30–40, 40–50, 50–60, 60–70, 70–80, 80–90, 90–100 cm	1	10	Fe
Costa et al. (2009)	Caxiuanã, PA	AR	Plinthosols	Variable, depending on the soil profile layers	2	8	Mn, Zn
Macedo (2014)	Inraduba, AM	F	Acrisols	Variable, depending on the soil profile layers	1	5	Fe, Mn, Cu, Zn
Mendoza (2011)	Autaz Mirim, AM	F	Ferralsols	0–20, 20–40, 40–60, 60–80, 80–100 cm	3	15	Fe, Mn, Zn
Moline and Coutinho (2015)	Manacapuru, AM	AS, F	Ferralsols	0–20 cm	1	1	Fe, Mn, Cu, Zn, B
Ribeiro (2006)	Manaus, Rio Preto da Eva and Iranduba, AM	F	Ferralsols	0–10, 10–20, 20–30 cm	4	12	Fe, Mn, Cu, Zn
Silva (2006)	Iranduba, AM	AR	Ferralsols, Acrisols	0–20, 20–40 cm	3	6	Fe, Mn, Zn
This study	Iranduba, AM, Belterra, PA and Porto Velho, RO	AS, F	Acrisols, Ferralsols, Plinthosols	0–10, 10–20, 20–30, 30–60, 60–90 cm	9	45	Fe, Mn, Cu, Zn, Ni

*Number of comparisons between ADE vs. ADJ soils included in the dataset of Sátiro et al. (2021) per micronutrient evaluated (generally equal to the number of sites multiplied by the number of depth intervals evaluated). The total number of samples collected in the studies may have been larger, but only those that provided adequate comparisons (based on criteria described in Materials and Methods) were considered.

where: ADE effect is the effect of ADE on micronutrient contents in relation to ADJ soils, ADE is the extractable micronutrient content in ADEs (mg kg^{-1}) and ADJ is the extractable micronutrient content in ADJ soils (mg kg^{-1}). Equation (1) represents the ADE Response Ratio (i.e., the ratio of ADE to ADJ nutrient concentrations), and the values are reported in log normal. Equation (2) was used after calculating the mean ADE response ratio for each micronutrient, and represents the number of times the value in ADE is larger (positive values) or smaller (negative values) than in ADJ soils. When ADE effect (ln) values were negative, the numbers were transformed to positive (i.e, by multiplying by −1) before taking the exponent, and then after the calculation was completed, the result (ADE effect times) was transformed back into a negative value (by multiplying by −1 again).

All the data obtained from the 21 studies (including the present field study), including the sampling depth, land use system, soil type, different micronutrient extractors and forms (available/ extractable, total and pseudo-total, oxide) are available for download (Sátiro et al., 2021).

3. Results

3.1. Extractable Cu and Ni

At Iranduba, both secondary forests (i.e., OF and YF) under ADE showed higher Cu contents compared to the ADJ soils throughout most of the soil profile (Fig. 1A), and the highest absolute values were found in YF-ADE at greater depths (60 cm: 2.2 mg kg^{-1}; 90 cm: 2.4 mg kg^{-1}). In the AS, differences in Cu contents between ADE (higher) and ADJ (lower) were more pronounced below 30 cm, but only significant at the 30-60 cm depth. All three land-use systems showed trends of higher Ni contents in ADE than ADJ soils, but significant differences were observed only in the 30–60 cm layer (Fig. 1B) for all systems and the 20–30 cm layer in the maize crop on ADE.

At Belterra, the Cu contents in ADE were lower than at Iranduba, and there was only one significant difference between OF-ADJ (0.8 mg kg^{-1}) that had higher values than OF-ADE, in the 20–30 soil layer (Fig. 1C), opposite to what was observed at Iranduba. Ni contents were again

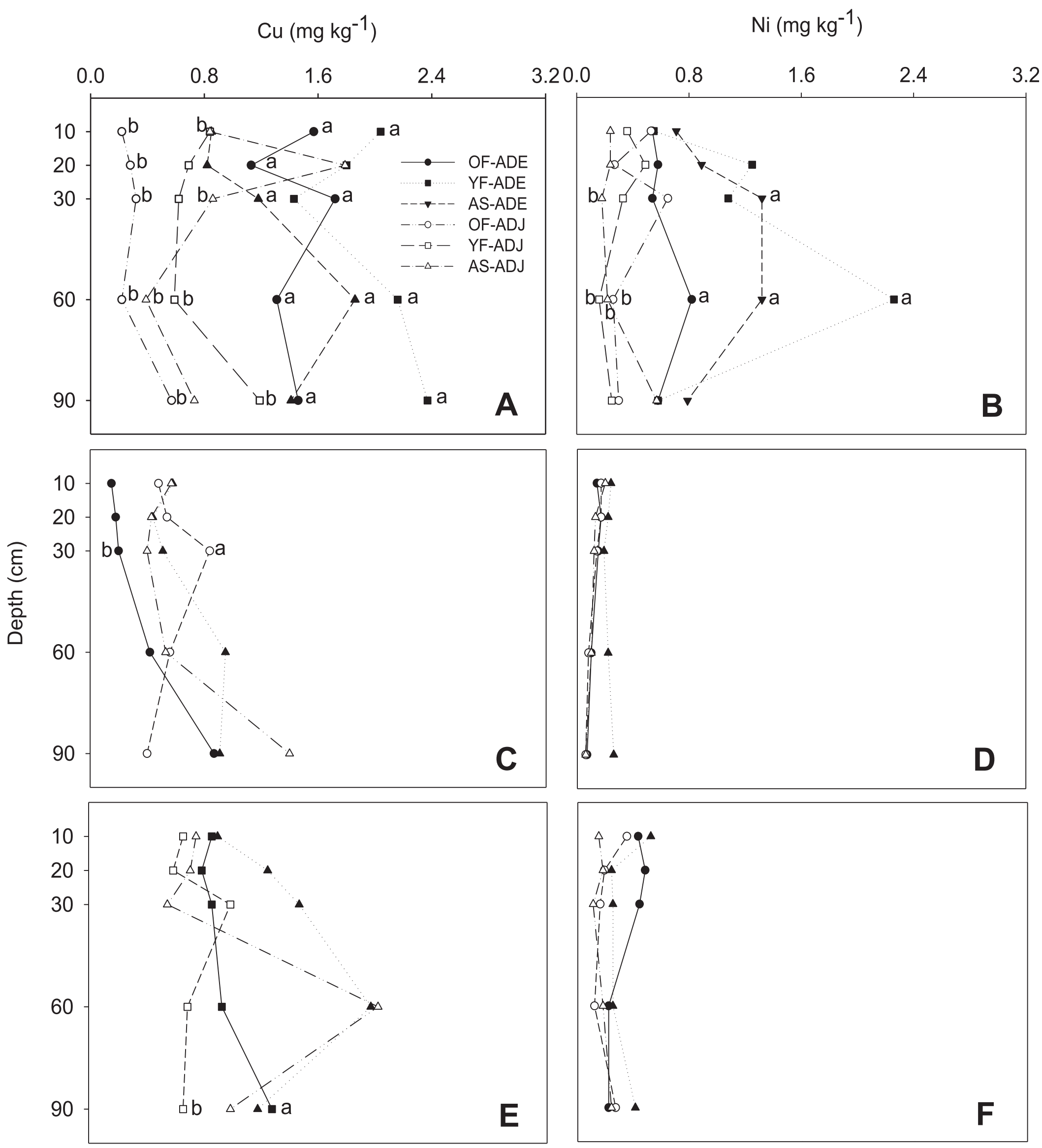

Fig. 1. Availability of Cu and Ni (mg kg^{-1}) in Amazonian Dark Earths (ADE) and adjacent soil (ADJ) in different land use systems in Iranduba, AM (A, B), Belterra, PA (C, D), and Porto Velho, RO (E, F). OF-ADE = old forest on ADE soil; YF-ADE = Young forest on ADE; AS = Agricultural system on ADE; OF-ADJ = old forest on ADJ soil; YF-ADJ = young forest on ADJ soil; AS-ADJ = agricultural system on ADJ. Different lower-case letters indicate significant differences between ADE and ADJ soils within each land use system.

lower than in Iranduba, showed little variation in the soil profile (contrary to Iranduba), and no significant differences were observed (Fig. 1D).

At Porto Velho, Cu contents were highly variable within the soil profile of the AS (and highest values were observed in the 30–60 cm layer), but less variable in the YF in both ADE and ADJ soils. Significant differences between ADEs and ADJ soils were only observed for YF-ADE, which had higher Cu contents than the YF-ADJ in the 60–90 cm soil layer (Fig. 1E). Although ADEs showed a tendency of higher Ni contents than ADJ soils, there was little variation along the soil profile, and no differences between soils or among land use systems were observed (Fig. 1F).

3.2. Extractable Mn and Zn contents

At Iranduba, both Zn and Mn contents were higher in ADEs in all land use systems compared to ADJ soils (Fig. 2A, B), but for Mn, they were significantly higher only in the top 30 cm layers, with no differences in deeper layers (Fig. 2A). For Zn, differences ADE and ADJ were observed throughout the soil profile, and were not significant only for the AS below 30 cm depth (Fig. 2B).

At Belterra, like in Iranduba, Mn contents were significantly higher in the OFs and the AS in ADEs than ADJ soils only in the top 30 cm layers (Fig. 2C). Soil Zn contents were significantly higher in ADEs compared to ADJ in both land use systems in the 0–10 cm layer (Fig. 2D), and in the AS, differences were significant at all depths evaluated.

At Porto Velho, Mn contents in ADEs were significantly higher than in ADJ soils up to 30 cm depth (Fig. 2E) in the AS, and up to 60 cm depth in the YF. The land-use system significantly affected Mn availability in ADEs, with higher values in forests than agroecosystems. On the other hand, Zn contents were not significantly affected by land use system and only YF-ADE had higher values than YF-ADJ in the 20–30 cm layer (Fig. 2F).

A sharp decrease in Mn contents with increasing depth was observed for ADEs at all sample sites, while in ADJ soils only minimal decreases in both Mn and Zn contents were observed. For Zn, decreases in contents with depth were much smaller than for Mn in ADEs.

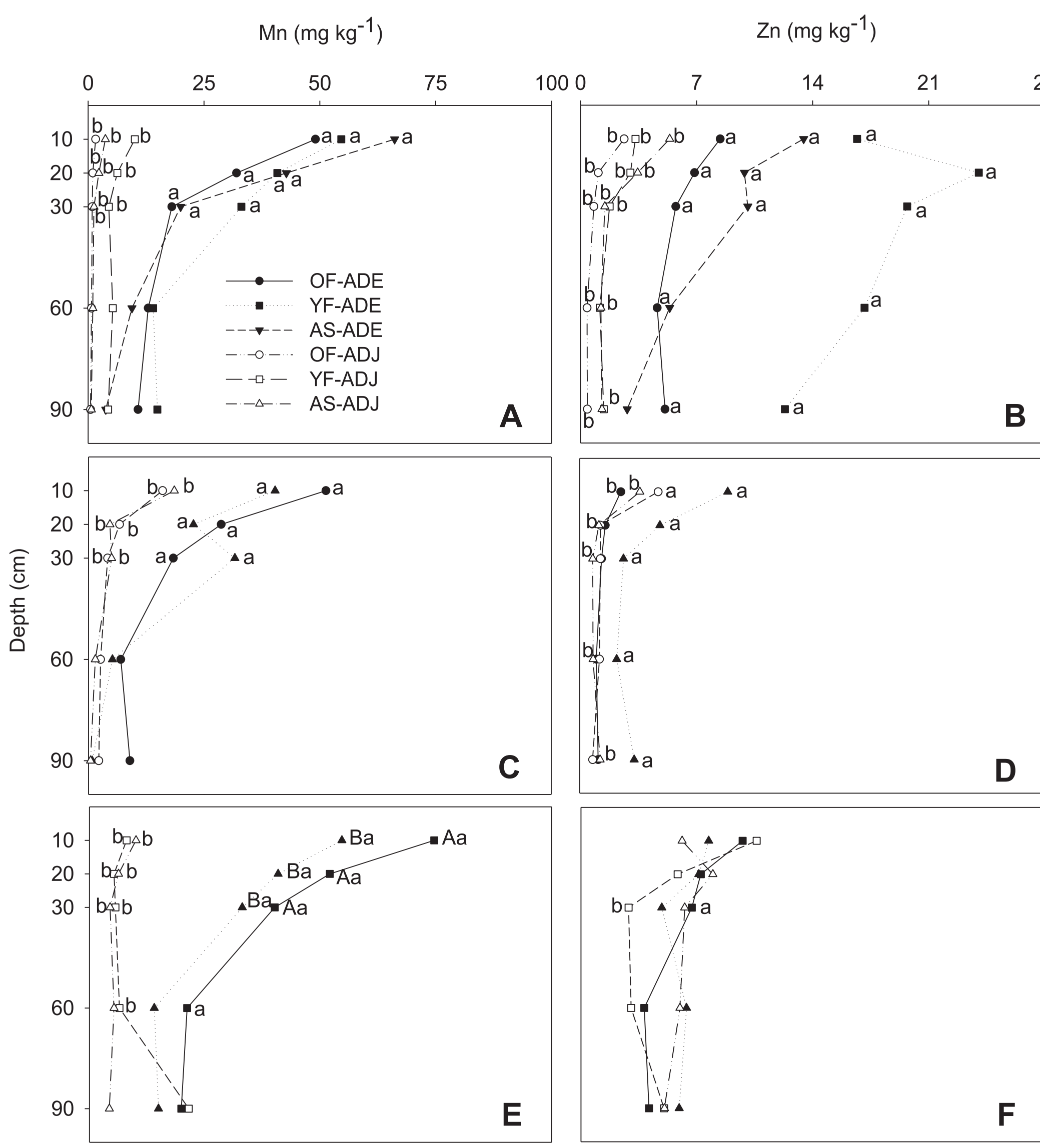

Fig. 2. Availability of Mn and Zn (mg kg^{-1}) in Amazonian Dark Earths (ADE) and adjacent soil (ADJ) in different land use systems in Iranduba, AM (A, B), Belterra, PA (C, D), and Porto Velho, RO (E, F). OF-ADE = old forest on ADE soil; YF-ADE = Young forest on ADE; AS = Agricultural system on ADE; OF-ADJ = old forest on ADJ soil; YF-ADJ = young forest on ADJ soil; AS-ADJ = agricultural system on ADJ. Different lower-case letters indicate significant differences between ADE and ADJ soils within each land use system, while different upper-case letter indicate significant differences between the land uses (OF, YF, ADJ) within each soil type.

3.3. Extractable Fe content

At Iranduba, all land use systems on ADJ soils had significantly higher Fe contents than ADEs (Fig. 3A), with a sharp decrease in availability below 30 cm depth, although differences were detected for all land use systems up to 30–60 cm depth and for both forest systems throughout the soil profile.

As in Iranduba, Fe contents at Belterra were higher in ADJ than ADE soils in both OF and AS, but significant differences were detected only in the top 30 cm depth in AS and up to 60 cm depth in OF (Fig. 3B). Furthermore, differences were observed between land-use systems, with higher Fe contents in OF than AS up to 60 cm depth in the ADEs, and throughout the soil profile in ADJ soils. Fe contents in the ADJ soils in Belterra tended to be lower than in Iranduba and Porto Velho (Fig. 3C), but with little change in depth.

Like at the other two sites, Fe contents in Porto Velho were significantly higher in ADJ soils than ADEs, but differences were observed in both YF and AS throughout the soil profile (Fig. 3C). A clear reduction of Fe contents with depth was observed in ADJ soils, particularly in YF, while a slight increase was seen in Fe availability over depth in YF on ADEs.

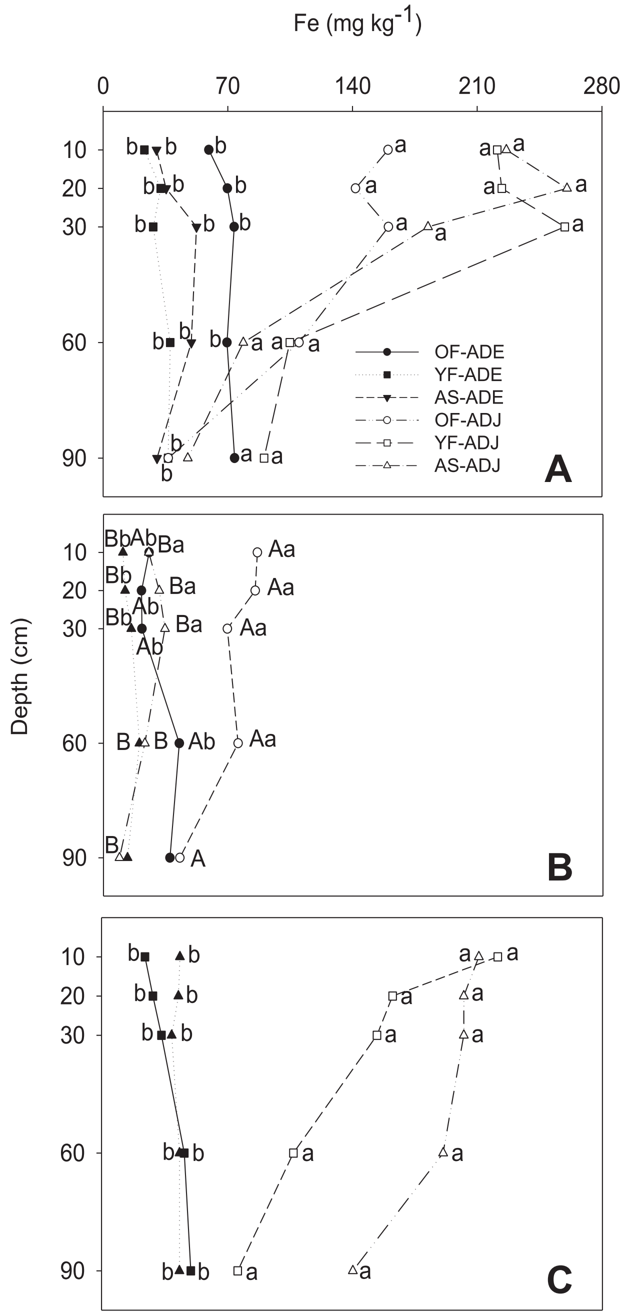

Fig. 3. Availability of Fe (mg kg^{-1}) in Amazonian Dark Earths (ADE) and adjacent soil (ADJ) in different land use systems in Iranduba, AM (A), Belterra, PA (B), and Porto Velho, RO (C). OF-ADE = old forest on ADE soil; YF-ADE = Young forest on ADE; AS = Agricultural system on ADE; OF-ADJ = old forest on ADJ soil; YF-ADJ = young forest on ADJ soil; AS-ADJ = agricultural system on ADJ. Different lower-case letters indicate significant differences between ADE and ADJ soils within each land use system, while different upper-case letter indicate significant differences between the land uses (OF, YF, ADJ) within each soil type.

3.4. Micronutrient contents overall in ADEs vs. ADJ soils: Principal component analysis

The first two axes of PCA analysis accounted for 64.3% of the total variance (Fig. 4). The first axis (PC1) separated the sites according to mainly Zn and Ni, but also Mn and Cu contents (Fig. 4A), while axis 2 (PC2), was correlated with Fe contents (Fig. 4B). The PCA separated the samples based on soil type, with ADJ soils related to extractable Fe, and ADEs mainly related to Mn and Zn contents. Separate PCA analyses for each region revealed similar trends overall, with ADJ soils mainly related to higher Fe contents (Supplementary Figs. 1–3).

3.5. Micronutrient meta-analysis

Of the seven other studies (besides the present one) that included extractable micronutrients, most measured them only in the top 0–30 cm layer, and only five of them included Mn, Fe and Zn, two of them Cu and one B (Table 2). The data from the literature survey (Fig. 5, black circles) showed enhanced extractable Mn, Zn and Cu contents in ADEs at all depths evaluated, but these were slightly higher for Zn and Cu in the 0–30 cm layer, compared to the results of the present study (red circles). Extractable Zn contents in ADEs were 5 times higher than those in ADJ soils in the literature review, but lower in the present study (+1.9 times), while increases in Mn contents were around 10 times higher in the present study and 6.5 times higher in the literature data, respectively (Fig. 5A, Supplementary Table 2).

In the 30–60 cm layer (Fig. 5B), few data were available, with only two studies (Mendoza, 2011; Macedo, 2014) to compare with the present one (see data in Sátiro et al., 2021). ADE effects in both the literature data and the present study were positive for Mn (2.5 and 5 times higher, respectively), as well as for Zn and Cu (around 2 times higher) in the literature and the present study. As in the intermediate soil depth, few results were available from the literature for depths > 60 cm (Fig. 5C), but contents of Mn, Zn and Cu showed positive effects of ADEs, that were very similar in both the literature and the present study (around 4 times higher for Mn, 3 times higher for Zn and 1.5 times higher for Cu).

Extractable Ni contents were evaluated only in the present study, and showed positive effects at all sampling depths (ranging from 1.9 times higher at 0–30 cm to 2.7 times higher at 30–60 cm) in ADEs compared with ADJ soils (Fig. 5; Supplementary Table 2). Only one study (Moline and Coutinho, 2009) evaluated extractable B in the topsoil horizon (0–20 cm), and there was only a minimal enhancement of its contents (1.2 times higher) in ADE than ADJ soil at the single study site (Manacapuru, AM).

Overall, for extractable Fe, ADE effects tended to be negative (Fig. 5), particularly in the top and intermediate soil layers (0–60 cm). Decreases in Fe contents at these depths ranged from a minimum of −1.5 times (literature data, 30–60 cm) to a maximum of −4.8 times (0–30 cm, present study) in ADEs compared with ADJ soils. Below 60 cm ADE effects were minimal and tended towards neutral (values close to 1.0, positive or negative).

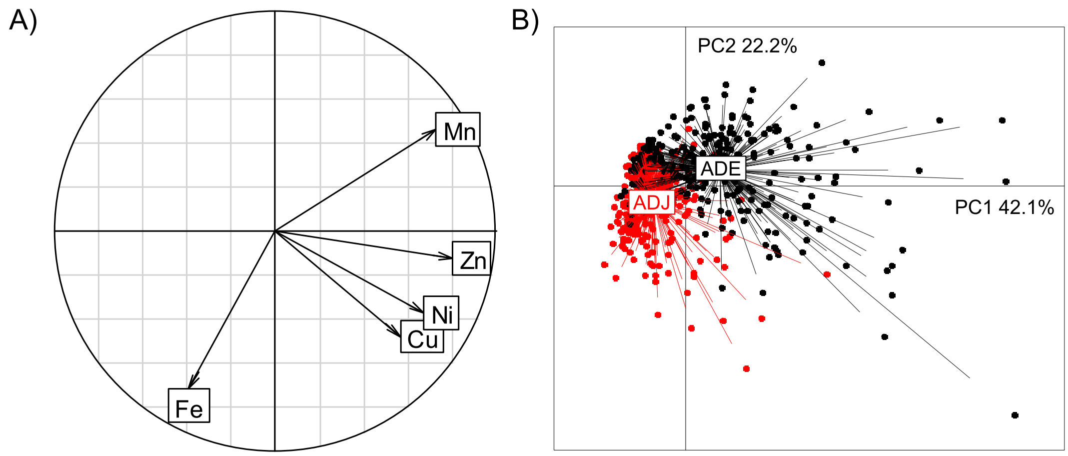

Fig. 4. Plot of first two axes of the Principle Component Analysis showing correlation circle of micronutrient concentrations (A) and distribution all of the sampling points (B) of ADE and ADJ soils, at all depth strata (0–10, 10–20, 20–30, 30–60 and 60–90 cm).

4. Discussion

4.1. ADE formation and micronutrient contents

Contrary to our hypothesis, micronutrient concentrations were not always higher in ADEs than ADJ soils, and depended on sampling depth, site and the nutrient in question. Since ADEs form from the top-down, available micronutrient contents in these soils are directly related to the amounts entering the soil, which is affected by both the duration and intensity of human occupation at each site and the nature and distribution of various agricultural and household practices of the Amerindian societies that created them (Schmidt, 2013; Kern et al., 2017). These phenomena can lead to very high variability both within and between ADEs, factors that pose important challenges to comprehending their formation and replicating their results (Schmidt, 2013; Kern et al., 2017; Alho et al., 2019). In this context, ADEs at Belterra had lower Mn, Zn, Cu and Ni contents than the other sites, which may be related to their younger age (between 450 and 530 years BP; Maezumi et al., 2018) compared to Iranduba (950 to 1780 years ago; Neves et al., 2004; Macedo, 2014) and Porto Velho ADEs (starting 6500 years BP; Watling et al., 2018). However, the overall time and intensity of occupation at each site is not fully known, and the Amazon basin was occupied by many different indigenous groups, and these processes were not uniform over time and space (Santos, 2018).

Extractable micronutrient contents in soils are also related to parent material types, and ADEs can form over many different kinds of soils, with different geological parent materials (Kern et al., 2017). These phenomena can also result in ADEs with different chemical characteristics, and different macro and micronutrient levels in different Amazonian regions (Smith, 1980; Eden et al., 1984; Kern and Kämpf, 1989; Segalla, 2017; Kern et al., 2017), as confirmed in the present study for the extractable micronutrients Mn, Zn, Ni, Cu and Fe. Nonetheless, all ADEs showed higher levels of extractable Mn and Zn and lower Fe contents than ADJ soils, although these varied according to depth and land use system evaluated. Although these results were already reported for some sites (Silva, 2006; Ribeiro, 2006; Moreira et al., 2009; Moline and Coutinho, 2015), only six studies besides the present one had systematically evaluated extractable micronutrient contents over different depths, and only four (Costa et al., 2009; Mendoza, 2011; Macedo, 2014; Albuquerque, 2017) had done so at depths over 40 cm (Table 2). Furthermore, only one other study had considered more than one land use system (Moline and Coutinho, 2015), and none of them had included Ni.

4.2. Extractable Mn and Zn

Both Zn and Mn have been shown to be relatively good indicators of anthropic occupation and ADE formation, although Zn appears to be less stable over time than Mn (Schmidt, 2013). Maintenance of micronutrients under plant-available forms in the soil–plant system depends on soil pH, the formation of secondary compounds in the soil, the intensity and strength of adsorption to clay, organic matter and/or charcoal and immobilization in organic matter fractions (Shuman, 1986; Sims, 1986; Nascimento et al., 2007; Motta et al., 2007). However, the ability of plants to cycle these nutrients in long-term components like wood and thick roots should also be considered (Bianchin, 2013). The importance of these phenomena to micronutrient availability varies depending on the micronutrient, and these issues are further explored below.

The higher increases in extractable Mn contents in ADEs observed in the literature and the present study occur despite the higher pH observed in ADEs (Segalla, 2017), compared with ADJ soils. These higher Mn contents are more likely due to the addition of burned plant remains (including wood, leaves, bark, etc.) from plants grown in acid soils containing high levels of Mn (Misra et al., 1993; Schmidt, 2013; Vogel et al., 2015; Heidak et al., 2014), than due to the addition of animal remains, that tend to have lower Mn content than many plant tissues (Lindow and Peterson, 1927). The long-term residual effect (e.g., over 150 years after abandonment) of large addition of plant charcoals to soils can lead to higher values of extractable Mn and Zn contents (Mastrolonardo et al., 2019). As a component of ash, Mn has high solubility when obtained at temperatures <400 °C (Pereira et al., 2011). Still, the soil heating process by human-induced fires can increase Mn availability, even at high values of organic matter and pH (Miyazawa et al., 1993), as observed here. Higher total Mn contents have also been observed in ADEs in relation to the ADJ soils, and these tend to decrease with depth (Barbosa et al., 2020). This decreased availability in the profile generally follows a decrease in organic matter contents, since Mn can be strongly complexed in organic matter (Kerndorff and Schnitzer, 1980; Shuman and Hargrove, 1985; Sims, 1986), but with less affinity than to Cu, Fe, Zn and Ni, thus determining greater availability. Agricultural soil management, including changes in land use, can also affect the input and quality of plant residues, and generally involves liming, which increases soil pH, thus influencing soluble forms of Mn in soil (Sims, 1986; Castro et al., 1992; Steiner et al., 2011). This may help explain the lower Mn contents found in the pasture than young forests in Porto Velho, although no differences between the land use systems (AS vs. forests) were observed in Iranduba and Belterra.

Similar to Mn, Zn was a good indicator of anthropic occupation, with

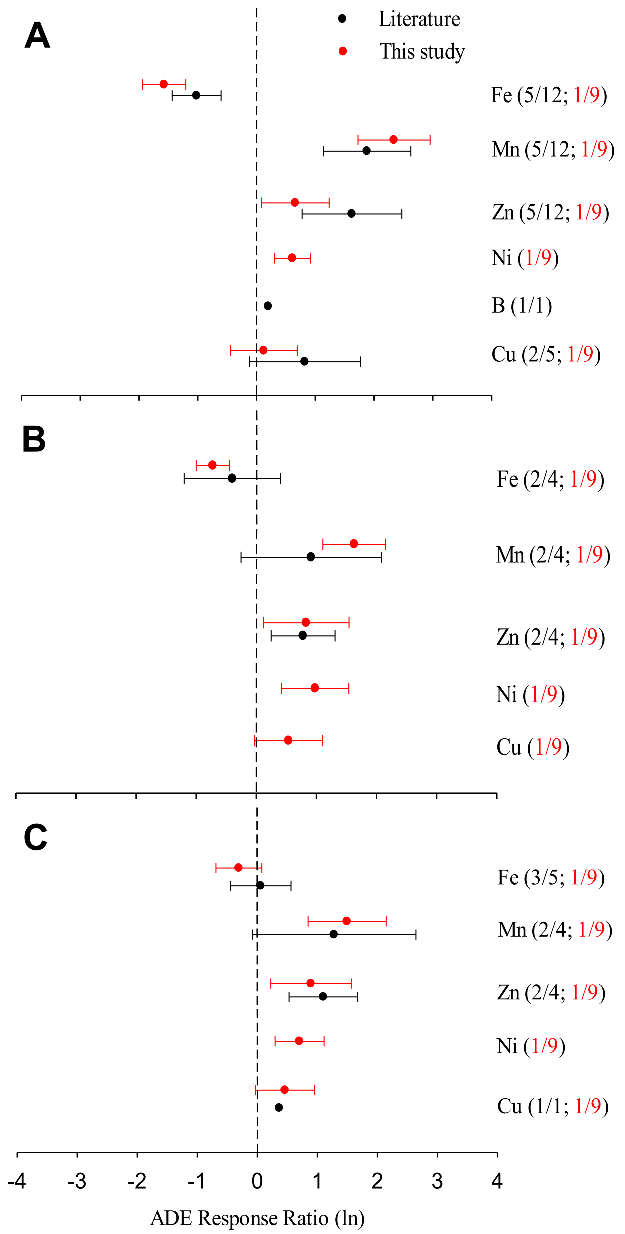

Fig. 5. Overall ADE Response Ratios, i.e., differences in the micronutrient concentrations in Amazonian Dark Earths compared with ADJ soils in the topmost (0–30 cm; A), intermediate (30–60 cm; B) and deeper (>60 cm) soil layers (C), based on a literature meta-analysis (black circles) compared with the results of the present study (red circles). In parenthesis are the number of studies/observations. Fe = iron, Mn = manganese, Zn = zinc, B = boron, Ni = nickel, Cu = cooper. Bars represent the 95% confidence intervals.

significantly higher levels in ADE than in ADJ soils. There is usually a negative relationship between Zn plant uptake and soil pH (Motta et al., 2007; Nascimento et al., 2007). Despite this, it has been reported that Mehlich-1 extractor showed low or no sensitivity to Zn extraction when liming and pH were varied (Nascimento et al., 2007; Fonseca et al., 2010). Changes in the extraction process such as filtration after extraction proved to increase Mehlich-1 sensitivity to changes in pH (Menezes et al., 2010) such as was done in this study. Also, the Mehlich-1 extractor showed high efficiency to recover Zn applied to the soil (Nascimento et al., 2007; Menezes et al., 2010). So higher values for extractable Zn for ADEs despite the higher pH values than the ADJ soils were observed and seemed to follow pseudo-total Zn accumulation in the soil (Segalla, 2017). The increase in total Zn contents in soils is likely related to the addition of Zn-rich animal remains, including skin and bones from fish and other vertebrates consumed by the Amerindians (Barbosa et al., 2020). However, the long-term addition of coal and ash through the burning of these residues may also have slightly increased extractable Zn (Hardy et al., 2017; Mastrolonardo et al., 2019).

4.3. Extractable Cu and Ni

Both Cu and Ni have been shown to be less useful indicators of anthropic occupation and ADE formation, due to their high variability between sites (Schmidt, 2013). In fact, extractable Cu in the present study was highly variable depending on the sampling region, the type of soil and the vegetation cover, as observed by other authors (Silva, 2006; Ribeiro, 2006; Moline and Coutinho, 2015). Higher values of extractable Cu in ADEs were found mainly in Iranduba, corroborating results of Moline and Coutinho (2015) from Manacapuru, only 60 km from Iranduba. However, the increase in extractable Cu contents did not follow those of pseudo-total and total Cu contents measured by other authors in Iranduba (Segalla, 2017; Barbosa et al., 2020) and the other sites (Segalla, 2017), which was higher on the surface and decreased with depth. In other words, higher total and/or pseudo-total Cu levels in ADEs did not necessarily indicate higher extractable Cu. The combination of higher organic matter contents and pH in the surface layers may be related to this absence of relationship, since Cu has a high adsorption force at pH close to 5.0 (Fe ≈ Cu > Ni ≈ Zn > Mn) (Kerndorff and Schnitzer, 1980). The increase in total Cu and a decrease in its extractable form was also observed in an area with charcoal accumulation (Hardy et al., 2017), indicating a high capacity of Cu adsorption by charcoal. In addition, the increase in Zn and Mn and no change in Cu contents in sites with high charcoal accumulation confirmed the high Cu adsorption capacity of this material (Mastrolonardo et al., 2019). Hence, Cu adsorption forces impact the accumulation of this nutrient in soils, but this also means that a small amount of Cu remains in available/extractable forms.

Similar to Cu, Ni levels were higher in ADEs than in ADJ soils only at Iranduba. Furthermore, extractable Ni did not follow the pseudo-total contents observed at the same sampling sites (Segalla, 2017), mainly in the surface soil layers. In fact, Ni does not seem to be much affected by ADE formation (Silva et al., 2012), although there are very few data on this micronutrient in ADEs (Sátiro et al., 2021), and this is the first study comparing extractable Ni contents in ADEs with ADJ soils. This element certainly warrants more attention in studies on ADEs, due to its importance as an essential nutrient in several plant functions and negative impact as a toxic element when excessive, although its role in the soil and plant system is still not fully understood (Yusuf et al., 2011).

4.4. Extractable Fe

Fe is generally found in high concentrations (thousands of mg kg^{-1}) in soils, particularly in tropical Ferralsols and most Amazonian soils (Falcão et al., 2019), and is also found in relatively high contents in plants (tens or hundreds of mg kg^{-1}). However, as opposed to Zn, Mn, Cu and Ni, all ADEs had lower extractable Fe contents than ADJ soils, which confirmed results reported in the literature (Silva, 2006; Ribeiro, 2006; Moreira et al., 2009; Moline and Coutinho, 2015; Albuquerque, 2017; Macedo et al., 2017). Interestingly, Mastrolonardo et al. (2019) also did not find greater extractable Fe in soils with long-term charcoal addition. The lower extractable Fe contents in ADEs may be due to the increase in organic fractions and charcoal in ADEs (Barbosa et al., 2020), although other changes such as higher pH and redox potential can influence Fe availability. Organic matter has a high Fe adsorption capacity (Kerndorff and Schnitzer, 1980), but extractable Fe in ADEs showed little change with depth while the organic matter contents decreased, so the participation of organic matter in Fe availability in these soils does not seem conclusive. Therefore, other factors may be associated with this variation, such as the changes in Fe minerals in ADEs, or even methodological aspects such as interactions with the chemical extractant (Moreira et al., 2009). Several studies indicated an increase in magnetic susceptibility of ADEs, generated by maghemite and magnetite formation, probably due to the burning practices involved in its genesis processes (Oliveira, 2017; Minervini et al., 2018). These mineralogical changes may decrease the solubility of Fe compounds, reducing Fe availability.

4.5. Micronutrient meta-analysis

The comparison of the results of the present study with those of the literature revealed very similar trends in extractable micronutrient contents, with highest increases for Zn and Mn, that can be associated with the addition of these elements in the ADE formation process. The notable exceptions were the lower increases in extractable Zn and Cu in the topmost soil layer (0–30 cm) of ADEs in the present study, although the values were still well within the range of standard deviations of the means of the literature data. Decreased extractable Fe contents were observed in ADEs, particularly in the uppermost soil layer (0–30 cm), which is related to the most recent activity of ADE formation. In terms of extractable Ni, this was the first study on this element in ADEs, so comparisons with previous studies were not possible.

Most studies on micronutrients in ADEs have focused on cations (like the present study), and few studies have addressed anion contents in these soils (Macedo et al., 2019; Barbosa et al., 2020; Segalla, 2017). Only three included extractable B contents (Rodrigues, 1998; Moreira et al., 2009; Moline and Coutinho, 2015). Although it is found in plant biomass in similar concentrations to Zn, B does not accumulate along the ADE profile, indicating non-permanence of B in the soil. Unlike the micronutrients presented so far, B has low retention to soil exchange sites, which determines its high mobility in the soil profile (Motta et al., 2007). Lower availability of B may also be due to its relationship with pH in ADEs (generally between 5.2 and 6.4) (Falcão and Borges, 2006), which modifies the number of exchangeable sites on clay surfaces, such as the distribution of ionic forms of B (H_3BO_3 and $H_4BO_4^-$) in the soil solution. The highest adsorption of B occurs between pH 6.0 to 8.5 in the form of $H_4BO_4^-$ (Goldberg et al., 1993).

4.6. Effects of land use

Land use had a smaller impact than expected on micronutrient availability in the present study, as we hypothesized to see lower contents in agricultural than forest systems in ADEs at all sites. However, this was the case only for Fe in both soils (ADE and ADJ) at Belterra and Mn in the ADEs of Porto Velho. Iron content in soybean plant tissue is relatively low (around 0.9 kg ha^{-1}; Bender et al., 2015), compared to the high amounts available in soils up to 1 m depth (around 300 kg ha^{-1}), so it is unlikely that grain export by annual soybean harvests at Belterra (at harvest, around 40% of plant Fe is in grains; Bender et al., 2015) contributed to lowering extractable Fe contents in both ADJ and ADE soils. Therefore, these lower contents of extractable Fe must be due to other phenomena, associated with impacts of land use and cover change, such as alteration in redox potential, forest clearing and burning, sunlight and rain impacts and erosion (Silva et al., 2003; Magalhães et al., 2013; Michelon et al., 2019). The same probably applies to the other micronutrients, which are also found in low contents in both maize (cultivated at Iranduba) and soybean plants (Bender et al., 2015; Gutiérrez et al., 2018), but that had high extractable contents in soils at our sampling sites.

Finally, the lower Mn contents in the ADE pasture at Porto Velho, are also unlikely to be due to plant biomass export by the cattle, despite the relatively high Mn uptake by Bahiagrass plants (around 1.6 kg ha^{-1}, under typical dry matter production rates; Mackowiak et al., 2017). The soils at the site contain important amounts of both available/extractable and pseudo-total Mn (Segalla, 2017), that could provide ample supply of Mn for the pasture. Nonetheless, an important topic deserving further attention in ADE research is the possible impact of very high micronutrient availabilities (particularly Zn and Mn) in these soils on plant nutrient uptake, balance and metabolism (Loneragan and Webb, 1993; Rabêlo and Borgo, 2016), particularly by high-value crops that may be sensitive to nutrient imbalances or high available metal (Mn, Zn) contents in soils (El-Jaoual and Cox, 1998; Millaleo et al., 2010). Possible impacts of these imbalances on potential consumers at higher levels of the food chain are also topics worth further investigation.

5. Conclusions

Both pre-Columbian and modern human activities affect extractable micronutrient contents in Amazonian soils. Land-use conversion together with modern agriculture can reduce available micronutrients (Fe at Belterra and Mn in ADEs at Porto Velho), while Mn and Zn levels tend to be enhanced in ADEs and can be used as indicators of Amerindian occupation and ADE occurrence. Extractable Fe has reduced levels in ADEs, despite its high concentration Amazonian ferralitic soils. Considering the very high contents of some extractable nutrients in ADEs, and potential interactions in nutrient uptake and cycling in these soils by plants, special care is needed to avoid nutrient imbalances in crops grown on these soils. Furthermore, additional work is warranted, particularly concerning the micronutrients (especially Ni, Cu and B) for which information is still scarce. Finally, further research is needed on soil fertility management and conservation of ADEs (which are considered Natural Heritage sites in Brazil), as well as on the mechanisms involved in micronutrient enhancement in these soils, in order to achieve a better understanding of how to replicate these soils in a modern world in need of a more productive and sustainable agriculture.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The study was supported by the Newton Fund and Fundação Araucária (grant Nos. 45166.460.32093.02022015, NE/N000323/1), Natural Environment Research Council (NERC) UK (grant No. NE/M017656/1), a European Union Horizon 2020 Marie-Curie fellowship to LC (MSCA-IF-2014-GF-660378), by CAPES scholarships to JNS, WCD and RFS, and by CNPq grants and fellowships to GGB and EGN (Nos. 307486/2013-3, 401824/2013-6, 310690/2017-0, 307179/2013-3). We thank INPA, UFOPA, Embrapa Rondônia, Embrapa Amazônia Ocidental and Embrapa Amazônia Oriental and their staff for logistical support and the farmers for access to and permission to sample on their properties. Sampling permit for Tapajós National Forest was granted by ICMBio.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2021.115072.

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