Elemental signatures of an Amazonian Dark Earth as result of its formation process

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Abstract

Amazonian Dark Earths (ADEs) are soils studied for archaeological purposes and as a potentially agricultural model for the humid tropic. We investigated the chemical composition of an ADE in comparison to an adjacent Ultisol without anthropic influence for better understanding the origin of ADE fertility and formation process. Three hundred ADE and Ultisol samples were collected at 10 cm depths from 0 to 100 cm soil profiles on the Caldeirão site at the Solimões River, Brazil and analyzed for elemental composition in an inductively coupled plasma mass spectrometer (ICP-MS). Results showed significantly increased concentrations of P, Ca, K, Mg, Mn, Ba, Zn, Sr, Cu, Rb, Ni, Li, Cd, Cs, Co, Tl, and Be and reduced concentrations of Se along the ADE profile relative to the control Ultisol. Additionally, it was also detected reduced concentrations of Al, U, and V in ADE superficial layers. Elemental enrichment factors in ADE varied from 1.6 to 15.9 times and the enriched elements have mostly been associated with organic residues. Besides the common elements used to characterize ADE sites, our results have shown altered concentrations of other uncommon elements (Al, Be, Cd, Cs, Li, Se, Tl, U, and V) that can be also used to unveil ADE sites and differentiate them from Amazonian soils without anthropic influence.

Keywords: Anthrosols; geochemistry; trace elements; tropical rainforests; agriculture model; ICP-MS.

Introduction

Highly weathered soils such as Oxisols and Ultisols with low concentrations of nutrients and organic matter prevail on the central plateaus of Amazon, where spots of highly fertile soils give support to theories on the existence of large and sedentary pre-Colombian societies that had improved soil fertility. Land incorporation of wastes, ashes and charred material from cooking, warming and forest clearance would be the means of building patches of highly fertile soils in Amazon known as Amazonian Dark Earths – ADEs (Smith, 1980; Jorio et al., 2012; Sheil et al., 2012; Thomas et al., 2015; Kern et al., 2017).

ADEs have been found in various soil orders and they are characterized by the presence of layers rich in pyrogenic carbon (char), bones, ceramic artifacts and persistent fertility (Birk et al., 2011; Glaser and Birk, 2012; Costa et al., 2017; Macedo et al., 2017; Maezumi et al., 2018). There are two categories of ADEs: the first includes dark soils (*terra preta*) with abundant archaeological ceramics, primarily associated with refuse disposal near ancient settlements; the second category regards to brownish soils (terra mulata) with few artifacts and levels of fertility lower than those found in terra preta. *Terra mulata* is probably associated with agricultural practices in more peripheral areas of ancient settlements (Schmidt et al., 2014). Previous studies have associated ADEs to high levels of calcium (Ca), phosphorus (P), barium (Ba), potassium (K), copper (Cu), magnesium (Mg), manganese (Mn), strontium (Sr), and zinc (Zn) as a mean of assigning ADE geochemical signatures (Costa and Kern, 1999; Costa et al., 2013). Besides the pronounced archaeological interest, ADEs may be useful as a model for a sustainable and climate smart agriculture in the humid tropic if the process of building them would be unveiled and reproduced (Schmidt, 2013). Similar ADE anthropogenic soils have been reported in Africa, Australia and Europe, and they have been associated to indigenous populations as well (Solomon et al., 2016; Downie et al., 2011; Wiedner et al., 2015).

ADE's fertility is related to residue type, deposition rate, deposition period, and residue's specific element content (Glaser and Birk, 2012; Schmidt et al., 2014). Ashes, charcoal, food scraps, bones, human faeces and ceramic artifacts are the main residues associated with the formation of ADEs (Smith, 1980; Schaefer et al., 2004; Birk et al., 2011; Glaser and Birk, 2012; Schmidt et al., 2014; Maezumi et al., 2018; Oliveira et al., 2018).

Population habits played an important role on the quantity and quality of wastes added to ADEs (Glaser and Birk, 2012; Schmidt et al., 2014). Consequently, the elemental composition of ADEs may be a habit fingerprint of pre-Colombian societies that inhabited the Amazonian Region. ADEs show a geographic pattern distribution similar to that observed for Brazilian nut trees (*Bertholletia excelsa* Humb. & Bonpl.) (Thomas et al., 2015). *B. excelsa* seeds have taken part in human diet for millennia and they contain relatively high concentrations of selenium (Se), Ba, and Zn that may currently be traced in ADEs (Pacheco and Scussel, 2007; Gonçalves et al., 2009; Naozuka et al., 2010).

Despite ADEs share common attributes (Birk et al., 2011; Glaser and Birk, 2012; Costa et al., 2017; Macedo et al., 2017; Maezumi et al., 2018), they do not present a strictly homogenous set of characteristics because soil addition of elements can vary. The burning of organic wastes releases some elements at gaseous forms (Fletcher et al., 2014), and there is a natural variation among soils. Bone fragments are significant sources of P and Ca (Schaefer et al., 2004). Nutrient resident time in soil depends on some intrinsic soil and nutrient source characteristics, climate, biological activity (bioturbation) and the nutrient itself. P persistence in tropical soils is associated to its high specific adsorption capacity onto iron (Fe) and aluminum (Al) oxides (Schaefer et al., 2004; Costa et al., 2017). Concentrations of Ca, Mg, Mn, Zn, and Cu in ADEs are also significantly higher in ADEs than in other Amazonian soils (Mescouto et al., 2011; Glaser and Birk, 2012; Schmidt et al., 2014).

There are many studies on ADE fertility (Souza et al., 2009; Mescouto et al., 2011; Glaser and Birk, 2012; Pagano et al., 2016; Costa et al., 2017), but the knowledge on multielemental composition of ADEs is still limited, especially in regard to trace elements. Some studies have applied inductively coupled plasma optical emission spectrometry (ICP-OES) to analyze ADE elemental composition (Costa and Kern, 1999; Silva et al., 2012; Schmidt, 2013; Schmidt et al., 2014). Inductively coupled plasma optical emission spectrometry (ICP-OES) is less sensitive to detect trace elements than mass spectrometry (ICP-MS), which allows the most precise quantification of other trace elements, such as silver (Ag), arsenic (As), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), cesium (Cs), molybdenum (Mo), nickel (Ni), lead (Pb), thallium (Tl), uranium (U) and vanadium (V).

It has been estimated a few thousands ADE sites in the Amazonian region (McMichael, 2014; Maezumi et al., 2018), and this study aimed to investigate a 12 ha ADE site named Caldeirão, which is located in Western Amazon, Brazil. Caldeirão ADE pattern consists of mounds that form a ring surrounding circular and semi-circular terraces of approximately 10-20 m diameter, where activities related to households or yards might have concentrated in the past and mounds supposedly formed from discard of organic wastes (Schmidt et al., 2014; Maezumi et al., 2018). Despite the scientific interest in ADEs, there is still a lot of debate and very little uncontested knowledge in respect to the exact processes of ADE formation (Schmidt et al., 2014). Questions include whether mounds formed from the overlap of wastes dumped on soil and whether this waste dumping intentionally aimed to increase soil fertility (Macedo et al., 2017). The Caldeirão site was chosen for its background on interdisciplinary ADE research (Birk et al., 2011; Taube et al., 2013; Nakamura et al., 2014; Schmidt et al., 2014) and because it presents typical anthropic soil horizons that may provide information on key components and processes involved in soil genesis and evolution. Thus, this study aimed to evaluate the elemental composition of an ADE for better understanding the origin of its fertility and formation process.

Material and methods

Study area

The study site is located in Iranduba count (3°15'6.8" South and 60°13'46.9" West – datum WGS 84), State of Amazonas, Brazil, in the sedimentary basin of Amazon River, on Solimões River bank (Fig. 1), Amazonian Tertiary Plateau, 20 m above Solimões River shore. This site is currently under a 40 years-old evergreen secondary forest, which canopy is at 12 m high from ground level in an area of yellowish Ultisol (Xanthic Kandiudult) (Soil Survey Staff, 2014) or *Argissolo Amarelo* (Embrapa, 2013). Stable isotope analyses of ¹⁴C have dated 1,700–1,800 yr BP the Au₂ soil horizon (22–71 cm) on Caldeirão ADE site (Schellekens et al., 2017). The study area is under Af – equatorial climate (Köppen-Geiger), where annual mean temperature is 26.9°C and annual mean precipitation is 2,500 mm (Alvares et al., 2013).

Samples collection

Three sampling transects (A, B, and C) were established along the southwestnortheast direction crossing part of the ADE site and part of an Ultisol site without anthropic influence (control) (Fig. 1). The ADE and control Ultisol sites present similar pedological, topographic and forest cover conditions. Transects A, B, and C kept 100 m distance from each other. Ten soil sampling points were allocated every 10 m along each transect in order to locate sampling points 1 to 5 on ADE site and points 6 to 10 on the control Ultisol, totaling 30 sampling points. Soil samples of 200 g were collected from each of the 30 points at every 10 cm depth by using a Dutch auger. Samples were left to dry under shadow conditions for two weeks and passed through a 2.0 mm sieve before chemical analysis. Ceramic fragments from samples were separated and recorded upon sieving (Fig. 2; Supplementary Table 1).

Soil analysis

After sample homogenization, approximately 200 mg of soil sub-samples were digested in perfluoroalkoxy (PFA) vessels within 48-place teflon-coated graphite block digestor (Model A3, Analysco Ltd, Chipping Norton, UK). For digestion, it was added 2 mL of HNO₃ (69% AR) and 1 mL of concentrated HClO₄. Vessel contents were transferred to tubes placed in a block digester and kept at 80°C for 8 h, subsequently at 100°C for 2 h, and left overnight at room temperature (20°C). On the next day 2.5 mL of concentrated HF (40% AR) were added to tubes and temperature was raised to 120°C for 1 h, increased and maintained at 140°C for 3 h, 160°C for 4 h, and left overnight at room temperature. On the third day the block digester was set to 50°C and 2.5 mL of concentrated HNO₃ and 2.5 mL Milli-Q water (18.2 MΩ cm; Fisher Scientific UK Ltd, Loughborough, UK) were added to tubes and left at 50°C for an hour. Finally, we removed the tubes from the block digester and left them to cool at room temperature. Digested samples were washed with Milli-Q water in 50 mL plastic flasks and stored in 5% HNO₃ matrix at room temperature in universal sample bottles pending elemental analysis. Standard reference material (SRM 2711a Montana soil; National Institute of Standards and Technology-NIST, Gaithersburg, MD, USA) and blank were used every 48 batch. Analysis of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, P, Pb, Rb, Se, Sr, Tl, U, V and Zn was conducted in an Agilent 7500cx ICP-MS (Santa Clara, CA, USA). These elements were chosen for ADE elemental characterization because there are reference values for them in the SRM 2711a Montana soil. Elemental recovery from standard reference material varied between 77% and 112% (Supplementary Table 2).

Additionally, X-ray diffraction analysis was performed on < 2 mm air-dried soil samples, according to Aburto and Southard (2016).

Data analysis

Data from ADE and Ultisol were submitted to the Shapiro-Wilk normality test (Supplementary Table 3). Mean values (n = 15) of elemental concentrations at each 10 cm depth of ADE and Ultisol were pair-wised and compared by t-test (normal distributed data) or Mann-Whitney U test (non-normal distributed data) at p<0.05. Relations between elements were analyzed by Pearson correlations and statistical tests and graphs were performed in SigmaPlot 12.0 software.

Results

Elemental composition of Amazonian Dark Earth and control Ultisol

It was found significantly (Supplementary Table 4) higher concentrations of Ba, Ca, Cd, Co, Cs, Cu, K, Li, Mg, Mn, Ni, P, Rb, Sr, Tl, Zn and Be, and lower concentrations of Se along the ADE profile relative to the control Ultisol (Fig. 3; Fig. 4). Mo concentrations were higher in ADE at two depths and Al, Cr, U, and V concentrations were lower in ADE's upper soil layers than in Ultisol. As and Fe showed lower concentrations between 0–30 cm soil depth and higher concentrations between 90–100 cm (Fig. 3; Fig. 4). Twenty one out 27 analyzed elements presented concentrations dissimilar between ADE and Ultisol (Fig. 5a) and eleven of them showed higher accumulation in ADE topsoil than in underneath layers (Ba, Ca, Cd, Co, Cu, Cs, Mg, Mn, Rb, Tl, and Zn). Li and Sr showed steady concentrations along the 0–100 cm ADE layers, while K, Ni, P, and Se showed higher variations along the ADE profile, though their concentrations along soil layers were consistently different from the control Ultisol.

Concentrations of Al, As, Cr, Fe, Mo, Pb, U and V increased accordingly to soil depth in both ADE and Ultisol, while Ba, Ca, Cd, Co, Cu, Cs, K, Mg, Mn, Rb, Tl and Zn

concentrations decreased along ADE depth. There was no decrease of elemental concentrations in deeper Ultisol layers (Fig. 3; Fig. 4).

Element enrichment factor in ADE relative to control Ultisol

The enrichment factor in ADE relative to the control Ultisol (element concentration in ADE/element concentration in control Ultisol) along the 0–100 cm profile varied from 0.7 to 15.9 times depending on the element (Fig. 5a). Ca showed the highest enrichment factor value and Se was diluted in ADE (Fig. 5a). Concentrations of Cd and Rb were ten times higher in ADE than in Ultisol, Cs and Cu were from 7 to 8 times higher in ADE and Tl, Zn, Ba, P, and K appeared five times more concentrated in ADE than in the Ultisol (Fig. 5a). Seven other elements were from 2 to 3 times more concentrated in ADE than in Ultisol and ten other elements did not appeared enriched in ADE relative to the Ultisol (Fig. 5a). Considering the amount of elements accumulated in the ADE to reach the mentioned concentrations (Fig. 5b), P and Ca represent the highest inputs (15,681 kg ha⁻¹ and 15,315 kg ha⁻¹ respectively) while Al showed the highest output in the 0–100 cm soil profile (78,094 kg ha⁻¹).

Anthrosol element ratios and distribution

Ca/P ratio in the study ADE gradually decreased in depth, starting from 1.60 in the 0–10 cm layer to reach values of 0.37 in the 90–100 cm layer (Fig. 6). Similarly, the ratio between Ca and the other analyzed elements in ADE decreased as a function of depth (Supplementary Table 5). Contrary to Ca, P/Ba ratio increased twice along the 0–100 cm ADE profile (Fig. 6) as did the ratio between P and the other analyzed elements (Supplementary Table 5).

The amount of analyzed elements that significantly accumulated in ADE relative to the control Ultisol (Fig. 3; Fig. 4) was the greatest in ADE profiles closer to Solimões River bank, between sampling points A_1 and A_2 , sampling points B_3 and B_5 , and sampling points C_1 and C_2 (Fig. 1; Fig. 7). The highest accumulations of Ba, Ca, Cd, Mg, Ni, P, and Sr in ADE were measured along transect A, which is closer to Solimões River bank than transects B and C.

Discussion

Element accumulation in Amazonian Dark Earth (ADE)

Inputs of matter in study ADE were evidenced by the comparison of elemental concentrations with the control Ultisol without anthropic influence (Fig. 3; Fig. 4). The significantly higher concentrations of Ba, Be, Ca, Cd, Co, Cs, Cu, K, Li, Mg, Mn, Ni, P, Rb, Sr, Tl and Zn in ADE are regarded as a result of the addition of organic residues and due to mechanisms that favored the permanence of these elements in soil. The study site is at Solimões River bank and fishes and other food resources from the river may have contributed to the high levels of Ca and P in the ADE (Fig. 5). A great amount of organic residues from high population density or long residence time is a key factor to the genesis of ADEs (Lima et al., 2002; Souza et al., 2009; Birk et al., 2011; Glaser and Birk, 2012; Schmidt, 2013; Schmidt et al., 2014; Costa et al., 2017; Macedo et al., 2017; Maezumi et al., 2018).

Soil incorporation of organic residues with low solubility such as bones allow some elements to last for long time in ADEs (Lima et al., 2002; Glaser and Birk, 2012). Pyrogenic carbon (char) formed in fires can last for thousands of years in the environment (Sheil et al., 2012) and keep soil cation exchange capacity (CEC) at high levels over long periods (Kern et al., 2017) due to its complex morphology (Teixeira and Martins, 2003;

Birk et al., 2011; Jorio et al., 2012; Schmidt, 2013; Schmidt et al., 2014; Macedo et al., 2017; Maezumi et al., 2018).

High levels of Ca and P accumulated in ADE (Fig. 5) suggest that residues with high content of these elements were important for its formation. The main residues associated with ADE formation are bones that are significant sources of Ca (20 to 32%) and P (7 to 10%) (Schaefer et al., 2004; Wilson et al., 2008; Buddhachat et al., 2016). A micrometric scale analysis has revealed that Ca and P from bones are mainly accumulated in ADE in the form of Ca phosphate particles $[Ca_3(PO_4)_2, Ca(PO_4)6(OH)]$ (Oliveira et al., 2018). To a lesser extent, Ca accumulates in structures of charcoal particles and P is associated to soil Fe and Al oxides (Jorio et al., 2012; Oliveira et al., 2018).

Ca and P in the study ADE are statically correlated (r = 0.64; *p*<0.001) and spatially associated in the area, which may indicate a common source of these nutrients (Fig. 7). Ca/P ratio ranges from 0.4 to 1.6 in ADE, 3.6 to 18 in other ADEs (Fig. 6) (Costa and Kern, 1999; Silva et al., 2012), 2.0 to 3.3 in bones (Schaefer et al., 2004; Almeida et al., 2008), above 14 in wood ashes and charcoal (Wilson et al., 2008; Okmanis et al., 2015), and below one in human faeces (Rose et al., 2015; Torri et al., 2017). The low Ca/P ratio in the ADE of this study may be due to its higher clay content (Schaefer et al., 2004; Macedo et al., 2017) compared to other ADEs (Costa and Kern, 1999; Silva et al., 2012). Clay favors P adsorption and reduces P loss. Nordic Dark Earth (NDE) in Germany and Terra Preta Australis (TPA) in Australia (Downie et al., 2011; Wiedner et al., 2015) have also presented coarse texture. P/Ba ratios of Caldeirão ADE are 3–7 times higher than the P/Ba ratios of other ADEs and NDE as well (Fig. 6). It evidences a significant contribution of P-rich residues and element permanence in the system during Caldeirão ADE formation.

P makes up 8.5% of bones (Schaefer et al., 2004) and the input of 15,681 kg P ha⁻¹ in the study ADE (Fig. 5b) would demand a daily incorporation of 5.12 kg ha⁻¹ of bones for 100 years if bones were the major source of P. However, when Ca in bones is taken into account (28.3% Ca) (Schaefer et al., 2004), the input of 15,315 kg ha⁻¹ of Ca measured in the ADE (Fig. 5b) would demand a daily incorporation of only 1.52 kg ha⁻¹ of bones for the same 100 years. Such figures suggest that after residue incorporation Ca losses were higher than P losses in the course of ADE formation.

Decreases in Ca/P ratio and increase of P/Ba ratio along ADE profile (Fig. 6) were probably due to the increase of P concentrations in depth (Fig. 4). P enrichment in depth may be a result of vertical transport from surface due to saturation of soil adsorption capacity or due to higher solubility of organic-P under high P concentrations in soil (Souza et al, 2009). P in the study ADE was more concentrated from 30 cm to downwards (Fig. 4). Clay content also increases along ADE depth (Caldeirão site) (Schaefer et al., 2004; Macedo et al., 2017) and may have favored P adsorption onto clay minerals.

Higher concentrations and amounts of K in relation to Mg (Fig. 3, Fig. 5) in the ADE are reported as a consequence of higher levels of K in meat, fruits (USDA, 1989), bones (Schaefer et al., 2004), ash, and charcoal made of plants (Schaefer et al., 2004; Okmanis et al., 2015). In addition, the presence of ceramic fragments (Fig. 2, Supplementary Table 1) consisting of micaceous (K-rich) material (Schaefer et al., 2004) may have contributed to K enrichment in the ADE. Constant burning of residues on soil surface can cause melting of organic materials and mineral particles (Teixeira and Martins, 2003), which could contribute to keep some elements such as alkali metals (Cs, K, Li and Rb) in ADEs. This can be especially important for highly mobile elements in soils such as Li, which is not as adsorbed by soil particles as Ca, Mg, Ba and K.

ADE enrichment with Mn, Zn, and Cu (Fig. 3; Fig. 4) has been frequently reported in other studies (Costa and Kern, 1999; Mescouto et al., 2011; Costa et al., 2013). The input of 1,490 kg ha⁻¹ of Mn in study ADE relative to control Ultisol (Fig. 5b) was greater than the inputs of Cu and Zn. Contents of Mn are high in foliar tissues of trees and in ashes of different species (Pitman, 2006; Dibdiakova et al., 2015). Under high temperatures during ash formation, Mn presents low solubility and may last long in soils (Pereira et al., 2011). The higher Cu enrichment in the study ADE compared to Zn (Fig. 5a) can be explained by the very low Cu content in control Ultisol and the higher adsorption capacity of Cu to organic matter and soil mineral components (Kabata-Pendias, 2011). Levels of Zn in plant and animal tissues are generally higher than Cu (Ferreira et al., 2012; Ferreira et al., 2014; Joy et al., 2015; Buddhachat et al., 2016) and it justifies the total amounts of Cu and Zn found in the study ADE (Fig. 5).

Ba enrichment (Fig. 3; Fig. 5) has also been reported in other ADEs (Costa and Kern, 1999; Schmidt, 2013). Plant charcoal and bones are the main sources of Ba and Sr in anthropogenic soils (Wilson et al., 2008) and Ba concentrations of up 5,000 mg kg⁻¹ have been measured in Brazilian nuts and seeds of *Bertholletia excelsa* (Smith, 1971; Gonçalves et al., 2009). This species has been historically used by Amazonian populations and it is associated to the distribution of ADE sites in the region (Thomas et al., 2015). Although charcoal and bones are the main sources of Ba, it is possible that Brazilian nut residues and human faeces have enriched the study ADE with Ba.

Cd, Cs, and Tl presented a high enrichment factor in the study ADE also due to the low concentrations naturally present in the control Ultisol (Fig. 5). There are significant contents of Cd in the bones (Buddhachat et al., 2016), charcoal (Fletcher et al., 2014), and ashes (Okmanis et al. al., 2015) and it is possible that residues from these materials were significant sources of Cd in the study ADE (Fig. 3). On the other hand, Co, Cs, Li, Rb

and Tl presented a high association with K, Cu, Mn and Zn (Supplementary Table 6; Fig. 7), being probably more influenced by the addition of plant residues via ash and charcoal.

Element decrease in Amazonian Dark Earth (ADE)

Fire has been a common tool for the management of forest and residues in the Amazon region (Schmidt, 2013), and the burning of organic materials added to ADE is the probable cause of decreased concentrations of Se relative to the control Ultisol (Fig. 4; Fig. 5). Se boiling point is at 685°C and up to 60% of this element can volatilize when organic residues are subject to fire (King et al., 1977; Fletcher et al., 2014). Consequently, it was not possible to establish a relation between the amount of Brazilian nut incorporated into the soil and the concentrations of Se measured in the study ADE (Fig. 4). Concentrations of Se (1.19–1.89 mg kg⁻¹) measured in the control Ultisol (Fig. 4) are higher than concentrations measured in native Amazonian soils (Gabos et al., 2014) and in soils around the world (Kabata-Pendias, 2011). Despite the lower concentrations of Se in ADE relative to the control Ultisol, the values 0.96 to 1.48 mg kg⁻¹ can be considered high (Fig. 4).

Lower concentrations of U in ADE compared to the Ultisol (Fig. 4) may be a result of dilution effect from soil incorporation of organic residues and charcoal (Birk et al., 2011; Schmidt et al., 2014; Macedo et al., 2017). The largest fractions of U are in immobile forms in soils and their contents in plant and animal materials are insignificant (Kabata-Pendias, 2011). There was not a consistent behavior of U concentrations in ADEs and reports on this element are controversial in anthropogenic soils (Entwistle et al., 1998; Vukašinović et al., 2010).

Al had undergone the highest loss from ADE profile (78,094 kg ha⁻¹) (Fig. 5) and lower concentrations of Al in ADE topsoil compared to adjacent soils have been reported in

other works (Silva et al., 2012; Schmidt et al., 2014). Such a characteristic is attributed to Al_2O_3 disaggregation caused by high concentrations of organic matter in ADE upper layers (Silva et al., 2012). However, Al did not accumulated in ADE deeper layers in concentrations beyond the levels measured in the control Ultisol (Fig. 3).

Al, Fe, and V originate from parent material, they present low mobility in soils and V is usually associated with Fe (Costa and Kern, 1999; Kern et al., 2017). Therefore, dilution effect may explain Al lower concentrations in ADE upper layers as Fe and V showed similar concentration pattern along the ADE profile (Fig. 3). Finally, Al, Fe, and V volatilization caused by fires is unlikely to had occurred due to high Al (2,470°C), Fe (2,862°C), and V (3,407°C) boiling points.

Elements with similar concentrations in Amazonian Dark Earth and control Ultisol

Concentrations and distribution of Ag, As, Cr, Fe, Mo, and Pb in ADE and Ultisol profiles were similar (Fig. 3; Fig. 4) as reported in other studies (Costa and Kern, 1999; Silva et al., 2012; Costa et al., 2013; Schmidt et al., 2014). The mineral fraction of ADEs and Amazonian soils are 97% composed of SiO₂, Al₂O₃, Fe₂O₃ (Costa and Kern, 1999). As a major part of soils, concentrations of Al and Fe from 30 cm to deeper layers were similar between the study ADE and the Ultisol (Fig. 3). Similarities between the deeper layers of ADEs and surrounding soils point to a common mineral matrix on which ADEs have formed by inputs of organic material and further pedogenetic transformations (Supplementary Figure 1) (Costa and Kern, 1999; Silva et al., 2012).

Distribution of elements in Amazonian Dark Earth

The seventeen elements that significantly enriched the study ADE have shown a spatial variability of concentrations on the site (Fig. 7). Element accumulation has

occurred in hotspots and it is more evident along transect B (Fig. 7). Contrasting results have been reported in the literature regarding element distribution on ADE sites, including distribution in circular forms (Costa et al., 2013; Schmidt, 2013; Schmidt et al., 2014), linear pattern (Schmidt et al., 2014), and absence of pattern (Kern et al., 2015). Where element accumulation pattern exist, site occupation is reported as it was intense in the past. On the other hand, absence of element accumulation patterns in ADEs can indicate different cycles of occupation and re-occupation of these sites. The distribution of elements (Fig. 7) points to a probable variability in ADE formation processes, since the accumulation of some elements was similar, while others showed significant variations between sampling points. Factors subsequent to ADE formation such as bioturbation, biosphere cycling, loss, and translocation can affect element dynamics in soil. Even tough, elemental distribution pattern may indicate the source of residue added to soil that still exerts a strong influence on the current elemental composition and signature of the study ADE. This pattern of anthrosol formation can be associated with occupation where the terraces were domestic areas (houses or yards) surrounded by refuse disposal areas in middens which built up into mounds over time, forming large deposits of Amazon Dark Earth (Schmidt et al., 2014).

ADE fertility and plant production

The highly weathered Amazonian soils are too infertile to support most crops, and the incorporation of domestic residues had been the mechanism of pre-Columbian societies to increase soil fertility and produce food crops (Doughty et al., 2013). Land application of organic materials is a traditional way of building soil fertility because organic matter increases nutrient stocks in plants' rooting zone, reduce nutrient leaching and generally

improve crop production, especially on acidic and highly weathered tropical soils (Steiner et al., 2007; Torri et al., 2017).

Many ADE sites have been abandoned and covered by forests following declines of indigenous populations, while some sites remain farmed by current inhabitants who try to make most from ADE fertility (Lehmann et al., 2004; Doughty et al., 2013). The study ADE showed enriched concentrations of seventeen elements (Fig. 5b), which are not necessarily availability for plant growth (Lehmann et al., 2004). Nutrient availability in ADEs rely on the mineralization of organic residues incorporated in soils, and the high stability of ADE organic matter (Jorio et al., 2012) may delay the release of nutrients for crop production (Falcão et al., 2009). Yet, organic residues are unbalanced sources of nutrients it may harm plant growth (Torri et al., 2017). High fertility is the most ascribed feature of ADEs, forecasted from their total concentrations of plant nutrients (Fig. 3 and 4), especially P (Glaser and Birk, 2012). However, plant nutrition does not solely depend on the total contents of nutrient in soils (Torri et al., 2017) and shortage of plant available nutrients has been reported in many ADEs (Falcão et al., 2009).

Even though, crop yields are usually higher on ADE sites than from adjacent soils (Lehmann et al., 2004), But low availability K, B, Cu and Fe and unbalanced concentrations of K relative to exchangeable Ca and Mg have been an issue in the contemporary use of ADEs for plant production (Falcão et al., 2009). Likewise, high concentrations of available P, Ca and Mg reduce plant absorption of Zn and Mn and this is another drawback for crop production on ADE sites (Falcão et al., 2009). Mineral N is marginally higher or even lower in ADEs relative to adjacent soils, despite the high concentrations of total N in ADEs (Lehmann et al., 2004). Physical protection of organic matter, high C/N ratios and N immobilization are the probably causes of low plant availability of N in ADEs (Lehmann et al., 2004; Jorio et al., 2012).

A study has shown unsatisfactory foliar concentrations of Cu and Fe in rice cultivated on ADE due to its respective high levels of exchangeable Ca and available P (Falcão et al., 2009). Crops with high demand for K such as banana (*Musa sp.*) do not appropriately develop on ADE sites. Corn has shown similar poor performance on ADE, but crops with a high demand for P, such as legume, beans, and manioc have grown beyond the yields harvested from adjacent soils (Lehmann et al., 2004). Regarding forest species, there was a slightly higher biomass production on an ADE site compared to a control Oxisol (Doughty et al., 2013).

Unbalanced concentrations of nutrients slowly released from ADEs may be enough for supplying subsistence crops but they have not appropriately sustained cash crops. Further research is necessary to bring ADEs into contemporary agricultural systems by supplementary fertilization and development of appropriate management.

Conclusion

Out of 27 analyzed elements there was a significant concentration enrichment in the study Amazonian Dark Earth (ADE) with Ba, Be, Ca, Cd, Co, Cs, Cu, K, Li, Mg, Mn, Ni, P, Rb, Sr, Tl, and Zn and dilution of Al, Se, U, and V relative to an Ultisol used as control. Organic residues are regarded as the main sources such elements, which portrait elemental signatures to the ADE and give clues to its formation process. Decreased concentrations of Se in ADE may be associated with the large addition of residue from complete (ashes) or incomplete burning (charcoal). Fire has been long in use in the Amazon region and Se is lost along with smoke. Our study contributes to broaden the knowledge about the composition of ADEs, indicating that besides the common elements used for its characterization, such as P, Ca, Mg, and Zn, altered concentrations of Al, Be, Cd, Cs, Li, Se Tl, U, and V can also unveil ADE sites and differentiate them from Amazonian soils without anthropic influence.

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Fig. 1. Study ADE site in Iranduba county, State of Amazonas (Brazil). Letters from A to C indicate sampling transects on ADE site (1–5) and on the reference Ultisol without anthropic influence (6–10). Images obtained from the United States Geological Survey.



Fig. 2. Soil samples collected at 0–10 cm depth from ADE (a) site and from the control Ultisol (b) and details of ceramic fragments (c; d) found in ADE.



Fig. 3. Concentrations of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cu, Cr, Cs, Fe, K, Li and Mg in Amazonian Dark Earth (ADE) and Ultisol. Bars indicate standard deviation for each depth (n=15). For Al and Fe the "k" along the scale of content indicate times 1,000. Asterisk indicates significant difference between ADE and Ultisol (p<0.05).



Fig. 4. Concentrations of Mn, Mo, Ni, P, Pb, Rb, Se, Sr, Tl, U, V, and Zn in Amazonian Dark Earths (ADE) and Ultisol. Bars indicate standard deviation for each depth (n=15). Asterisk indicates significant difference between ADE and Ultisol (p<0.05).



Fig. 5. Mean values of ADE enrichment factor (a) and nutrient input (b) considering the 0–100 cm soil layer.



Fig. 6. Ca/P and P/Ba ratios in some Anthrosols. ADE–Amazon Dark Earth; NDE–Nordic Dark Earth; TPA–Australis Dark Earth.



Fig. 7. Accumulated amounts (kg ha⁻¹) of analyzed elements (0–100 cm depth) in the study Amazonian Dark Earth (ADE).

Graphical abstract



Supplementary data



Fig. S1. X-ray diffraction of air-dried samples from Amazonian Dark Earth (ADE) and Ultisol (control) samples collected in the 40–50 cm depth layer. KAO: kaolinite; Qrtz: quartz; GOE: goethite; Cor: corundum.

Transact					Dep	oth (cm)					- Sum
Transect	0–10	20-30	20-30	30–40	40–50	50-60	60–70	70–80	80–90	90–100	Sum
A1	1	1									2
A2	1	1						1			3
A3	1										1
A4		1	1								2
A5	1	1	1								3
B1					1						1
B2			1				1	1			3
B3	1			1							2
B4		1			1	1					3
B5						1	1			1	3
C1	1	1	1	1							4
C2	1			1	1	1		1	1		6
C3											0
C4		1				1					2
C5	1	1	1								3
Sum	8	8	4	3	3	4	2	3	1	1	

Supplementary Table 1. Number of ceramic fragments found in ADE samples.

A, B, and C refer to transects and numbers (1–5) under letters refer to sampling profiles along each transect.

Element	Certified value (mg kg ⁻¹)	Recovered value (mg kg ⁻¹)	Recovery (%)
Ag	6	5.5	91
Al	67200	51999.8	77
As	107	114.8	107
Ba	730	693.8	95
Co	9.89	9.0	91
Ca	24200	21597.8	89
Cd	54.1	56.1	104
Cr	52.3	40.9	78
Cs	6.7	6.0	89
Cu	140	124.2	89
Fe	28200	26556.9	94
K	25300	22643.5	94
Mg	10700	8286.2	77
Mn	675	614.7	91
Mo	1.6	1.6	99
Ni	21.7	19.6	90
Р	842	853.2	101
Pb	1400	1228.1	88
Rb	120	111.5	93
Se	2	2.0	100
Sr	245.3	219.5	89
Tl	2.47	2.5	101
U	2.6	2.4	92
V	80.7	78.3	97
Zn	414	462.0	112

Supplementary Table 2. Certified soil concentrations and recovery of soil certified reference material (Montana II soil 2711a, NIST, Gaithersburg, MD, USA) from analysis by ICP-MS.

Element					Dep	th (cm)				
Element	0–10	10–20	20–30	30–40	40–50	50–60	60–70	70–80	80–90	90–100
Ag	No	No	No	No	No	No	No	No	No	No
Al	Yes	Yes	Yes	Yes	No	Yes	No	Yes	Yes	Yes
As	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Ba	No	No	No	No	No	No	No	No	No	No
Be	No	Yes	No	No	No	No	Yes	No	No	No
Ca	n No No No		No	No	No	No	No	No	No	No
Cd	No No No		No	No	No	No	No	No	No	No
Co	Yes	No	No	No	No	No	No	No	No	No
Cu	No	No	No	No	No	No	No	No	No	No
Cr	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Cs	s No		No	No	No	No	No	No	No	No
Fe	No	No	No	Yes	Yes	No	No	Yes	Yes	Yes
Κ	Yes	Yes	No	No	No	No	No	No	No	No
Li	Yes	No	No	No	No	No	No	No	No	No
Mg	No	No	No	No	No	No	No	No	No	No
Mn	No	Yes	No	No	No	No	No	No	No	No
Мо	No	Yes	No	No	No	Yes	No	No	No	No
Ni	No	No	No	No	No	No	No	No	No	No
Р	No	No	No	No	No	No	No	No	No	No
Pb	Yes	No	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes
Rb	No	Yes	No	No	No	No	No	No	No	No
Se	Yes	Yes	No	No	Yes	Yes	Yes	Yes	Yes	Yes
Sr	No	No	No	No	No	No	No	No	No	No
Tl	No	No	No	No	No	No	No	No	No	No
U	No	No	No	No	Yes	Yes	No	Yes	Yes	Yes
V	No	No	No	Yes	No	Yes	No	No	No	No
Zn	Yes	No	No	No	No	No	No	No	No	No

Supplementary Table 3. Results of data normality analysis by the Shapiro-Wilk test (p<0.05). Normal distributed data (yes) and non-normal distributed data (no).

Element	Depth (cm)												
Element	0–10	10–20	20–30	30-40	40–50	50-60	60–70	70–80	80–90	90–100			
Ag	0.178	0.852	0.300	0.561	0.144	0.066	0.772	0.135	0.560	0.605			
Al	0.013	0.001	0.002	0.164	0.419	0.080	0.590	0.255	0.959	0.857			
As	0.024	0.001	0.004	0.405	0.710	0.323	0.898	0.689	0.238	0.006			
Ba	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000			
Be	0.003	0.000	0.014	0.004	0.001	0.034	0.012	0.004	0.045	0.074			
Ca	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.007	0.000			
Cd	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.005	0.000			
Co	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.007	0.050			
Cu	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000			
Cr	0.449	0.039	0.002	0.123	0.154	0.040	0.251	0.114	0.763	0.294			
Cs	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000			
Fe	0.290	0.016	0.034	0.805	0.748	0.339	0.934	0.641	0.141	0.033			
К	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.008	0.019			
Li	0.000	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000			
Mg	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000			
Mn	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.009	0.029			
Мо	0.866	0.088	0.115	0.455	0.527	0.605	0.534	0.361	0.008	0.000			
Ni	0.012	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.031	0.004			
Р	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000			
Pb	0.829	0.561	0.161	0.831	0.983	0.557	0.854	0.629	0.322	0.276			
Rb	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000			
Se	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000			
Sr	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000	0.000			
T1	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.000			
U	0.051	0.147	0.009	0.001	0.001	0.001	0.034	0.001	0.033	0.092			
v	0.029	0.001	0.001	0.093	0.216	0.084	0.340	0.308	0.267	0.058			
Zn	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.006	0.000			

Supplementary Table 4. p values for the comparison between Amazon Dark Earth (Iranduba-AM) and Ultisol (control) by t test or Mann-Whitney U test. Gray highlight indicates significant values (p<0.05).

Datia	Depth (cm)											
Katio	0-10	1020	20-30	30-40	40-50	50-60	60-70	70-80	80-90	90-100		
P/Ag	13234	13404	16711	17129	18279	18775	17410	16790	17379	14626		
P/Al	0.04	0.04	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.02		
P/As	247	247	260	238	227	226	198	173	172	133		
P/Ba	16	17	19	22	24	25	27	29	31	37		
P/Be	5993	5752	6921	6498	7315	7345	7192	6579	6800	6673		
P/Ca	0.63 0.90 1.19		1.39	1.52	1.57	1.66	1.81	1.77	2.71			
P/Cd	1749	1733	2093	2423	2735	2962	3207	3431	3878	6446		
P/Co	1182	1175	1433	1634	1748	1844	1810	1859	1936	2001		
P/Cu	112	115	131	142	156	162	173	190	222	264		
P/Cr	36.68	36.43	41.22	39.78	39.34	39.01	35.88	31.69	31.53	25.24		
P/Cs	2198	2200	2675	3049	3411	3633	3868	4336	4727	6195		
P/Fe	0.05	0.05	0.05	0.05	0.05	0.05	0.04	0.04	0.04	0.03		
P/K	2.65	2.56	2.56	3.33	3.69	3.90	4.15	4.36	4.31	5.84		
P/Li	444	457	502	534	579	601	611	605	619	634		
P/Mg	3.29	3.70	4.45	5.22	6.01	6.41	6.49	7.07	8.66	8.59		
P/Mn	3.49	3.65	5.38	6.65	7.55	8.07	8.08	8.85	10.82	12.11		
P/Mo	1509	1540	1621	1507	1430	1547	1352	1186	1171	946		
P/Ni	337	252	276	334	372	393	384	371	430	392		
P/Pb	208	210	238	236	236	238	219	199	199	165		
P/Rb	203	213	256	300	327	345	366	394	439	554		
P/Se	1435	1498	1960	1998	2005	2050	1842	1633	1621	1295		
P/Sr	42.30	47.30	55.23	57.11	58.53	56.88	56.61	52.72	55.06	50.69		
P/Tl	14364	14823	20014	24272	27062	28896	29735	32701	35450	42682		
P/U	781	783	969	1027	1068	1091	992	946	962	804		
P/V	21.68	21.47	22.97	21.44	20.72	20.35	18.46	16.03	15.91	12.68		
P/Zn	26.04	25.88	31.68	35.49	39.83	42.36	43.99	48.07	54.60	55.87		
Ca/Ag	21111	14871	13994	12291	12006	11931	10482	9276	9832	5400		
Ca/Al	0.06	0.04	0.03	0.02	0.02	0.02	0.02	0.01	0.01	0.01		
Ca/As	394	275	218	171	149	143	119	96	97	49		
Ca/Ba	25.24	18.56	16.12	15.78	15.80	15.88	16.36	16.09	17.45	13.48		
Ca/Be	9560	6382	5796	4663	4804	4668	4330	3635	3847	2464		
Ca/Cd	2791	1923	1753	1738	1796	1882	1931	1896	2194	2380		
Ca/Co	1885	1304	1200	11/2	1148	1172	1090	1027	1095	739		
Ca/Cu	179	127	110	102	102	103	104	105	125	97		
Ca/Cr	58.52	40.42	34.52	28.54	25.84	24.79	21.60	17.51	17.84	9.32		
Ca/Cs	3506	2441	2240	2188	2241	2309	2329	2396	2674	2287		
Ca/Fe	0.08	0.05	0.04	0.04	0.03	0.03	0.03	0.02	0.02	0.01		
Ca/K	4.23	2.84	2.14	2.39	2.42	2.48	2.50	2.41	2.44	2.16		
Ca/Li	/08	507	420	383	380	382	368	334	350	234		
Ca/Mg	5.25	4.10	3.72	3.74	3.95	4.07	3.91	3.90	4.90	3.17		
Ca/Mn	5.50 2.407	4.05	4.50	4.//	4.96	5.13	4.8/	4.89	6.12	4.47		
	2407	1708	1357	240	939	985	814	000	002	549 145		
	JS7 1.60	260	251	240	244	230	251	205	245	145		
Ca/P	1.00	1.11	100	160	155	151	120	110	112	61		
Ca/PU	201	233 227	199	215	133	210	132	210	240	205		
	524 2280	207 1661	213 1642	213 1/3/	213 1317	219 1302	220 1100	210	249 017	203 178		
Ca/St Ca/St	2209 67 18	52 / 8	46.25	40 98	38 //	36.15	34 08	202	31.15	+/0 18 71		
Ca/Tl	22914	16444	16760	17416	17774	18362	17903	18067	20055	15757		
Ca/U	1246	869	812	737	701	693	597	523	544	297		
Ca/V	34.58	23.82	19.23	15.39	13.61	12.93	11.12	8.86	9.00	4.68		
Ca/Zn	41.55	28.71	26.53	25.47	26.16	26.92	26.48	26.56	30.89	20.63		

Supplementary Table 5. Ratio of P/elements and Ca/elements in Amazonian Dark Earth (Iranduba-AM).

Supplementary Table 6. Pearson	i correlation co	efficients between	elements in the	Amazonian
Dark Earth and the significance (p	values in italic	c) of each correlation	on (continue).	

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	Al	As	Ba	Be	Ca	Cd	Co	Cu	Cr	Cs	Fe	К	Li	Mg	Mn	Мо	Ni	Р	Pb	Rb	Se	Sr	TI	U	v	Zn
Ag	0.534	-0.028	-0.067	0.469	0.079	-0.016	0.288	0.248	0.274	0.205	0.222	0.096	0.132	0.006	0.083	0.047	0.054	0.195	-0.091	0.133	0.156	0.135	0.059	0.128	0.212	0.334
	0.000	0.732	0.412	0.000	0.335	0.843	0.000	0.002	0.001	0.012	0.006	0.243	0.109	0.946	0.312	0.570	0.515	0.017	0.268	0.105	0.056	0.100	0.474	0.118	0.009	0.000
Al		0.762	-0.470	0.228	-0.445	-0.479	-0.288	-0.325	0.927	-0.438	0.918	-0.351	-0.221	-0.544	-0.645	0.715	-0.145	0.101	0.536	-0.423	0.707	0.002	-0.582	0.601	0.914	-0.299
		0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.000	0.000	0.000	0.077	0.220	0.000	0.000	0.000	0.981	0.000	0.000	0.000	0.000
As			-0.467	-0.047	-0.516	-0.518	-0.556	-0.574	0.876	-0.668	0.942	-0.514	-0.389	-0.627	-0.817	0.852	-0.209	0.006	0.835	-0.619	0.852	-0.043	-0.707	0.700	0.942	-0.567
			0.000	0.567	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.942	0.000	0.000	0.000	0.599	0.000	0.000	0.000	0.000
Ba				0.457	0.858	0.922	0.782	0.859	-0.477	0.819	-0.426	0.773	0.822	0.874	0.769	-0.395	0.658	0.669	-0.008	0.803	-0.507	0.787	0.870	-0.322	-0.458	0.836
				0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.922	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Be					0.435	0.453	0.620	0.602	0.122	0.568	0.125	0.566	0.661	0.422	0.350	0.028	0.400	0.632	0.163	0.542	-0.087	0.564	0.462	0.100	0.102	0.596
					0.000	0.000	0.000	0.000	0.139	0.000	0.128	0.000	0.000	0.000	0.000	0.731	0.000	0.000	0.046	0.000	0.291	0.000	0.000	0.224	0.216	0.000
Ca						0.897	0.698	0.758	-0.481	0.726	-0.454	0.691	0.709	0.819	0.747	-0.389	0.531	0.635	-0.090	0.723	-0.448	0.770	0.831	-0.395	-0.471	0.796
						0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.275	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cd							0.777	0.852	-0.488	0.790	-0.461	0.748	0.795	0.840	0.797	-0.392	0.620	0.678	-0.072	0.787	-0.522	0.712	0.880	-0.350	-0.484	0.842
							0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.380	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Co								0.941	-0.376	0.939	-0.417	0.901	0.894	0.853	0.861	-0.446	0.577	0.606	-0.245	0.939	-0.558	0.562	0.898	-0.232	-0.442	0.934
								0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.004	0.000	0.000
Cu									-0.425	0.933	-0.434	0.859	0.904	0.847	0.851	-0.458	0.636	0.661	-0.233	0.902	-0.600	0.636	0.895	-0.333	-0.465	0.959
									0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr										-0.541	0.962	-0.391	-0.257	-0.593	-0.713	0.815	-0.172	0.098	0.666	-0.476	0.802	-0.036	-0.615	0.735	0.969	-0.421
										0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.035	0.234	0.000	0.000	0.000	0.662	0.000	0.000	0.000	0.000
Cs											-0.557	0.908	0.882	0.896	0.879	-0.542	0.561	0.552	-0.318	0.958	-0.657	0.563	0.934	-0.331	-0.582	0.912
											0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe												-0.414	-0.258	-0.586	-0.756	0.850	-0.133	0.134	0.784	-0.523	0.813	0.057	-0.642	0.702	0.997	-0.428
												0.000	0.001	0.000	0.000	0.000	0.105	0.101	0.000	0.000	0.000	0.491	0.000	0.000	0.000	0.000
к													0.909	0.849	0.761	-0.403	0.571	0.602	-0.173	0.921	-0.581	0.589	0.860	-0.213	-0.436	0.836
													0.000	0.000	0.000	0.000	0.000	0.000	0.034	0.000	0.000	0.000	0.000	0.009	0.000	0.000
Li														0.811	0.705	-0.266	0.612	0.735	-0.019	0.875	-0.508	0.714	0.829	-0.134	-0.282	0.862
														0.000	0.000	0.001	0.000	0.000	0.818	0.000	0.000	0.000	0.000	0.101	0.000	0.000
Mg															0.868	-0.531	0.590	0.503	-0.276	0.901	-0.625	0.597	0.921	-0.385	-0.610	0.844
															0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn																-0,707	0.482	0.329	-0.512	0.852	-0,706	0.396	0.945	-0.487	-0.772	0.859
																0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Me																	-0.143	0.131	0.755	-0.511	0.751	0.008	-0.581	0.619	0.860	-0.458
																	0.080	0.111	0.000	0.000	0.000	0.920	0.000	0.000	0.000	0.000
																	0.000	0.111	0.000	0.000	0.000	0.720	0.000	0.000	5.000	0.000

		-	Juii	X LA		unu	the	516	mm	cun		<i>)</i> vu	iiuo	,	nun	c) 01	u		iiciu	1011.						
	Al	As	Ba	Be	Ca	Cd	Со	Cu	Cr	Cs	Fe	K	Li	Mg	Mn	Mo	Ni	Р	Pb	Rb	Se	Sr	Tl	U	V	Zn
Ni																		0.540	0.097	0.536	-0.262	0.563	0.553	-0.080	-0.158	0.609
																		0.000	0.237	0.000	0.001	0.000	0.000	0.329	0.054	0.000
Р																			0.375	0.556	-0.139	0.772	0.499	0.040	0.112	0.622
																			0.000	0.000	0.090	0.000	0.000	0.631	0.171	0.000
Pb																				-0.303	0.689	0.395	-0.323	0.619	0.772	-0.227
																				0.000	0.000	0.000	0.000	0.000	0.000	0.005
Rb																					-0.627	0.549	0.926	-0.289	-0.545	0.880
																					0.000	0.000	0.000	0.000	0.000	0.000
Se																						-0.139	-0.630	0.655	0.828	-0.546
																						0.089	0.000	0.000	0.000	0.000
Sr																							0.560	-0.020	0.021	0.653
																							0.000	0.806	0.799	0.000
Tl																								-0.374	-0.660	0.891
																								0.000	0.000	0.000
U																									0.705	-0.334
																									0.000	0.000
v																										-0.458
																										0.000

Supplementary Table 6. Pearson correlation coefficients between elements in the Amazonian Dark Earth and the significance (p values in italic) of each correlation.