CHEMICAL SIGNATURES OF ARCHAEOLOGICAL SOILS

Ph.D. Thesis

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Chemical Signatures of Archaeological Soils
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Declaration

The author hereby declares that this thesis titled "Chemical signatures of archaeological soils" includes original text written independently by the author except for chapters 2-6 where all the co-authors of included articles were declared and all of them agreed that the articles will be published as a part of this thesis. Moreover, the author declares that all sources used have been quoted and acknowledged employing the complete reference list in the chapter General references according to the citation rules of the FZP. The author states that the work has not been submitted for any other degree to this or any other university within and outside the Czech Republic.

In Prague

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Michael Opare Asare

Abstract

Past human activities are connected with the accumulation of elements (anthropogenically-induced), and to some extent, alter the physical attributes of archaeological soils. The classes of archaeological soils (e.g., dark earth, settlement soil, and necrosol) relate to the kind of human activities, physical characteristics, and geographical location. This study adopted multi-analytical methodologies to trace the extent of past anthropogenic imprints of the physicochemical properties of soils from past human habitations and answer many unresolved questions, e.g., (i) can the chemical signatures of medieval settlements in soils be masked by recent mineral fertilizer applications? (ii) which method is most appropriate in calculating enrichment factors of elements? (iii) which elements best indicate soft tissue and bone decomposition of buried human bodies? Different types of Archaeological dark earth (ADE) soil: European dark earth (EDE) and African dark earth (AfDE) were characterized, according to the dark color, corroborated by homogenously-mixed high amounts of charcoal. The ADE soils were chemically composed of relatively neutral reactions (pH [H_2O]) and a substantial accumulation of organic C and total N, P, Ca, Mg, S, Mn, Fe, Cu, Zn, Sr, and Rb. Additionally, the ADE soils have a high accumulation of available P, K, Ca, S, Cu, and Zn compared to neighboring soils of the same geological substrates, without the mark of past human activities. The intensive application of mineral fertilizers can not easily mask the chemical signatures obtained from EDE, even after thousands of years of abandonment of the site. The total P, Ca, Mn, Fe, Cu, Zn, Sr, and Rb contents were 3-14 times higher in EDE and AfDE compared to 2-3 times reported for *Terra preta* (Amazonian dark earth), indicating probably high intensity and duration of human activities and the size of the settlements. Past human activities were well-reflected by the accumulation of total P and trace elements (Mn, Cu, Zn, and Sr) in EDE and AfDE in both the Tropics and Temperate zone. The accumulation of the elements related to organic wastes, excrement, and biomass ash depositions, as ashes have a high content of elements with relatively low releasability (plant-available content ÷ total content), thus can retain in archaeological soils for millennia. In estimating the enrichment factors of elements in soils, even from different geographical regions, the total element content is preferred, especially in the field for geoarchaeological purposes. It is difficult to provide straightforward inferences as the contents of plant-available elements are affected by many soil chemical properties, which may be hard to perform in the field. The study also revealed that the decomposition of buried human bodies can cause significant enrichment of necrosols by several elements for thousands of years. However, in grave infills, Zn and P contents are the most suitable indicators of soft tissues and bone decompositions, respectively, within space and time. Although some types of archaeological soils so far are neglected, these soils remain an adventure for sustainable agricultural production and a vital repertoire of information for archaeological, geoarchaeological, and soil science studies.

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CHAPTER 1

General Introduction

Contemporary arable field (Archaeological dark earth soil) on Neolithic to High Middle Ages (early 1200 AD) settlement, Dřevíč hillfort, Czech Republic.

Archaeological soil (archaeo-anthrosol) is a class of anthropogenic soils developed as a result of past human activities (FAO, 2015). The genesis of archaeo-anthrosols development dated from prehistory up to Medieval ages and beyond. Anthrosols from past human activities are characterized by the accumulation, and to some extent, the depletion of anthropogenically-induced elements (Lehmann et al., 2003; Golyeva et al., 2012; 2016; Šmejda et al., 2017, 2018). Past human activities can change the soil system as the natural fluxes of elements are disturbed, from the input of bio-essential chemical compounds like phosphorous (P), potassium (K), calcium (Ca), zinc (Zn), copper (Cu), or changes in the configuration of chemical compounds (Entwistle et al., 1998, 2000; Fleisher and Sulas, 2015). These changes are stored in the soil archive and detectable even after thousands of years of abandonment of sites. The complexity of soil-forming processes (e.g., post-depositional soil processes) and soil chemistry in space and time requires robust analytical data and reference materials to reflect these changes (Wilson et al., 2009). Nevertheless, the rate of inorganic and organic matter inclusions by past human activities to soils are higher than the removal by natural soil processes.

Although different archaeological timelines relate to the onset of peculiar human activities leading to the formation of different archaeo-anthrosols, some activities can be considered universal. For example, the deposition of organic wastes, biomass ashes, together with agricultural practices, craft, and manuring of arable fields were frequent human activities in past settlement sites (Parnell et al., 2002; Knudson et al., 2004; Wilson et al., 2008). Meanwhile, mining and metallurgy thrived in specific locations (Grattan et al., 2013; Lopez-Merino et al., 2014). The form (i.e., the total or plant-available) and level of element accumulation have a direct bearing on the type of human activity and may influence its persistence in the ecosystem. Although different types of ancient human activities are connected to the accumulation of specific elements, there are no such studies that quantitatively assessed the exact level of their inputs from an archaeological perspective. For example, Hejcman et al. (20110) attributed high biomass production in an ancient waste pit abandoned after thousands of years in the Czech Republic to the deposition of biomass ashes as ashes contain a high accumulation of P, Ca, K, and many other elements. Thus, a detailed elemental analysis of such organic wastes is vital. Meanwhile, there are no studies that explore why the elements accumulated in biomass ashes persist-in the soil over centuries. Such studies can further provide the fertilizer values of biomass ashes and their suitability in applying on arable fields.

Although elements such as P was previously used as traditional elements to mark the input of human activities, it can mostly be affected by post-depositional processes such as gleying, pH, podzolization, and leaching, which influence its retention and distribution (Ottaway and Matthews, 1988; Pierce et al., 1998). Hence, pertinent in the identification of other elements to reliably trace anthropogenic input in the pedo-stratigraphy across the world. Additionally, the use of anthropogenically-induced elements in soils in tracing past anthropogenic imprints is a relatively new approach especially in many parts of Africa over previous field surveys for tangible artifacts such as collapsed clay/daub houses and wooden crafts. The use of artifacts in such environmental conditions to detect ancient existence can be problematic due to their complete decomposition within some time frame. Hence, this study hypothesized that anthropogenically-induced elements in soils may not necessarily be different in abandoned settlement sites even with different geographical and environmental conditions.

The different types of archaeological soil, for example, cemetery (necrosols), settlement, and dark earth soils are related to the cultural settings, type of activities, and to some extent the climatic conditions of a given locality. For example, a characteristic physical feature of Archaeological dark earth soils (ADE) is the black, dark brown, or dark grey color (Lehmann et al., 2003; Solomon et al., 2016). However, in some regions, ancient settlement soils (settlement soil) are light in color without any accumulation of black soil organic matter. Although the large-scale accumulation of P, K, Zn, and Cu was recorded in former settlement site in comparison to adjacent rangelands and arable fields at Tel Burna in Israel, even more than 2000 years after its abandonment, the color of the soil was light grey (Šmejda et al., 2017). Thus, may indicate that ADEs can hardly develop in semi-arid and arid regions, probably because of the high decomposition rate of accumulated organic matter. Different types of Archaeological dark earth (e.g., European, African, and Amazonian (*terra preta*) dark earth soils) can be traced according to their geographical locations. The unique physical (such as porosity and grain size distribution) and chemical (e.g., soil reactions, cation exchange capacity, and element contents) attributes of ADEs (Lehmann et al., 2003) have, therefore, called for more studies in the tropics and temperate regions serving the purpose sustainable agricultural production (Glaser et al., 2001; Glaser, 2007). Moreover, the extent of elemental accumulation in soils from ancient localities in connection with the duration of settlement activities is so far not studied. For instance, several authors have studied the development of archaeo-anthrosols (e.g., ADEs from the Amazon) taking thousands of years for their development (Whitehead et al., 2010; Nicosia et al., 2012). However, at what duration ADE with substantial elemental accumulation develops is still missing in the academic discourse. Meanwhile, necrosols have been a neglected category by soil scientists without any multi-elemental study of prehistoric graves. Few studies relating to prehistoric graves were only connected with the analyses of P in grave infills (Hlavica et al., 2011; Limburský, 2015). Thus, several questions, such as how long can the buried human body decompose in soils? is still unresolved. In archaeological studies, different anatomical positioning/orientation of the dead body can also provide some knowledge on the culture, internment, and burial practices of a group of people.

In the last decade to date, studies on the geochemistry of archaeological soils in the hinterlands drew the patterns between ancient land use and management (Storozum et al., 2020). The elemental composition of archaeological soils in connection with sustainable agricultural management is not well-known. Studies on the elemental composition of most archaeological soils relate to the total element contents (Šmejda et al., 2017; Horák et al., 2018). However, total element content is of little value in the determination of element deficiencies of plants. Therefore, the fertility of archaeo-anthrosols on current arable fields requires a detailed analysis of available nutrients to plants. The analysis of the content of plant-available elements in arable fields of previous settlements can further provide knowledge on the required amount of mineral fertilizers application.

Several environmental factors influence the preservation of anthropogenic pedoturbations. For example, the topography of ancient sites can reduce the spatial dispersion of chemical disturbances in soil. However, soil chemistry has come to offer a steadily more important role in tracing the geochemical patterns in archaeological localities. Several analytical techniques have enabled the identification of archaeological prospection, where disciplines, such as environmental archaeology, geoarchaeology, and archaeo-pedology, take part. Chemical data are becoming more easily acquired by several analytical techniques, enabling the acquisition of large amounts of pragmatic data. However, to theoretically and practically understand these data, traditionally managed indigenous soils or sites active for long enough periods are compared to a background soil (control), where disturbances have little or no influence. Even with the increasing scope of geochemistry in archaeology, many localities remained abandoned. Once a site gets deserted, post-occupation biogeochemical processes, e.g., mineral weathering, litterfall, and soil leaching commence, which may transform the previously occupied surfaces (Totsche et al., 2010). These processes can blur the imprint of archaeological features and render their identification problematic, at the scale of centuries. Yet, occupational surfaces preserve, to some extent, the physicochemical signatures of past human activities. Pedoturbations, anthro-perturbations, e.g., through plowing, digging, can stop or redirect the development of soil. Meanwhile, after the abandonment of sites, the progressive pathway takes over as post-occupational processes get established, resulting in surface soil containing the chemical and mineralogical imprints or both genesis vectors.

However, several multi-analytical techniques can be adopted to trace the chemical imprints of past human activities in archaeo-anthrosols in the absence of visible artifacts (archaeological remains). Different analytical approaches from dry (using X-Ray fluorescence spectrometry) to wet (e.g., extraction by different acids) methods are currently in use to determine the content of total and plant-available elements, respectively, in archaeological soils (Holliday and Gartner, 2014; Horák et al., 2018). However, which method is most suitable in estimating the enrichment factors of elements for geo-archaeological studies in the field remains not well-known and has evoked amounting concerns. The enrichment factor of elements is estimated by a direct comparison of the level of each element in the anthrosols to the control unaffected by past human activities. In most cases, the study adopted the use of portable X-ray fluorescence spectrometry (pXRF) for the analysis of total or near-total element contents in soils due to its cost-effective, accurate, and precise measurements (Šmejda et al., 2017). That said, the use of X-Ray fluorescence spectrometry in the analysis of soils is relatively new, especially in archaeological studies. Notwithstanding, it has been in use in the last decades for environmental monitoring (Kalnicky and

Singhvi 2001; Ulmanu et al. 2011; Parsons et al. 2012), but it is still experimental to some degree, and the instrument methodologically contested (Speakman and Shackley 2013). However, it is increasingly becoming established as an efficient and effective means for multi-elemental analysis with minimal sample preparation. The use of the pXRF is supported widely by a rapidly increasing volume of published studies on archaeology and agricultural soils (Grattan et al. 2014; Šmejda et al. 2017).

In the case of available elements, the Mehlich-3 (M-3) extraction was used as a conventional methodology for the arable, forest, and even archaeological soil analysis (see Holliday and Gartner, 2007).

In the context of this study, I mainly contrast the chemical properties of soils from past localities in the temperate zone and the tropics with reference soils not affected by past human activities to understand how humans alter their surroundings through space and time. The properties of previous human sites with undisturbed soil can define the chemical and mineralogical signatures. The investigated sites cover the periods from prehistory to Medieval age up to sub-recent timelines in the tropical and temperate zones.

Owing to this, large-scale mapping of the chemical composition of the upper and subsoil layers of archaeological localities was studied aiming to; (a) To determine chemical signatures of ancient soils compared with modern cultivated and non-cultivated soils (Chapter 2-4), (b) To compare the effect of modern mineral fertilizer application and signatures of medieval settlement activities on arable soils (Chapter 2), (c) To determine the elements suitable to indicate the impact of past human activities on current arable fields in different geographical locations (Chapter 2-4), (d) To determine which method is more suitable in estimating the enrichment factors of elements, especially for geoarchaeological purposes (Chapter 2-4), (h) To determine the elemental composition of wood ashes as well as the releasability (proportion of available elements from the total) and whether they are suitable fertilizers for agricultural soils (Chapter 5).

Lastly, the next part of the thesis (Chapter 6) is connected to the analysis of the elemental composition of necrosol to evaluate; (g) The effect of the prehistoric buried human body on the elemental composition of the soil and (h) which elements best indicate the decomposition of the human body tissues and bones.

CHAPTER 2

A medieval hillfort as an island of extraordinary fertile Archaeological Dark Earth soil in the Czech Republic

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Michael O. Asare (third from right) in front of the Baroque chapel of St. Wenceslas, Dřevíč hillfort, Czech Republic.

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ORIGINAL ARTICLE

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Abstract

Archaeological Dark Earth soil is a category of archaeological anthrosols that has gained much attention because it exhibits higher nutrient content and organic matter stocks and a characteristic dark color and enables higher crop yields in comparison to neighboring soil. However, much is unknown about the chemical properties of Archaeological Dark Earth soils in Central Europe. Therefore, we studied a European Dark Earth (EDE) soil, a type of Archaeological Dark Earth soil, in the territory of the early medieval Drěvíč hillfort, Czech Republic, aiming to compare the chemical properties of EDE with a control soil unaffected by settlement activities. The black color of EDE soil contrasted highly with the light grey Cambisol of the control. Soil reaction and total element contents (N, P, Ca, Mn, Fe, Al, Cu, Zn, Sr, and Rb) were substantially larger in the EDE soil compared with the control and vice versa in the case of the C/N ratio. Also, the content of plant-available (Mehlich III) P, Ca, K, and Mg was larger in the EDE soil than in the control. In contrast to Ca, plant-available and total P and K were not well correlated. Total element contents are highly suitable for geoarchaeological purposes as enrichment factors can be easily calculated. The increased contents of these elements, together with pieces of charcoal visible in the EDE soil, indicate the deposition of organic waste and biomass ash during the existence of the hillfort. Thus, medieval hill- forts can represent extraordinary nutrient-rich islands in the cultural landscape of Central Europe. The chemical signatures generated by past settlement activities are so intense that they cannot easily be masked by short-term intensive application of mineral fertilizers.

Highlights

- Settlement activities increased soil pH and the content of anthropogenic elements.
- Enrichment by P, Ca, Mn, Fe, Al, Zn, Cu, Sr, and Rb may indicate settlement activities.
- Analysis of total element contents is suitable for geoarchaeological purposes.
- Application of mineral fertilizers cannot easily mask the signatures of medieval settlement activities.

Keywords
Anthrosol, biomass ash, Cambisol, dark earth, macro element, medieval, microelement, mineral fertilizer, trace element

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INTRODUCTION

Past settlement activities are related to the accumulation of different elements such as phosphorus (P), calcium (Ca), potassium (K), manganese (Mn), iron (Fe), and copper (Cu) (referred to as “anthropogenic elements”) in soil (Wells et al., 2000; Fernández et al., 2002; Gojda & Hejcman, 2012), and long-term intensive settlement activities can result in the formation of archaeological anthrosols (FAO, 2015; Howard, 2017). These activities include domestic/organic waste disposal, craft production, prescribed burning of the forest, farming, animal husbandry, and agriculture (Entwistle et al., 1998; Devos et al., 2011; Hejcman et al., 2013a, 2013b). Chemical signatures generated from settlement activities are site-specific and are often difficult to interpret due to the combined effects of natural variations in background geology, soil-forming processes, site-use history, and methodological factors (Oonk et al., 2009; Wilson et al., 2009). Nevertheless, soil chemical analyses have become increasingly useful to help elucidate ancient settlement patterns (Holliday, 2004; Goldberg & Macphail, 2006; Ackermann et al., 2015). This is mainly because anthropogenic activities alter the natural sediments in recognizable ways (Holliday, 2004), forming new soil characteristics that are traceable through multi- analytical methodologies (Šmejda et al., 2017).

Moreover, past anthropogenic activities have resulted in the formation of dark soil layers known as Archaeological Dark Earth soil (FAO, 2015; Howard, 2017), which are characterized by large amounts of charcoal and high plant- nutrient availability (Glaser & Birk, 2011; Nicosia et al., 2012). These soils are associated with high and stable organic matter contents, microbial abundance, reduced acidity and increased contents of both total and plant-available (Pav) Ca, P, Mn, and zinc (Zn) compared to the surrounding soils (Lehmann et al., 2003; Glaser et al., 2001; WinklerPrins, 2014; Lucheta et al., 2017). Archaeological Dark Earth soils have formed on Acrisols, Arenosols, Cambisols, Ferralsols, Latosols, Luvisols, Nitisols, and Podzols (Lehmann et al., 2003; Fairhead & Leach, 2009; Solomon et al., 2016). The identification and characterization of most Archaeological Dark Earth soils are connected with origin (Fairhead & Leach, 2009; Solomon et al., 2016) and formation processes (Macphail & Courty, 1985). The formation of Archaeological Dark Earth soils is associated with the unintentional deposition of organic and inorganic waste, as well as intentional amendments to improve home gardens and crop fields (Pape, 1970; Hecht, 2003; Schmidt & Heckenberger, 2009; Giani et al., 2014; van Gils & Mölder, 2019). Different types of Archaeological Dark Earth soils identified and dated so far include Amazonian Dark Earth (Terra Preta), African Dark Earth (AfDE), European Dark Earth (EDE), and Plaggen (WinklerPrins, 2014; Solomon et al., 2016). Terra preta is the legacy of the former settlement sites of pre-Columbian farmers (WinklerPrins, 2014). On the other hand, AfDEs formed around the edges of nucleated villages and ancient towns, especially in the rainforest zones (Solomon et al., 2016).

The time of origin of EDE soil mostly spans from the Roman to Medieval periods (Macphail et al., 2003; Nicosia et al., 2012). The formation of EDE is often related to repeated destruction of forts during medieval warfare, including the burning of ramparts and settlement timbers, wattle and thatched houses, crops, and wooden tools, all of which could result in charcoal in the soil (Macphail & Courty, 1985; Nicosia et al., 2012). Although EDE and plaggic soils originated from Europe during the medieval ages, the latter resulted from the fertilization of arable lands with manure and plaggen sods cut from the organic Ah horizon of surrounding soils (Pape, 1970; Giani et al., 2014; van Gils & Mölder, 2019). What is still missing is the chemical signatures of EDE soil formed on hillforts; that is, defended settlements, surrounded by one or more circuits of banks and ditches and generally placed on hilltops, ridges, and promontories (Vengalis, 2016). Archaeological Dark Earth soils may contain two to three times higher P, Ca, K, and Mn compared to surrounding soils (Kern & Kämpf, 1989; Glaser, 2007; Nicosia et al., 2012; WinklerPrins, 2014). However, there is no information regarding the extent to which mineral fertilizer application can interfere with the chemical signatures of medieval settlement activities.

According to our knowledge, there is no scientific paper comparing the chemical signatures of medieval settlement activities with the signatures generated by modern fertilizer applications. To study this, we analyzed soil from the grassland experiment established on the same geological substrate as the studied hillfort with a developed EDE soil. Also, different analytical approaches are used for the analysis of Archaeological Dark Earth soils to determine the plant-available to total contents of “anthropogenic elements” (see Holliday & Gartner, 2007). In the Czech Republic, the method used for the testing of plant-available elements in agricultural and forest soils is Mehlich III extraction (Mehlich, 1984), which was successfully used for the analyses of archaeological soils (Hejcman et al., 2011, 2012a, 2012b, 2013a, 2013b). We, therefore, used this method and compared the plant-available contents of P, K, and Ca with total contents of the same elements obtained by energy-dispersed portable X-ray fluorescence spectrometry (pXRF).

We tried to answer the following research questions.

(a) To what extent is EDE soil enriched by anthropogenic elements, especially by macro- (carbon (C), nitrogen (N), P, K, Ca, sulphur (S) and magnesium (Mg)), micro- (Mn, Fe, Cu, and Zn) and trace elements (strontium (Sr), rubidium (Rb) and lead (Pb)), in comparison to the control soil on the same geological substrate? (b) Can 5 years of intensive NPK fertilizer application increase the contents of anthropogenic elements to the same level as medieval settlement activities? (c) Can the recent application of mineral fertilizers mask the chemical signatures of medieval settlement activities? (d) Are there, in addition to traditionally determined elements in geoarchaeological studies, other elements that can indicate medieval settlement activities? (e) To what extent are comparable patterns obtained by the analysis of plant-available and total contents of selected elements, and which method is more suitable for geoarchaeological purposes?

2 MATERIALS AND METHODS

2.1 Study area

The Dřevíč hillfort (50°14‘51‘‘N, 13°49‘33‘‘E; Figure S1) is located 50 km west of Prague and 1 km SE of Kozojedy village in the Rakovník district, Czech Republic. The size of the fortified area with the occurrence of EDE soil is 11 ha. The elevation of the fortified area ranges from 455 to 464 m a. s. l., with mean annual temperature and precipitation of 7.1○C and 550 mm, respectively.

To compare the EDE soil with the original soil not modified by settlement activities, we took advantage of a fertilizer experiment (see Hejcman et al., 2012a for a detailed description of the fertilizer experiment) established on the same marlstone bedrock (Chytrý, 2012; Czech Geological Survey, 2012) and at a similar elevation (480 m a. s. l.). The fertilizer experiment site was close to the former forest office “Tok167” in the village of Mšec (50°12‘24‘‘N, 13° 51‘40‘‘E; Figure S1), located 6 km SE from the Dřevíč hillfort. The experiment ran from 2007 to 2011 with five treatments: unfertilized control and application of mineral N, P, NP, and NPK fertilizers (see Figure S2) at annual application rates of N, P, and K at 300, 80, and 200 kg ha^{-1}, respectively. In the late 1990s, the fertilizer experiment site was managed as a species-poor meadow established on previously arable land with the application of mineral fertilizer. Farmyard manure was occasionally applied to fertilize the meadow before the experiment started. The application of conventional mineral fertilizers on the arable field in the hillfort and the area of the fertilizer experiment was similar, at least in the last 50 years before the establishment of the experiment in 2007. However, during the period of the fertilizer experiment in Mšec, the mean annual application of mineral N, P, and K fertilizers in the hillfort was 120, 10, and 60 kg N, P, and K per year, respectively, using the same fertilizers as in the fertilized experiment.

The soil in the fertilizer experiment site was Luvic Cambisol, with a light grey-coloured A horizon. The color of the soil in the hillfort was black, surrounded by Modal Cambisol in the valleys, visually identified as reddish-brown (Figure 1a and Table 1; Němeček & Kozák, 2005). However, we did not sample the Modal Cambisol as it developed on much older red sandstone sediment and, therefore, has a different elemental composition

2.2 Study site description

The Dřevíč hillfort was an early to high medieval hillfort from the 8th to 13th century AD (Profantová et al., 2012). In the 12th century AD, the fortified settlement was the center of administration of the neighbouring regions (Kabát & Moucha, 1971; Čtverák et al., 2003). The internal area of the hillfort, with homogeneously mixed pottery fragments in the soil due to ploughing, has been used as an arable field at least for the last 200 years, and probably much longer. Despite this, the EDE soil has not eroded because of no or slight inclination of the arable field in the central part of the hillfort (Figure 1b). Still detectable archaeological features in the landscape were collapsed ramparts made from marlstone and soil (Figure 1c) and relicts of two gates, of which the southern one is called Iron Gate. The Baroque chapel of St. Wenceslas in the northern part of the fortified area is on the position of the formerly much larger church that existed during the use of the hillfort (Figure 1d). An early medieval graveyard is in the surroundings of the chapel.

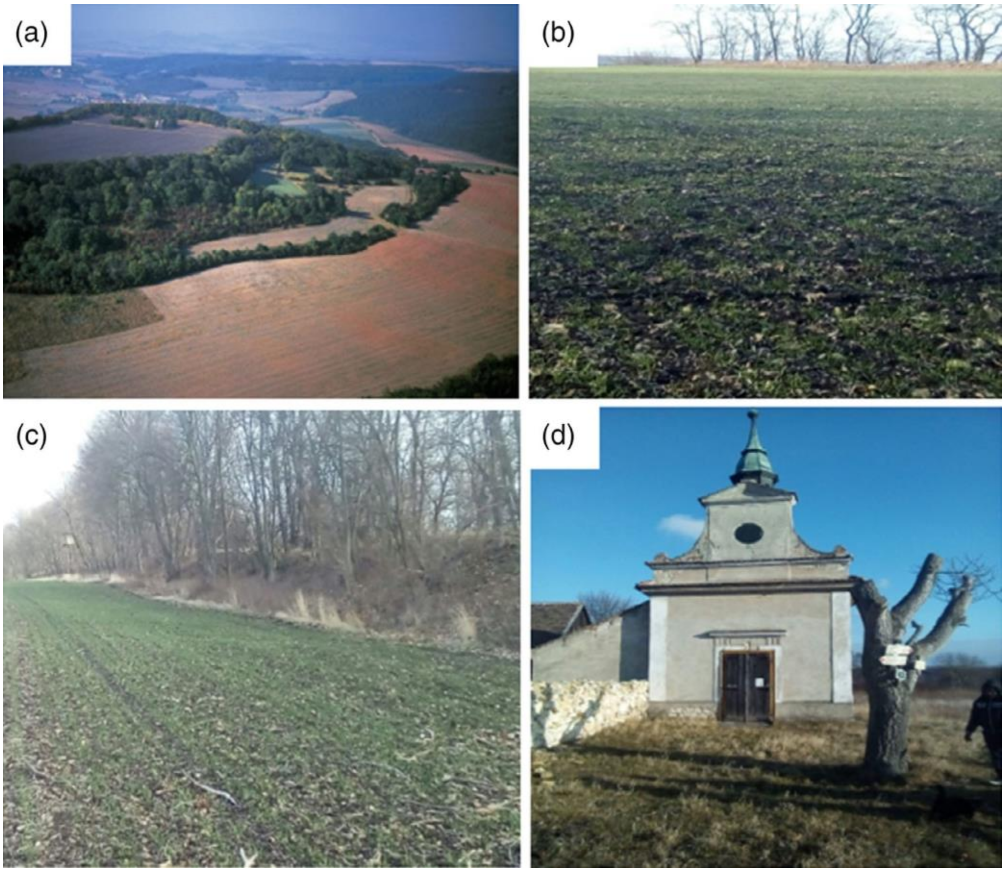

FIGURE 1 Relicts of the deserted Dřevícˇ hillfort, Czech Republic. (a) Aerial view of Dřevícˇ hillfort, whose internal area with early to high medieval settlement activities is characterized by black arable soil (European Dark Earth soil), surrounded by trees on the rampart and surrounding slopes. Arable soil in the surroundings of the hillfort is reddish-brown coloured (photo by Zdeneˇ Smrž). (b) The flat area of the internal area of the hillfort on a marlstone bedrock is used as an arable field (photo by Michael O. Asare). (c) Collapsed fortification: rampart made from marlstones and soil currently covered by trees and shrubs (photo by Michael O. Asare). (d) Baroque chapel of St. Wenceslas is at the location of the former medieval church (photo by Michael O. Asare).

The Drěvíč hillfort was inhabited during the Neolithic, Late Bronze Age Knovíz Culture (1300–950 BC), Early Iron Age Hallstatt period (750–450 BC), and Early Middle (700–1100 AD) to High Middle Ages (early 1200 AD) (Sábl, 1973; Profantová et al., 2012), confirmed by evidence from discovered artefacts such as stone battle axes, split tools, pottery fragments, S-shaped earrings and coins from the 10th and 11th centuries AD, and the graveyard (Sábl, 1973; Profantová et al., 2012). The first written record about the hillfort comes from the Czech chronicler Kosmas (1045–1125 AD) and refers to the Dřevícˇ hillfort as a well-fortified castle in the year 1004.

2.3 Sampling design

Soil samples from the 0–10-cm depth were collected from the internal area of the hillfort and the fertilizer experiment site in September 2011. Soil samples collected from both sites were compared in terms of their chemical signatures. We divided the internal area of the hillfort with a developed EDE soil into four quarters. For this, a mixed soil sample from each soil layer of each quarter was randomly collected from the hillfort. As the fertilizer experiment was established in four complete randomized blocks of five treatments (with a total of 20 plots; Figure S2), we randomly collected a mixed soil sample from each fertilizer treatment. Each mixed soil sample was composed of 10 subsamples taken with a soil probe. In total, 24 mixed soil samples were collected. We collected mixed samples as an accepted procedure to average out short-range variation, making the results, and generalization more reliable.

2.4 Soil sampling

All the soil samples were air-dried and subsequently oven-dried at 40°C for 24 hr. Soil samples were ground in a porcelain mortar and passed through a 2-mm sieve after the removal of roots and debris.

2.4.1 Particle size distribution

We analysed 10 g of each soil sample to determine the percentage particle sizes. The particle size distribution of soil samples from the hillfort and the fertilizer experiment was determined using sieves with 2, 1, 0.5, 0.25, 0.1, 0.05, and 0.002 mm (sieve analysis) and compared.

2.4.2 Soil chemical analysis

Total contents of P, K, Ca, S, Mn, Fe, Al, Si, Cu, Zn, Sr, Rb, and Pb, were determined via pXRF analyser -Delta Professional, manufactured by Olympus (Waltham, MA, USA). The Soil Geochem mode was used for all measurements. The pXRF is used to obtain total or near-total contents of elements in the matrix (see Canti & Huisman, 2015, for the application of pXRF spectrometer). The quality of our device result was successfully tested by the BAS Rudice Ltd Company, Blansko, Czech Republic (https://www.bas.cz) on 55 reference materials (e.g., SRM 2709a, 2710a, 2711a, OREAS 161, 164, 166, RTC 405, 408). The pXRF performed each measurement over a period of 1 min, with 30 s of a 10-kV beam and 30 s of a 40-kV beam; each sample measured was in triplicate and the values were averaged. The S content was not determined (three times) in all samples as it was below the detection limit, and thus missing values were replaced by half of the detection limit. However, the total contents of elements such as Mg, Cl, Cr, Mo, Co, Ni, Se, Sb, Y, Cd, Sn, Ti, In, Sn, Sb, Ba, W, Bi, Ag, Tl, Au, Th, and Hg in all samples were omitted from further analysis as they were either not detected or above the detection limit only in a few cases. The contents of organic C and total N in all soil samples were measured using a Skalar Primacs SNC-100 analyzer produced by Skalar (Breda, The Netherlands). The pH (H2O) of all soil samples was determined at ratio 1:1 (soil/water) using a Voltcraft PH-100 ATC pH meter (pH 212; I & CS spol. s r.o., Czech Republic).

The reliability of data obtained by the pXRF was assessed by randomly selecting five soil samples from the hillfort (*n* = 2) and the fertilizer experiment (*n* = 3). These samples were analysed to determine the total contents of P, K, Ca, S, Mn, Fe, Si, Al, Cu, Zn, Sr, Rb, and Pb in an independent accredited laboratory where extractions of elements in Aqua regia extract (3 ml HCl and 1 ml HNO3, International Organization for Standardization USEPA 3052) were analysed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700x, Agilent Technologies Inc., Santa Clara, CA, USA). Additionally, the content of Pav (Mehlich III extraction; Mehlich, 1984) P, K, Ca, and Mg was determined using the same ICP-MS as in the case of the total contents of elements.

2.5 Data analysis

Data for soil particle sizes and chemical properties were tested using the Shapiro–Wilk W-test for normality and met the assumptions for the use of parametric tests. One-way ANOVA was used to evaluate the differences in the soil chemical properties between all analysed sites. In the case of significant ANOVA results, we applied a post hoc comparison using Tukey´s honest significant difference (HSD) test to identify significant differences among the sites. To analyse the relationship between the contents of different elements as well as between elements obtained from the pXRF, Mehlich III, and Aqua regia ICP-MS data, we used Pearson's correlation. The software package STATISTICA 13.3 (www.statistica.io) was used to perform all statistical analyses in this study.

3 RESULTS

3.1 Quality of the pXRF dataset

The results obtained from the comparison of pXRF and Aqua regia ICP-MS revealed a strong linear correlation among the total contents of the studied elements. We obtained the following correlations for P (r = 0.99, p < .001), K (r = 0.97, p < .001), Ca (r = 0.99, p < .001), S (r = 0.92, p = .024), Fe (r = 0.96, p < .001), Mn (r = 0.99, p = .001), Al (r = 0.97, p < .001), Sr (r = 0.99, p < .001), Rb (r = 0.98, p = .002), Cu (r = 0.99, p = .005), Zn (r = 0.99, p < .001) and Pb (r = 0.94, p = .052). The lowest correlation coefficient was recorded for total silica (Si) (r = 0.55, p = .337), which is not fully soluble in Aqua regia. Based on the comparison of the contents obtained by both methods, we conclude that pXRF data were of adequate precision for this study (Figures S3-S5; Šmejda et al., 2017, 2018).

3.2 Particle size distribution and other physical characteristics of soil

Except for fractions of very coarse particles (≥2 mm), there were no differences in the proportion of other size fractions of soil among the hillfort and the fertilizer treatments (Table 1). The proportions of ≥2, <2–1, <1–0.5, <0.5–0.25, <0.25–0.01, <0.01–0.05, <0.05–0.002 and <0.002 mm fractions across all sites were 12.1, 20.8, 22, 10.9, 5.4, 3.8, 11.2 and 13.7%, respectively. Although not significant, there were marginally larger proportions of the very fine fraction of soil (<0.25 to

<0.002 mm) in the hillfort compared to the fertilizer experiment. The soil texture was mostly sandy loam with sub-rounded particles (Table 1).

3.3 Soil chemical properties

Of the 38 analysed elements, only total P, K, Ca, S, Mn, Fe, Al, Si, Sr, Rb, Cu, Zn, and Pb, together with organic C and total N, were identified as relevant for this study as they were above detection limits. There was also a clear difference between the content of most of the studied elements in the hillfort and the fertilizer experiment. Significantly higher pH values and contents of total N, P, Ca, Mn, Fe, Al, Sr, Rb, Cu, and Zn, were recorded in the hillfort in comparison to all treatments of the fertilizer experiment (Figures 2–6). The soil was neutral in the hillfort and slightly to moderately acidic in the fertilizer experiment (Figure 2a). Contents of total N, P, Ca, Mn, Fe, aluminium (Al), Sr, Rb, Cu, and Zn were enriched by 40, 350, 900, 100, 140, 100, 35, 40, 30, and 90%, respectively, in the hillfort in comparison to the unfertilized control of the fertilizer experiment. Except for total S, there were no significant differences in the contents of elements among the fertilizer treatments. However, the N treatment recorded the lowest total S content in comparison to the other fertilizer treatments and the hillfort (Figure 3d). On the other hand, a significantly lower C/N ratio, as well as total Si and Pb contents, were recorded in the hillfort compared to the fertilizer experiment (Figures 2d, 4d, and 6). There were no significant differences between soils from them hillfort and the fertilizer experiment in terms of C and total K contents (Figures 2b and 3b). Except for the P-fertilizer treatment, there was a significantly larger content of Pav P in the hillfort compared to the other fertilizer treatments. The Pav K, Ca and Mg contents were significantly greater in the hillfort compared to all treatments of the fertilizer experiment (Table 2). The content of total P positively correlated with total Al, Mn, Fe, Cu, Sr, and Rb contents (Figures S6–S8).

The correlation between total P and Mn was the strongest ($r = 0.86$, $p < .001$; Figure S6a). The content of total Si was correlated negatively with total Ca and Fe contents (Figures S7c and S7d). We recorded no significant correlation between the contents of total and Pav P ($r = 0.31$, $p = .136$) and Pav K ($r = 0.28$, $p = .183$). There was a significant correlation between the contents of total and Pav Ca ($r = 0.9$, $p < .001$; Figure S9).

TABLE 1 Particle size distribution (mean percentage ± SD) and physical properties of the upper 10-cm soil layers from the Dřevícˇ hillfort and the fertilizer experiment (unfertilized control, N, P, NP, and NPK treatments)

Site use	Particle size distribution (%)								Colour ^{a}	Texture	Consistency	Description of soil particles
	≥2 mm	**<2–1 mm**	**<1–0.5 mm**	**<0.5–0.25 mm**	**<0.25–0.1 mm**	**<0.01–0.05 mm**	**<0.05–0.002 mm**	**<0.002 mm**				
Dřevícˇ Hillfort	10.1 ± 0.1^{a}	20.5 ± 0.1^{a}	22.2 ± 0.1^{a}	10.5 ± 0.4^{a}	6.0 ± 0.3^{a}	4.1 ± 0.1^{a}	12 ± 0.2^{a}	14.5 ± 0.2^{a}	Black (7.5YR 2.5/1)	Sandy loam + pottery fragments + Charcoal	Firm, slightly sticky + plastic	Mostly rounded black humus-rich sediment
Fertilizer experiment												
Unfertilized Control	12 ± 0.1^{b}	21 ± 0.3^{a}	22.3 ± 0.6^{a}	10.1 ± 0.05^{a}	5.1 ± 0.7^{a}	3.7 ± 0.01^{a}	11.1 ± 0.1^{a}	13.7 ± 0.2^{a}	Light grey (7.5YR 7/1)	Sandy loam	Firm, slightly sticky + slightly plastic	Mostly sub-rounded particles
N treatment	12.1 ± 0.1^{b}	21.1 ± 0.2^{a}	22.2 ± 0.2^{a}	11.1 ± 0.07^{a}	5.3 ± 0.07^{a}	3.6 ± 0.2^{a}	11 ± 0.3^{a}	13.5 ± 0.5^{a}	Light grey (7.5YR 7/1)	Sandy loam	Firm, slightly sticky + slightly plastic	Relatively sub-rounded particles
P treatment	13.5 ± 0.2^{c}	20.5 ± 0.1^{a}	21.5 ± 0.2^{a}	11.1 ± 0.07^{a}	5.1 ± 0.1^{a}	4.0 ± 0.2^{a}	10.9 ± 0.2^{a}	13.3 ± 0.4^{a}	Light grey (7.5YR 7/1)	Sandy loam	Firm, slightly sticky + slightly plastic	Relatively sub-rounded particles
NP Treatment	12.5 ± 0.2^{bc}	20.6 ± 0.07^{a}	21.7 ± 0.3^{a}	11.4 ± 0.1^{a}	5.4 ± 0.2^{a}	3.7 ± 0.1^{a}	11 ± 0.3^{a}	13.4 ± 0.4^{a}	Light grey (7.5YR 7/1)	Sandy loam	Firm, slightly sticky + slightly plastic	Relatively sub-rounded particles
NPK Treatment	12.4 ± 0.1^{bc}	20.7 ± 0.07^{a}	22.3 ± 0.5^{a}	11.1 ± 0.1^{a}	5.3 ± 0.1^{a}	3.4 ± 0.02^{a}	11.2 ± 0.2^{a}	13.4 ± 0.3^{a}	Light grey (7.5YR 7/1)	Sandy loam	Firm, slightly sticky + slightly plastic	Relatively sub-rounded particles
Mean	12.1 ± 1.1	20.8 ± 0.3	22 ± 0.4	10.9 ± 0.5	5.4 ± 0.3	3.8 ± 0.3	11.2 ± 0.4	13.7 ± 0.5				
p value	.002	.487	.308	.265	.250	.280	.990	.910				

Note: Using the Tukey HSD post hoc test, mean values with the same superscript letters (a, b, and c) were not significantly different.

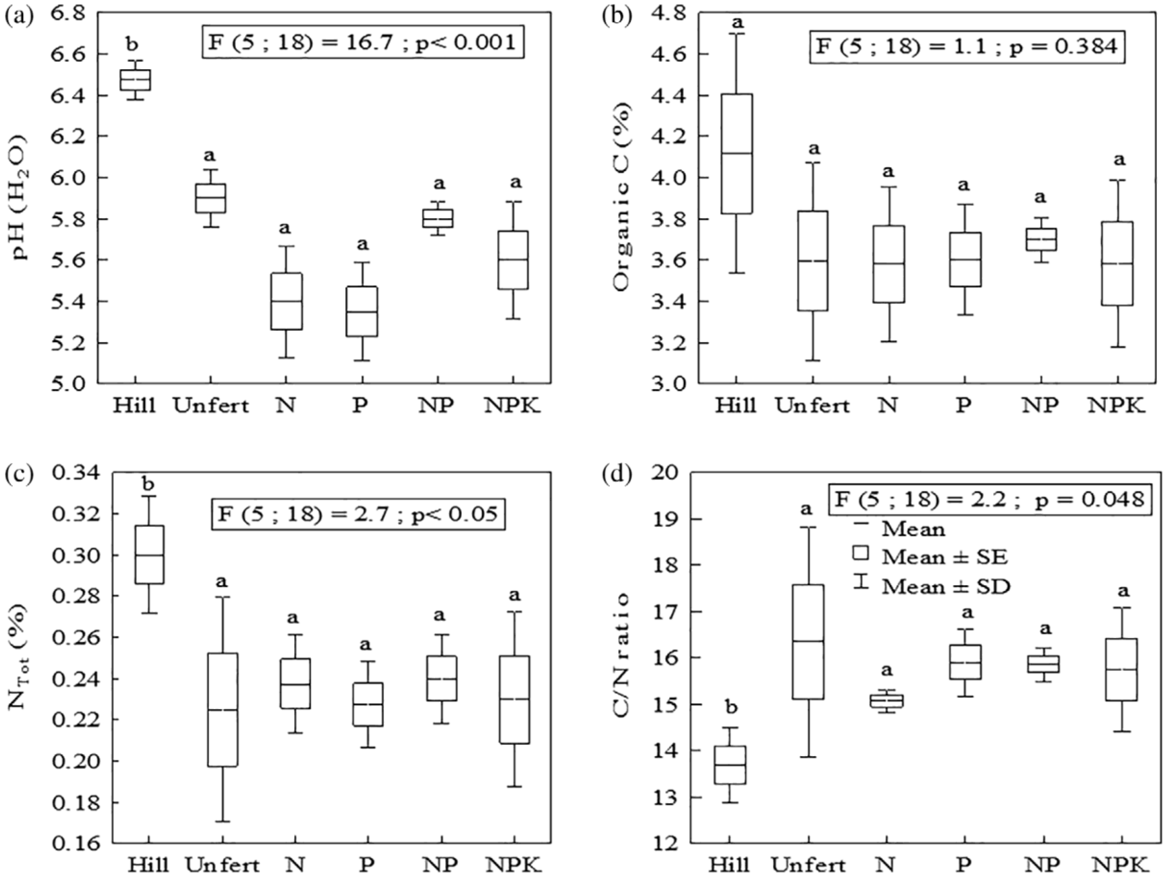

FIGURE 2 Effects of different site use on (a) pH, (b) organic C, (c) total N, and (d) C/N ratio in the 0-10-cm depth soil layer. “Hill” (internal area of the hillfort) was compared with the unfertilized control (Unfert) and N, P, NP, and NPK application treatments of the fertilizer experiment by Hejcman et al. (2012a). The F and p values were obtained by one-way ANOVA. Using Tukey´s HSD post hoc test, fields with the same letter were not significantly different. Error bars indicate standard deviation.

4 DISCUSSION

Although settlement activities in the studied hillfort stopped in the 13th century AD, there is still a visible change in the soil colour, from light grey in the control to black in the hillfort, as well as an increased soil Ph (neutral reaction) and larger contents of macro (N, P and Ca), micro (Mn, Fe, Cu, and Zn) and trace elements (Sr and Rb). Moreover, the past settlement activities affected plant availability of P, K, Ca, and Mg, as indicated by increased Mehlich III values for these elements in the hillfort in comparison to the unfertilized control. The enrichment of the soil from the hillfort by total N, P, Ca, and K was larger in comparison to the fertilizer experiment, and even recent short-term intensive mineral N, P and K fertilizer applications could not mask it. We, therefore, infer that 5 years of intensive N, P, and K fertilizer application cannot increase the total contents of anthropogenic elements to the same level as intensive long-term settlement activities. This result is important in answering the frequently asked question “To what extent can the chemical signatures of soils, formed as a result of ancient settlement activities, be masked by modern agricultural practices?". Based on our results and previous research of ancient settlements on contemporary arable fields in the Czech Republic (Hejcman et al., 2012b, 2013a), we can conclude that the signatures of intensive and long-term past settlement activities are generally stronger than the recent short-term footprint of modern fertilizers. Again, farmers frequently disregard ancient settlement sites by applying

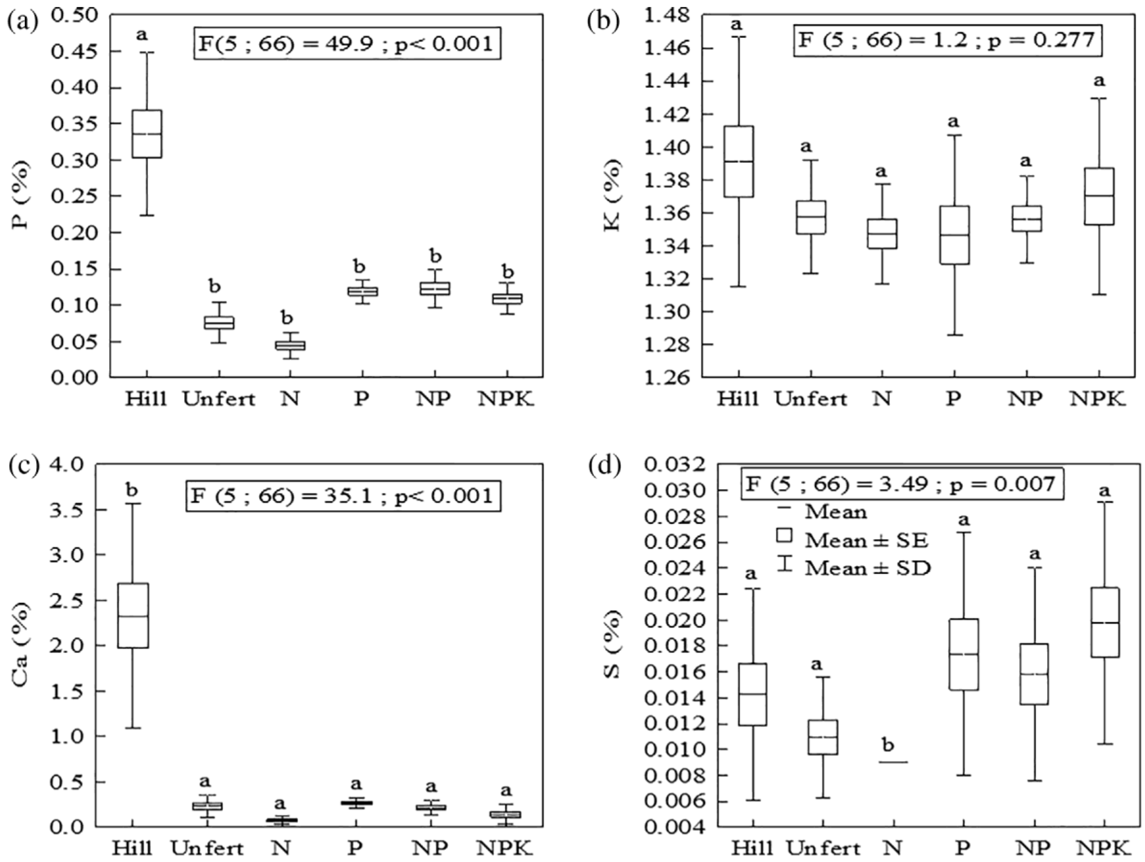

FIGURE 3 Effects of different site use on (a) P, (b) K, (c) Ca, and (d) S in the upper 10 cm soil layer. "Hill" (internal area of the hillfort) was compared with the unfertilized control (Unfert) and N, P, NP, and NPK application treatments of the fertilizer experiment by Hejcman et al. (2012). The F and p values were obtained by one-way ANOVA. Using Tukey´s HSD post hoc test, fields with the same letter were not significantly different. Error bars indicate standard deviation.

the same amounts of fertilizers on arable fields of sites without settlement activities and ancient settlements due to the lack of detailed elemental analysis. Modern fertilizer application is thus the same on sites with different ancient activities and cannot, therefore, mask the ancient chemical signatures preserved in the soil.

4.1 Soil physical properties

The relatively similar percentage size of soil particles (especially from <2 to <0.002 mm), texture, and other physical properties, together with the same geology in the hillfort and the fertilizer experiment site, indicated that the soils from both sites are similar (see Table 1; Jahn et al., 2006; Czech Geological Survey, 2012; FAO, 2015). The lack of a significant difference between the proportion of clay particles (<0.002 mm) in the hillfort and the fertilizer experiment soils indicates that the two sites are located on the same geological bedrock.

However, the marginally larger amount of fine soil particles (<0.25 to <0.002 mm) in the hillfort compared to the fertilizer experiment contributed to the retention and reduced leaching of the studied elements (Acosta et al., 2011). The black colour of the soil within the hillfort was predominantly due to incomplete combustion (black carbon), mainly derived from heating and cooking fires, unintentional fires, and deliberate destruction by burning, as well as accumulation of domestic wastes. The effect of charcoal on the black colour of the soil in the hillfort was corroborated by the homogenously high number of charcoal pieces found, which is consistent with the findings of other authors from different past settlements (Lehmann et al., 2003; Macphail, et al., 2003; Glaser, 2007). The high sorption capacity of charcoal played a significant role in sustaining the higher fertility of the soil in the hillfort.

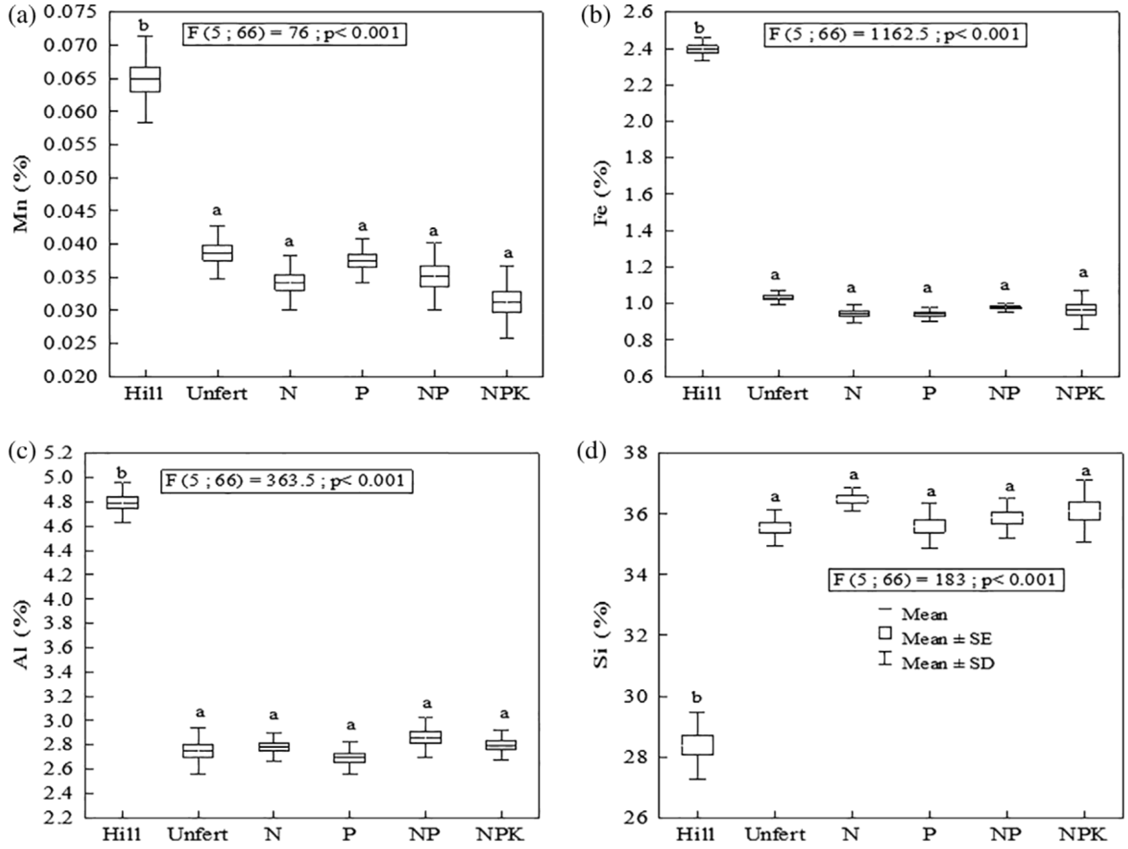

FIGURE 4 Effects of different site use on (a) Mn, (b) Fe, (c) Al, and (d) Si in the upper 10-cm soil layer. "Hill" (internal area of the early medieval hillfort) was compared with the unfertilized control (Unfert) and N, P, NP, and NPK application treatments of the fertilizer experiment by Hejcman et al. (2012). The F and p values were obtained by one-way ANOVA. Using Tukey´s HSD post hoc test, fields with the same letter were not significantly different. Error bars indicate standard deviation.

4.2 Soil chemical signatures

The increased total and Pav Ca contents, together with C, N, and high amounts of charcoal, in the hillfort are responsible for the increased and retained pH compared to the fertilizer experiment (Hejcman et al., 2012b). The increased acidity of the soils from the fertilized treatments in comparison to the hillfort and the unfertilized control is a result of the intensive application of N, P, and K fertilizers (Arsova, 1995). Moreover, the comparatively lower pH of the unfertilized control compared to the hillfort is related to the long-term application of mineral fertilizer (Li et al., 2018). The marginally enhanced organic C and the significantly larger total N contents in the soil from the hillfort in comparison to the unfertilized control and all the fertilizer treatments indicate the deposition of organic waste, manuring, and tool/house manufacturing or destruction (Deotare & Joshi, 1981; Bogaard et al., 2007). The larger organic matter content, identified by increased organic C and total N contents increased plant-available nutrients, high amount of charcoal, and the higher soil pH in the hillfort compared to the unfertilized control are typical features of EDE (Courty et al., 1990; Nicosia et al., 2012). The larger organic C content in the hillfort is associated with a higher CEC, responsible for the lesser leaching of many elements from

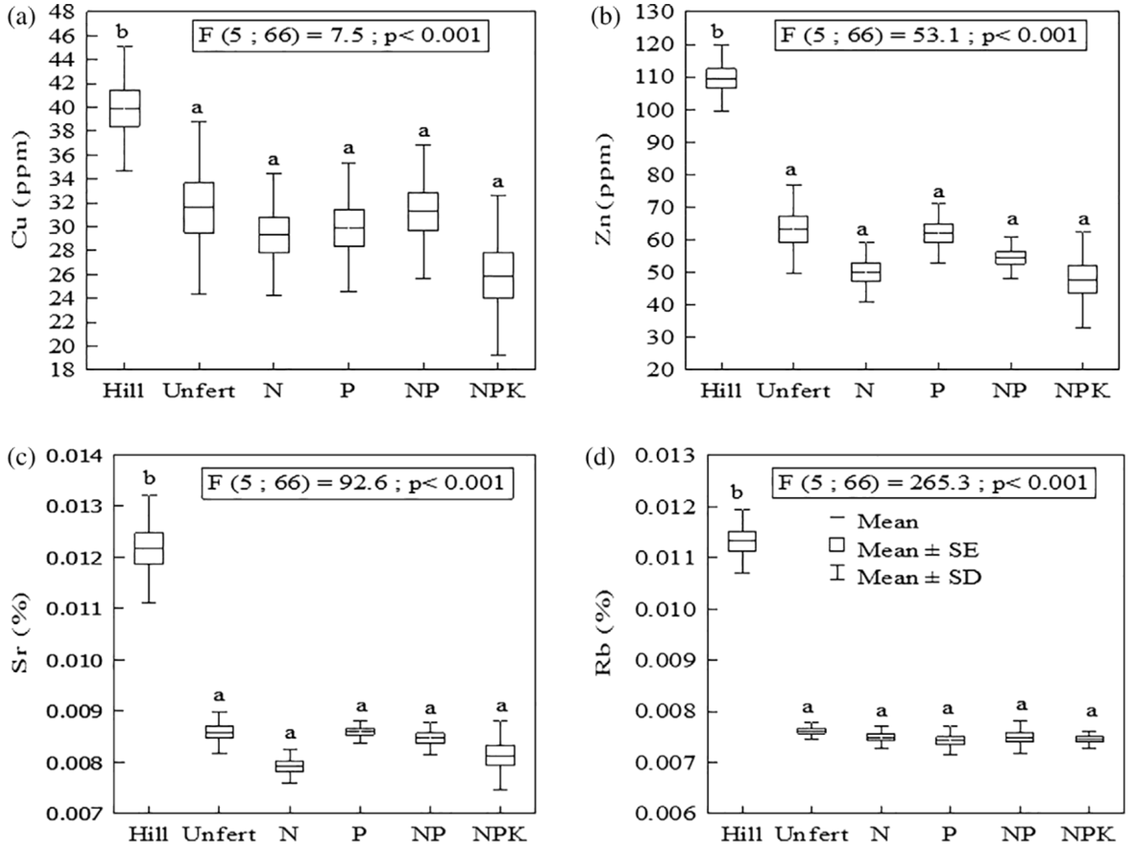

FIGURE 5 Effects of different site use on (a) Cu, (b) Zn, (c) Sr, and (d) Rb in the upper 10-cm soil layer. "Hill" (internal area of the hillfort) was compared with the unfertilized control (Unfert) and N, P, NP, and NPK application treatments of the fertilizer experiment by Hejcman et al. (2012). The F and p values were obtained by one-way ANOVA. Using Tukey´s HSD post hoc test, fields with the same letter were not significantly different. Error bars indicate standard deviation.

the soil (Glaser et al., 2001; Lehmann et al., 2003; Glaser, 2007). The high amount of charcoal from wood-burning for heating and cooking in the hillfort is connected with an increased organic C content in the soil and is also responsible for the binding of the studied elements. The lowest C/N ratio recorded in the hillfort, in comparison to the unfertilized control and all fertilizer treatments, is a direct effect of the deposition of ash, excrements, and biosolids. A lower C/N ratio is also an indicator of high mineralization and nutrient supply in the soil from the hillfort (Kanokporn, 2015) and explains the higher crop yields in comparison to the surrounding soils, as reported by local farmers.

The total P content in the hillfort was approximately five times greater in comparison to the unfertilized control. Again, the hillfort was 8.5 times enriched by total P in comparison to the N fertilizer treatment and approximately three times greater in comparison to the P, NP, and NPK treatments. The sources of P in the hillfort resulted from the deposition of domestic waste, especially animal bones and excrements, kitchen waste, and biomass ash (Holliday & Gartner, 2007; von Oheimb et al., 2008). These possible sources of P related to the sources of Mn, Fe, Al, Cu, Sr, and Rb, and were, therefore, positively correlated (see Figures S6a, b, S7a, b, and S8a, b). However, the lowest P content in the fertilizer treatments in comparison to the hillfort resulted from the short duration of the experiment (only 5 years). Additionally, P fertilizers are highly soluble and are easily available for uptake by plant roots (McKenzie & Middleton, 2013).

Although P fertilization only slightly increased the contents of total P, it highly increased the contents of Pav P in the soil in our experiment.

The content of total Ca was 9.5 times greater in the soil from the hillfort in comparison to the unfertilized control. In comparison to the N, P, NP, and NPK fertilizer treatments, the total Ca content in the hillfort was 24, 9.5, 8, and 12 times greater, respectively. The elevated total Ca content suggests deposition of biomass ash from burnt wood and woody biomass, energy crop, agricultural biomass, and forest residues, which contain approximately 5 to 45% Ca (Gaskin, 2002; Kofman, 2016; Simniškytė-Strimaitienė et al., 2017; Zając et al., 2018). The larger content of total Ca in the hillfort may be related to clay imported for the construction of houses and the manufacturing of crafts during its existence, similar to the case of deserted medieval villages in the Czech Republic (Hejcman et al., 2012b). Conversely, the smaller total Ca content in the fertilizer experiment may be a result of the effect of long-term mineral fertilizer application (Lungu & Dynoodt, 2008). Although K is a highly mobile ion in soils and rapidly taken up by plants, we only observed slightly larger total K values in the hillfort, mainly because most of the K could be fixed in minerals and was, therefore, relatively immobile. The content of total K was slightly larger in the hillfort than in the unfertilized control and fertilizer treatments, which is connected to the deposition of ashes, which contain, depending on the burnt organic material, approximately 2 to 7% of K (Wilson et al., 2009; Kofman, 2016; Zając et al., 2018). Potassium enrichment in archaeological localities with the deposition of biomass ash has also been reported by Entwistle et al. (1998) and Misarti et al. (2011). The content of total S in the hillfort was 1.5 times greater in comparison to the unfertilized control and the N treatment. This is most likely to be a result of biomass ash deposition and the larger content of soil organic matter (Tisdale et al., 1993). Sulphur also readily reacts with Fe during the decomposition of organic matter, which may contribute to the black colour of the soil (Walker, 1968). There was slightly higher S content in the P, NP, and NPK treatments in comparison to the hillfort, which can be explained by the application of superphosphate with a high S content (Vitosh, 1996).

Total Mn was also twice as high in the hillfort compared to the unfertilized control and all fertilized treatments, which may be due to the deposition of biomass ashes, which can contain approximately from 1 to 3% of Mn (Brais et al., 2015; Kofman, 2016; Zając et al., 2018).

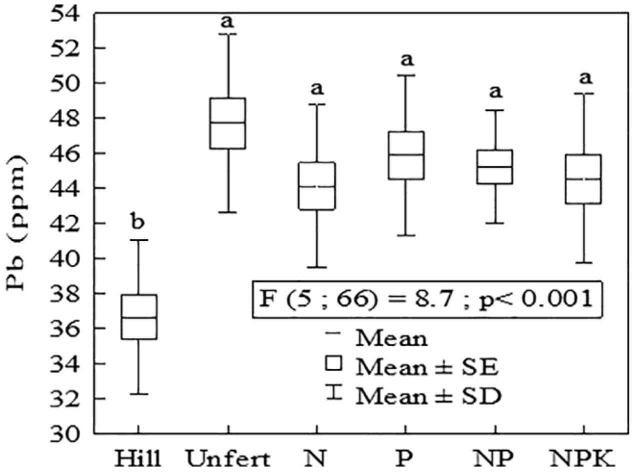

FIGURE 6 Effects of different site use on Pb in the upper 10-cm soil layer. "Hill" (internal area of the hillfort) was compared with the unfertilized control (Unfert) N, P, NP, and NPK application treatments of the fertilizer experiment by Hejcman et al. (2012). The F and p values were obtained by one-way ANOVA. Using Tukey´s HSD post hoc test, fields with the same letter were not significantly different. Error bars indicate standard deviation.

Other authors have reported Mn accumulation because of the deposition of animal excrements and organic waste (e.g., Wilson et al., 2008; Mescouto et al., 2011; Vassilev et al., 2013). Among all elements identified in this study, the total content of Mn was most significantly positively correlated with total P ($r = 0.86$, $p < .001$). Therefore, we infer that total Mn can be a strong indicator of settlement activities, especially in the case of EDE soil.

The total Fe content was approximately 2 to 2.5 times greater in the hillfort in comparison to the unfertilized control and all the fertilized treatments, suggesting a high accumulation of organic waste. Iron is relatively abundant in many cultivated soils, with an average total content from 2 to 4% (Cornell & Schwertmann, 2003). Many organic materials, such as livestock manure, are also sources of Fe. However, when organic matter is decomposed by microorganisms, the Fe previously tied up in organic compounds is released into the soil, which may have contributed to the enrichment in the hillfort. Iron accumulation has also been reported in biomass ash by Pitman (2006).

The larger total content of Al in the soil from the hillfort than in the fertilizer experiment may be due to the deposition of wood ashes, as ash contains approximately 2 to 4% Al (Pitman, 2006; Dibdiakova et al., 2015). The lowest content of total Si in the hillfort in comparison with the fertilizer experiment may be due to the enrichment of the hillfort by many other elements and, consequently, the decreased proportion of total Si (see Figure S7c, d). Again, the lowest content of total Si in the hillfort is related to the lower proportion of coarse sand, and a marginally larger percentage fraction of very fine soil particles, especially silt (<0.05–0.002 mm) and clay (<0.002 mm), compared to the fertilizer experiment.

The content of total Sr was twice as high in the hillfort in comparison to the unfertilized control and all fertilized treatments, which is related to the accumulation of biomass ash and organic waste. Strontium is present in microorganisms, plants, and animals, especially in bones (Lengfelder et al., 2018). We observed approximately 1.5 times increased content of total Rb in the hillfort compared with the unfertilized control and the fertilized treatments. The accumulation of Sr and Rb can be linked with the deposition of different biomass ash (Wedepohl & Simon, 2010; Oroian et al., 2015; Simniškytė-Strimaitienė et al., 2017) and of excrements, as suggested by Nielsen and Kristiansen (2014).

As the total Fe, Al, Sr, and Rb strongly correlated positively with total P (Figures S6b, S7a, S8a, b), which is a reliable indicator of past settlement activities, they can also be used as indicators of past anthropogenic activities.

TABLE 2 Mean contents (±SD) of plant-available elements in the upper 10-cm soil layers from the Dřevícˇ hillfort and the fertilizer experiment (unfertilized control, N, P, NP, and NPK treatments)

Element	Hillfort	Unfertilized control	N treatment	P treatment	NP treatment	NPK treatment	*p*-value
P (ppm)	450.5 ± 90.6^{a}	180 ± 53^{b}	130 ± 18^{c}	450 ± 60.8^{a}	360 ± 22.3^{d}	350 ± 59^{d}	<.001
K (ppm)	383.8 ± 58.8^{a}	160 ± 65.8^{b}	110 ± 22.7^{c}	200 ± 38.6^{d}	110 ± 45.2^{c}	260 ± 44.5^{e}	<.001
Ca (ppm)	7,494 ± 1736^{a}	1,740 ± 432^{b}	1,020 ± 360^{c}	2,240 ± 420^{d}	1,490 ± 158.8^{e}	1,490 ± 364.8^{e}	<.001
Mg (ppm)	188.3 ± 29.6^{a}	120 ± 33.9^{b}	150 ± 28.4^{c}	110 ± 28.4^{b}	110 ± 16.1^{b}	110 ± 26.3^{b}	<.001

In comparison to both the unfertilized control and all fertilized treatments, the content of total Zn in the soil from the hillfort was approximately 1.8 times greater. The increased Zn content is a testimony of its accumulation in biomass ashes, as ashes contain from 0.2 to 0.9% of Zn (Hejcman et al., 2011; Nielsen & Kristiansen, 2014; Kofman, 2016; Zając et al., 2018). The contents of total Zn in all the soils were within the commonly recorded range in agricultural soils, from 50 to 300 mg kg^{-1} Zn (Alloway, 2008). Total Cu was increased from 1.2 to 1.6 times in the soil from the hillfort in comparison with both the unfertilized control and the fertilized treatments. The high Cu content is probably due to its accumulation in biomass ashes, which contain approximately 200 ppm of Cu, and deposition of excrements (Campos et al., 2016). Its accumulation via deposition of biomass ash has also been recorded in ancient settlements in the Czech Republic (Hejcman et al., 2011; Hejcman et al., 2012b). On a global scale, the estimated baseline total Pb content for surface soil is 25 mg kg^{-1}; levels above this threshold suggest an anthropogenic influence, especially from mining and metallurgy (Kabata-Pendias & Pendias, 2001). The Pb contents (Figure 6) in all analysed samples were above this threshold. The lower content of total Pb in the hillfort was a result of its larger distance from the main road in contrast to the fertilizer experiment, which was established in close vicinity to the main road 16/1 with heavy traffic. In the 1930s up to the year 2000, lead gasoline was used, and the accumulation of Pb in soils of the fertilizer experiment occurred in this period. The contents of Pav P, K, Ca, and Mg were approximately 2.5, 2.4, 4.3, and 1.5 times, respectively, greater in the hillfort in comparison to the unfertilized control. The comparatively larger Pav P, K, Ca, and Mg contents in the soil from the hillfort than in the fertilizer treatments, except for the P treatment, clearly indicate that past settlement activities increased the availability of nutrients for crops and, consequently, the fertility of the soil (see Table 2). Thus, these elements can readily be taken up by plants.

The relatively low variability in the contents of the studied elements across all sampled locations in the hillfort was probably associated with the regular ploughing of the arable field, leading to a homogenization of the soil in the hillfort. The chemical signatures recorded in the soil are mostly connected with the early to the high medieval occupation, as witnessed by a high density of collected early/high medieval pottery fragments from the field.

4.3 The relationship between total and plant-available elements

The patterns for total and Pav P contents in the hillfort and the fertilizer experiment were not the same. Based on our results, the soil total P content is better suited for archaeological purposes, as we can easily calculate the enrichment factor in comparison to the control locality. In the case of Pav P, the content is dependent not only on total P content in the soil but also on other soil chemical properties such as pH value, the presence of Al and Fe oxides, total Ca and Mg contents, among others. Although there was a clear enrichment of Pav Ca in the hillfort in comparison to the fertilizer experiment, generally, Ca is mostly tied up in the exchange complex (not readily available) or with carbonates (unavailable). At alkaline pH values, for example, pH < 7.5, Pav P also tends to react quickly with Ca and Mg to form less soluble compounds.

These complicate the estimation of the enrichment factor of Pav for numerous elements, including K and S. Additionally, there was a weak correlation between the obtained data for plant-available and total elements in this study, except for Ca (Figure S9). The interpretation of such data is therefore complex; thus, the total contents of elements can be better interpreted in geoarchaeological studies.

5 CONCLUSIONS

1. We recorded substantial accumulation of the following elements (total N, P, Ca, Mn, Fe, Al, Cu, Zn, Sr, and Rb) and reduced acidity in the EDE soil from the hillfort compared to the control soil not affected by settlement activities. The range of the accumulation of the above-mentioned elements indicates intensive and long-term past settlement activities in the hillfort. In addition to the total contents, settlement activities in the hillfort still positively affect the availability of P, K, Ca, and Mg.

2. Five years of intensive mineral fertilizer application did not increase the total contents of anthropogenic elements to the same level as long-term and intensive past settlement activities. The recent application of mineral fertilizers could not mask the chemical signatures of intensive and long-term medieval settlement activities.

3. Besides traditionally analysed anthropogenic elements settlement activities can be associated with the accumulation of total Mn, Sr, Fe, Al, and Rb. These elements can, therefore, be used as indicators of past settlement activities in the Czech Republic. The accumulation of the studied elements in soils was a result of the deposition of biomass ash, domestic waste, and excrements. The retention of the accumulated elements was due to the favourable pH level, the high proportion of fine sand/loam, silt, and clay particles as well as the inclusion of charcoal in the EDE soil.

4. Comparing the contents of total and plant-available (Mehlich III) elements, we conclude that the analysis of total element content is highly suitable for geoarchaeological purposes, as the enrichment factors are easy to calculate. In the case of P and K, and other elements not analysed in our study, total and Pav contents are not well correlated, as each method revealed different patterns. The patterns recorded using Pav contents of elements are highly affected by some soil chemical properties. Hence, it is difficult to draw straightforward conclusions without a detailed analysis of soil properties, which may be hard to perform by geoarchaeologists in the field. Total contents are therefore more suitable for similar studies evaluating the intensity of settlement activities in the landscape.

5. We conclude that abandoned medieval settlements may represent an island of extraordinarily fertile EDE
soil in contemporary landscapes. In addition to routine P analysis performed in soils in archaeological localities, we strongly recommend multi-elemental analysis, as many elements are potential indicators of past human activities.

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CONFLICT OF INTEREST

We confirm that this work has no conflict of interest.

AUTHOR CONTRIBUTIONS

Study concept and design, data analysis, and interpretation of data: Michael O. Asare and Michal Hejcman. Data collection: Michael O. Asare, Michal Hejcman, and Martin Janovský. Critical revision of the manuscript for intellectual content: Michael O. Asare, Jan Horák, Ladislav Šmejda, and Michal Hejcman. Obtained funding and study supervision: Michal Hejcman.

DATA AVAILABILITY STATEMENT

Data available on request from the authors

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SUPPLEMENTARY MATERIAL

Fig. S1 Location of the studied hillfort Dřevíč and the fertilizer experiment in village Mšec, Czech Republic

Fig. S2 Aerial view of the fertilizer experiment in Mšec, Czech Republic. The individual plot size was 4 × 3 m. Plot abbreviations: the first digit indicates the number of the randomized block, the second digit indicates the number of the individual plot, and C indicates the unfertilized control, while N, P, NP, and NPK indicate the individual fertilizer treatments (photo by Michal Hejcman)

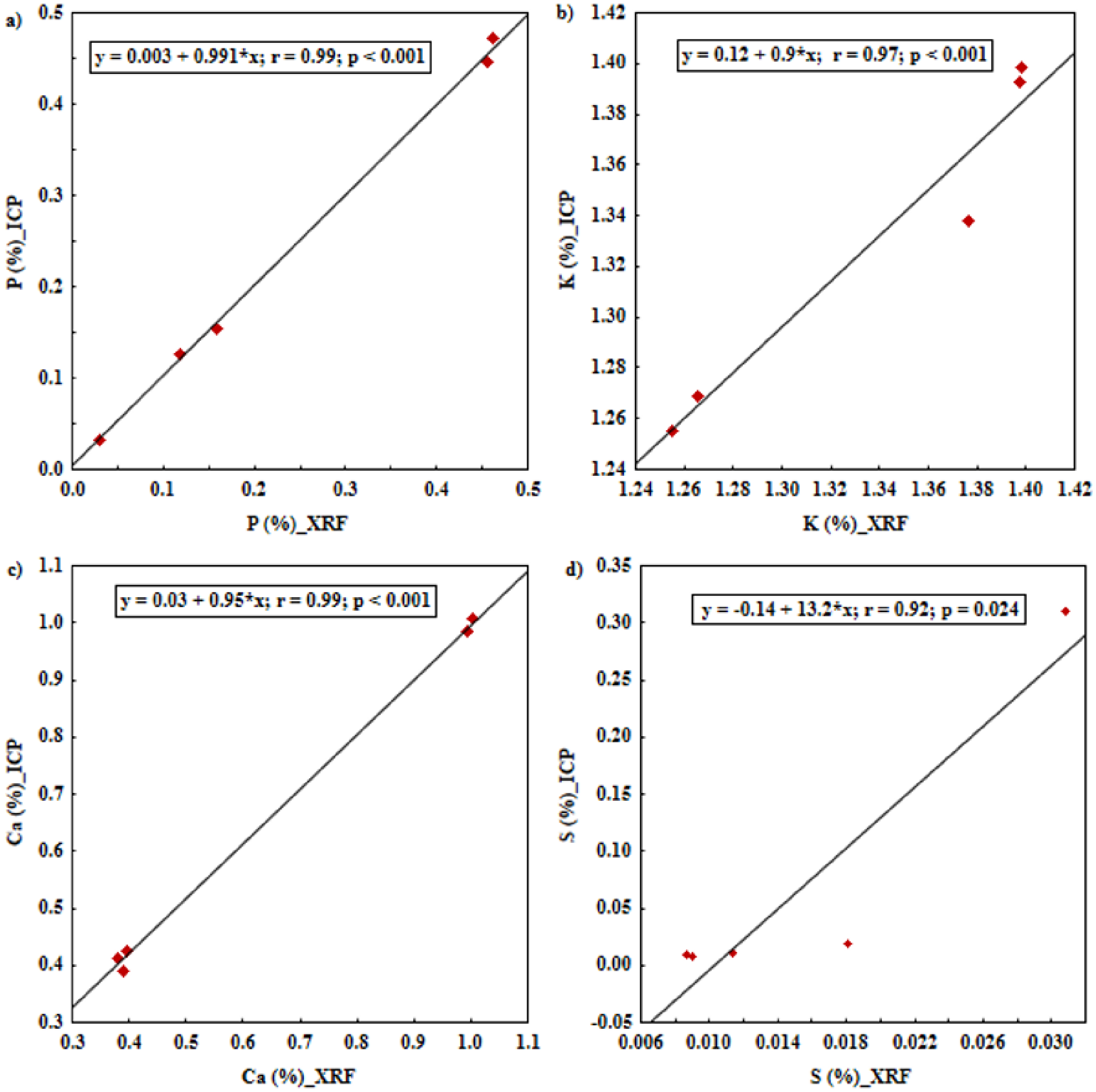

Fig. S3 Scatterplot correlation between pXRF and *Aqua regia* ICP data of a) P, b) K. c) Ca and d) S contents

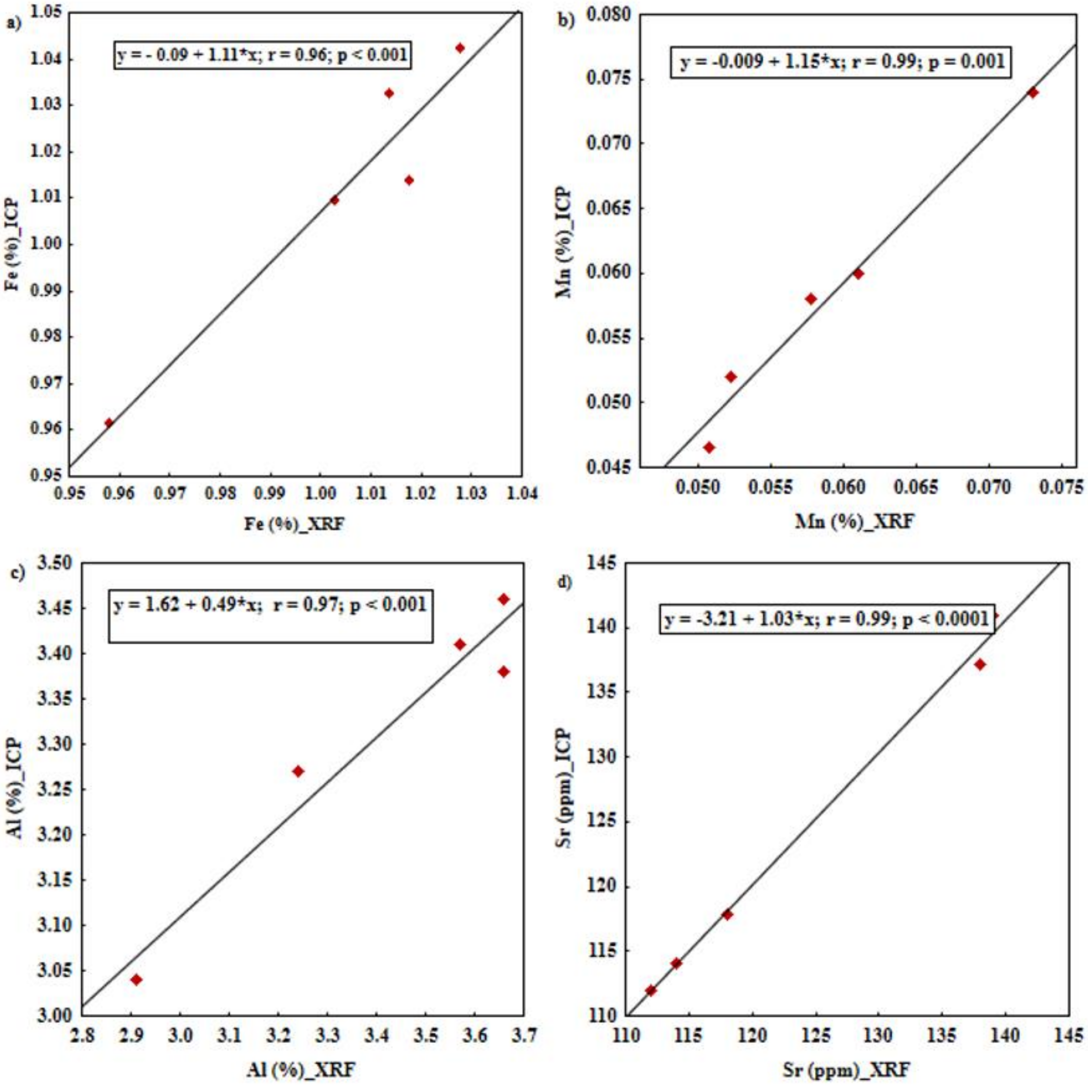

Fig. S4 Scatterplot correlation between pXRF and *Aqua regia* ICP data of a) Fe, b) Mn c) Al and d) Sr contents

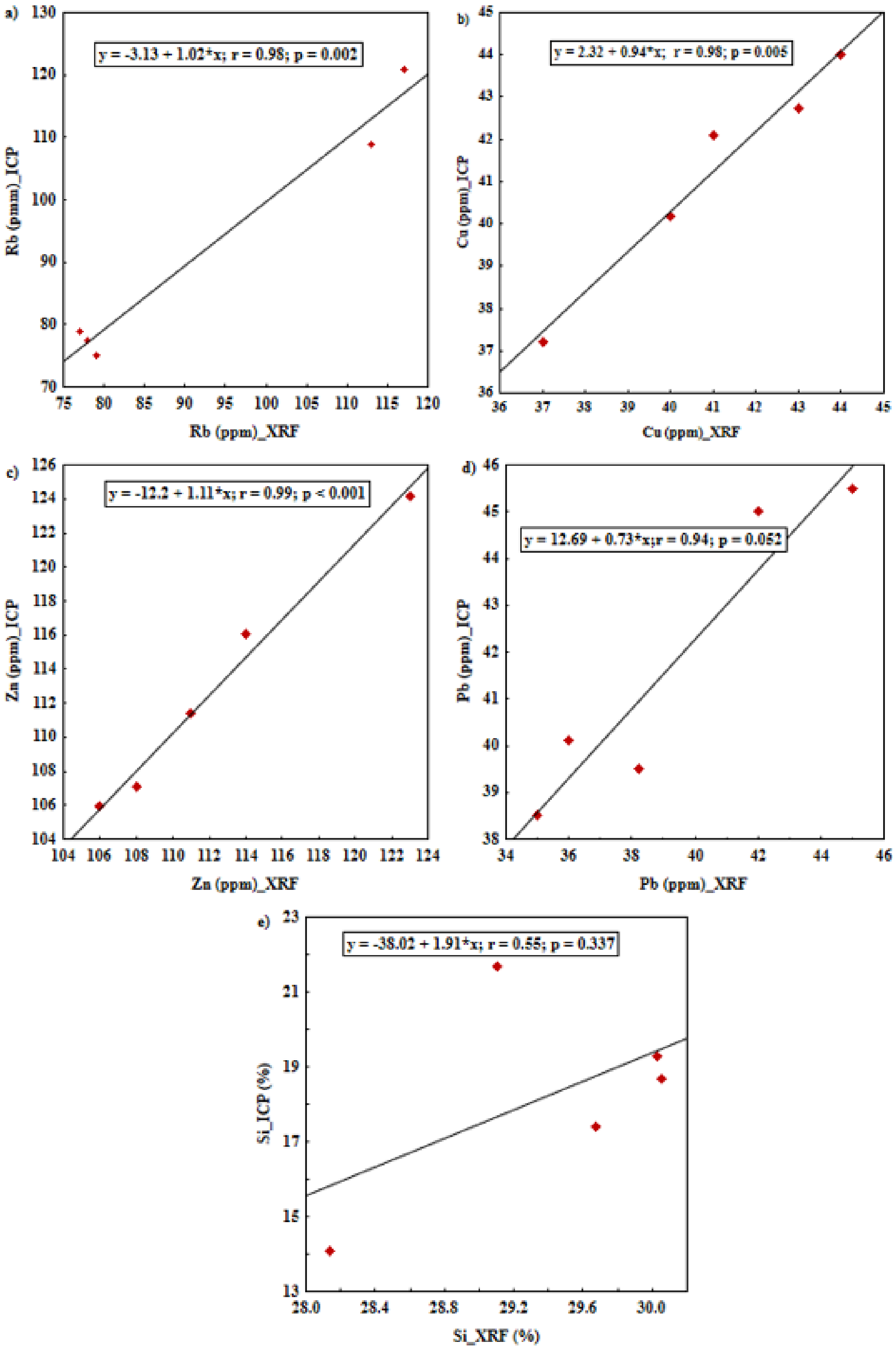

Fig. S5 Scatterplot correlation between pXRF and *Aqua regia* ICP data of a) Rb, b) Cu c) Zn, d) Pb and e) Si contents

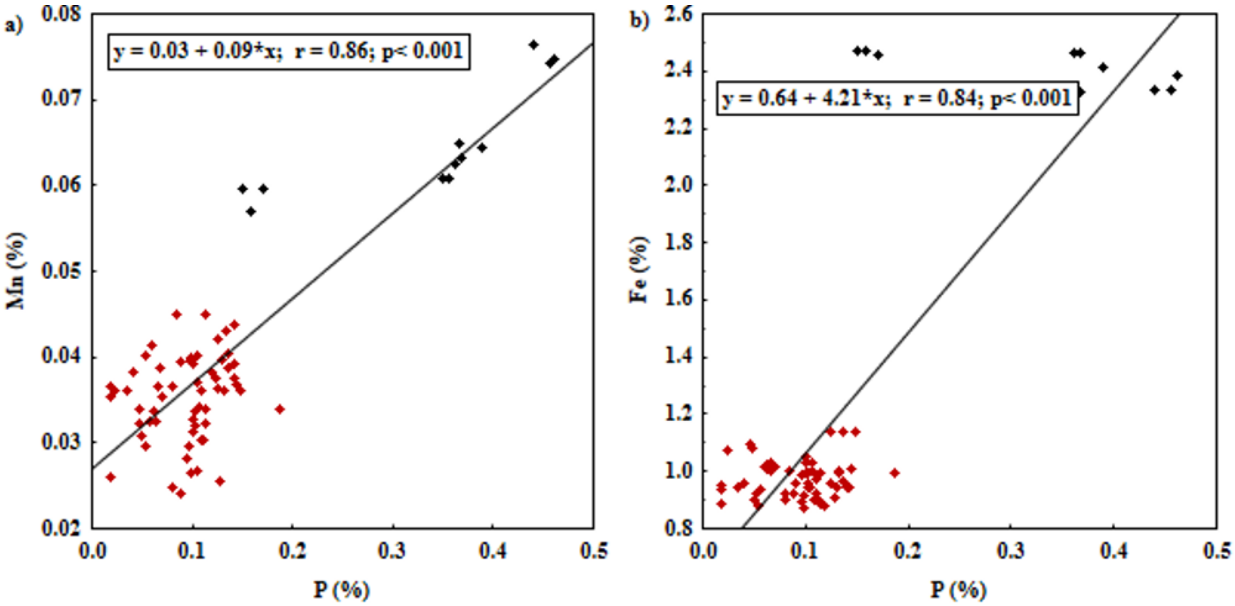

Fig. S6 Relationship between total a) P and Mn and b) P and Fe in all the sites. The black marks indicate values from the hillfort

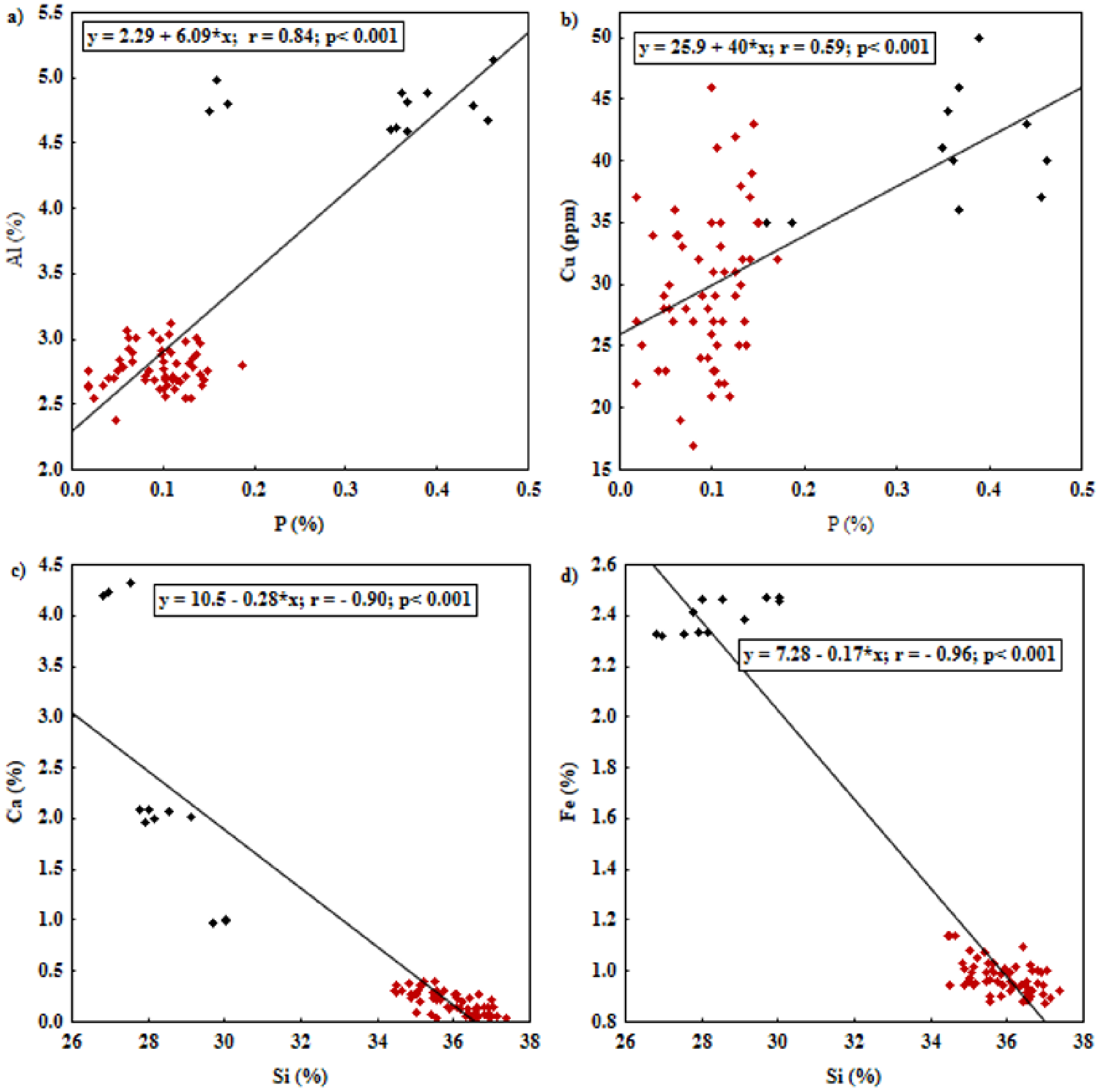

Fig. S7 Relationship between total a) P and Al, b) P and Cu, c) Ca and Si, d) Fe and Si in all the sites. The black marks indicate values from the hillfort

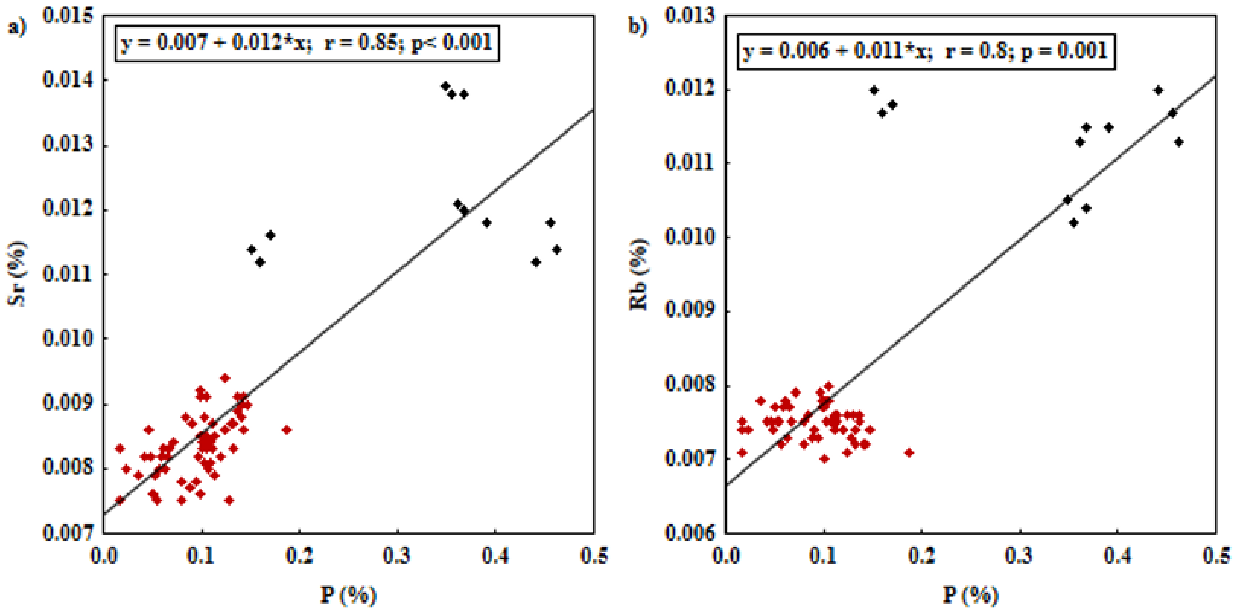

Fig. S8 Relationship between total a) P and Sr, b) P and Rb in all the sites. The black marks indicate values from the hillfort.

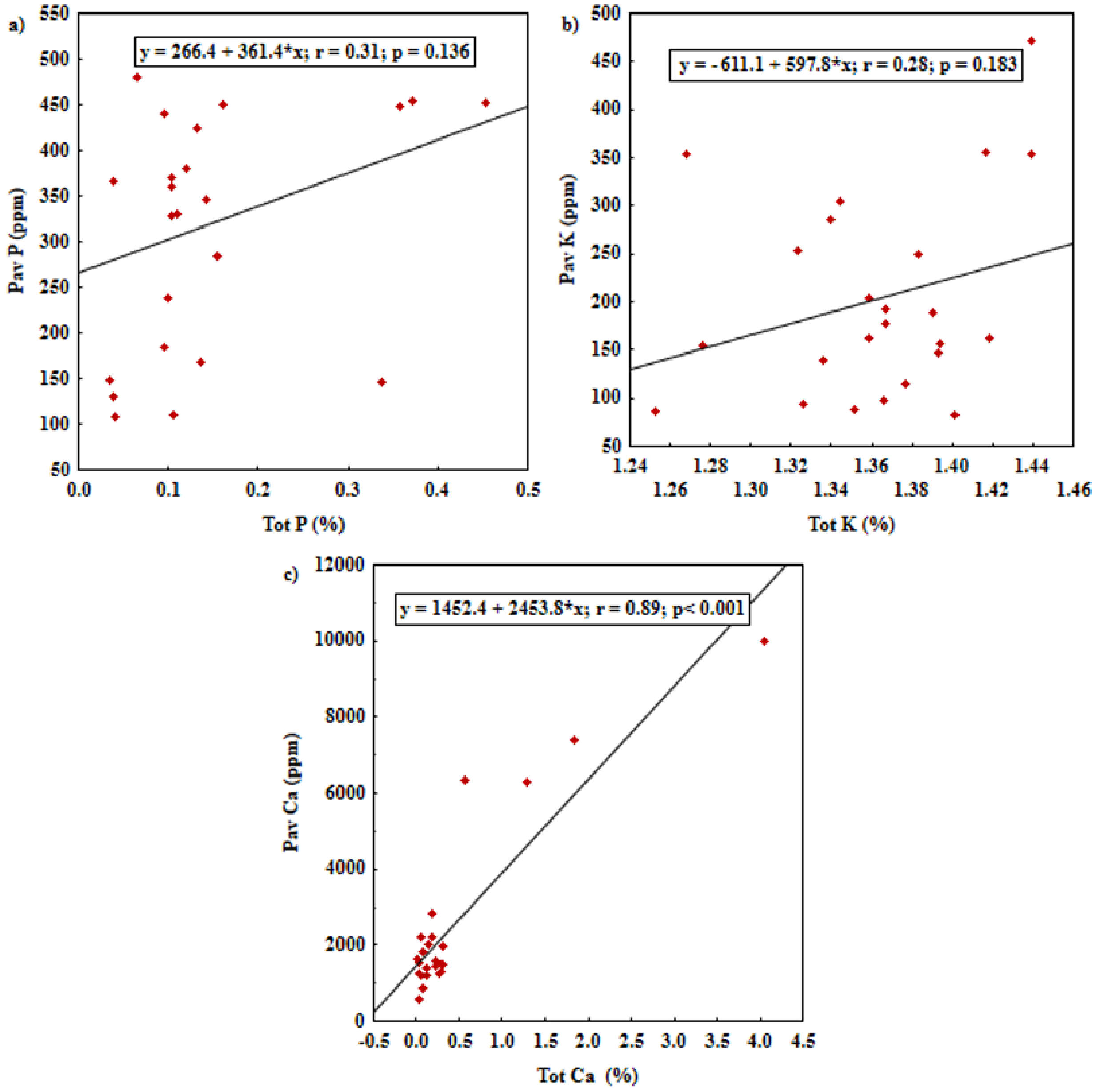

Fig. S9 Relationship between total (Tot) and plant-available (Pav), a) P, b) K, and c) Ca

CHAPTER 3

Traces of German and British settlement in soils of the Volta Region of Ghana

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Soil sampling by Michael Opare Asare in Ziavi Galenkuito, Ghana

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ABSTRACT

Can less than a hundred years of past settlement activities in former European settlements substantially increase the concentration of elements and result in the formation of African Dark Earth soil is a question not addressed. We performed a multi-element analysis of Africa Dark Earth soil from a late 19th to mid–20th century CE former German–Togoland settlement, Ziavi–Galenkuito in the Volta Region, Ghana. Relatively neutral reaction and black color of soil mainly from charcoal inclusion in the settlement site contrasted highly with moderately acidic brown Ferric Acrisol in the control located on the same metasedimentary/Voltaian bedrock. Organic C and total N, P, K, Ca, Mn, Fe, Cu, Zn, Sr, and Rb concentrations were substantially increased and vice–versa for the C/N ratio in the 0–40 cm layer of the settlement soil compared to the control without settlement activities. The concentrations of plant-available P, K, Ca, S, Fe, Cu, and Zn were higher in the settlement soil in comparison to the control. The increased concentrations of the elements mentioned above resulted in the disposition of organic waste and biomass ash. Significantly higher concentrations of total and plant–available elements in 0–10, 10–20, and 20–40 cm layers of settlement site compared to their respective control suggested that chemical signatures from past settlement activities can be determined even in the upper soil layer. Positive correlations between the concentration of P and K, Mn, Sr, Fe, Ca, Zn, Rb, Cu implied that these elements were indicators of past settlement activities. The concentrations of total and plant–available P, K, Ca, Fe, Cu and Zn were well correlated; however, total elements concentrations are much suitable for geoarchaeological purposes as it is easy to calculate enrichment factors. We concluded that intensive human settlement activities in even b100 years resulted in the development of Africa Dark Earth soil with a substantial accumulation of elements.

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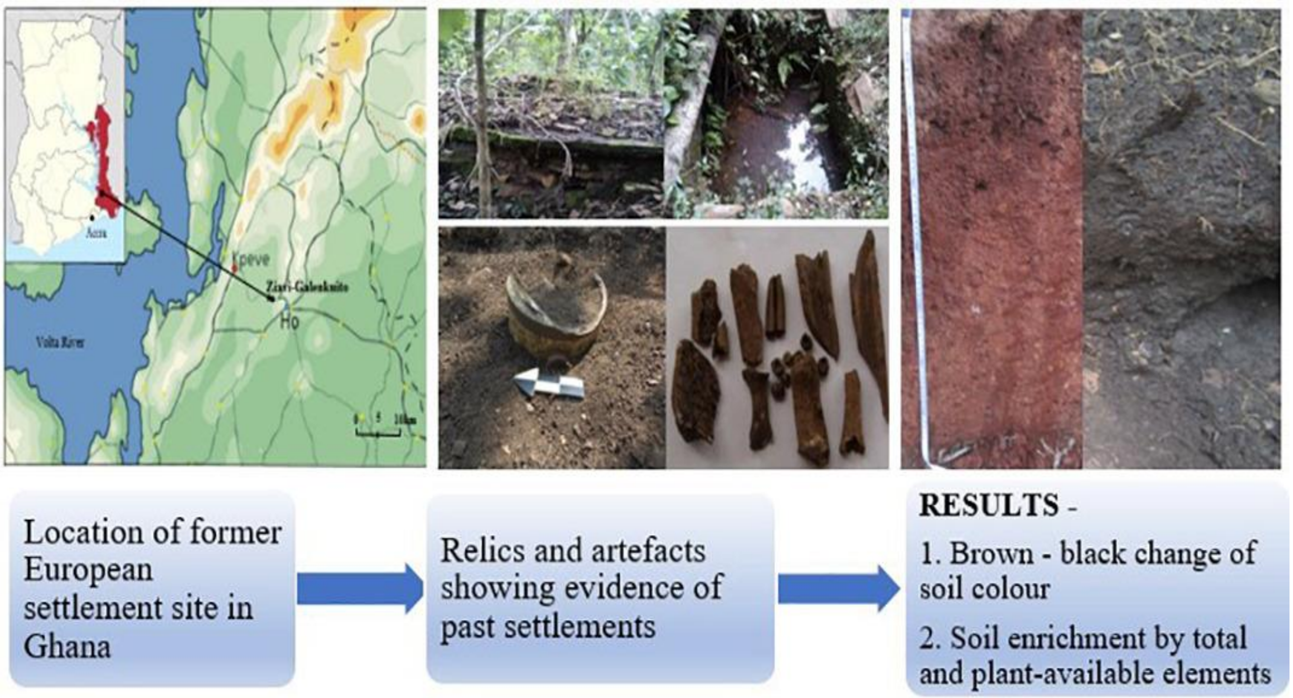
Graphical abstract



Location of former European settlement site in Ghana

Relics and artefacts showing evidence of past settlements

RESULTS -

1. Brown - black change of soil colour
2. Soil enrichment by total and plant-available elements

Introduction

Past settlement sites are associated with the accumulation of elements in soils due to human activities (Hejcman et al., 2013a, b; Golyeva et al., 2018; Šmejda et al., 2018), referred in this context as anthropogenic elements. So far, there are no studies on the elemental composition of soils from former European settlements in Ghana. Many studies in these sites were related to the dominance and influence of European imperial powers over local societies (Killingray, 1978; Laumann, 2003; Apoh, 2009; Pawlikova–Vilhanova, 2013). For example, former German settlements remain unforgotten through intangible oral accounts and structural relicts, especially in the Volta Region of Ghana, formerly part of German–Togoland territory (Fig. 1; Apoh, 2009; Apoh and Lundt, 2013).

However, the unintended and deliberate past settlement activities, including, domestic waste disposal, craftworks, and agriculture can elevate the elemental concentrations of soils (Entwistle et al., 1998; Hejcman et al., 2013a, 2013b; Golyeva et al., 2018). For example, some authors attributed Cu and Mn accumulation to biomass ash in the Czech Republic (Hejcman et al., 2011; Hejcman et al., 2012) and organic waste in Piedras Negras, Guatemala, (Parnell et al., 2002). Additionally, past settlement activities changed the soil's original color to black, dark grey, or dark brown, especially from the addition of charcoal resulting in the development of Archaeological Dark Earth soil (Lehmann et al., 2003; Nicosia et al., 2012).

Based on geographic origins, different types of archaeological dark earth soil are studied; Amazonian Dark Earth (Terra preta) from South American rainforest zones (Lehmann et al., 2003), European Dark Earth (Nicosia et al., 2012), and African Dark Earth (AfDE) mostly developed in the rainforest zones (Fairhead and Leach, 2009). Although few studies about the development of AfDE soil are dated 115–692 years BP, there is continual formation as the activities leading to the formation still occur, especially in rural areas (Frausin et al., 2014; Solomon et al., 2016).

Archaeological dark earth soils are anthropogenic soils characterized by high stable organic matter stocks, high cation exchange capacity (CEC), reduced acidity, and high concentration of total and plant–available P, Ca, Mn, Cu, and Zn compared to neighboring soils (WinklerPrins, 2014; Solomon et al., 2016). Several authors have reported the formation of Archaeological dark earth soil as a result of long–term settlements over hundreds of years on different soil types (Lehmann et al., 2003; Whitehead et al., 2010; Nicosia et al., 2012). According to our knowledge, no studies have reported the development of archaeological dark earth soil in less than a hundred years.

In the absence of landmarks, legacies (e.g., trade castles and forts), together with degrading archaeological remains in the tropical environment, soil chemical analyses can offer relevant information about past human activities (Holliday, 2004; Oonk et al., 2009; Šmejda et al., 2018). Such analyses are pertinent in making reliable inferences on what level some elements accumulate in the natural sediments. The combination of both traditional archaeological methods, together with analysis of soil properties, can assist in tracing anthropogenic imprints in the landscape (Holiday, 2004; Salisbury, 2013). Anthropogenic activities alter the natural sediments in recognizable ways (Holliday, 2004), forming traceable soil characteristics investigated through traditional phosphate (Salisbury, 2013), multi-elemental (Šmejda et al., 2018), and micromorphological analyses (Nicosia and Stoops, 2017).

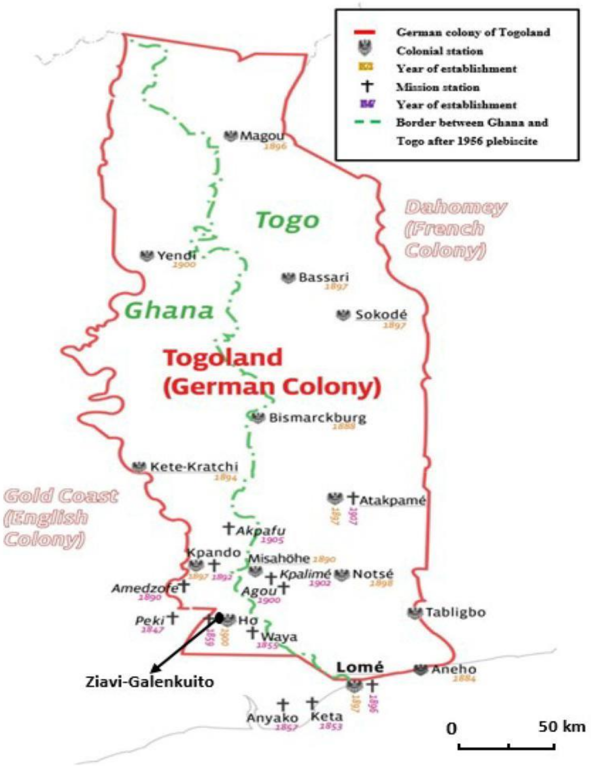


Fig. 1. Map of former German–Togoland showing the colonial and mission stations with their years of establishment. The red–full line indicates the borders of the former colony. The green dashed line indicates the current border between Ghana (formerly Gold Coast; left) and Togo (right) after its demarcation in 1956 (according to Heller and Dogbey, 2015).

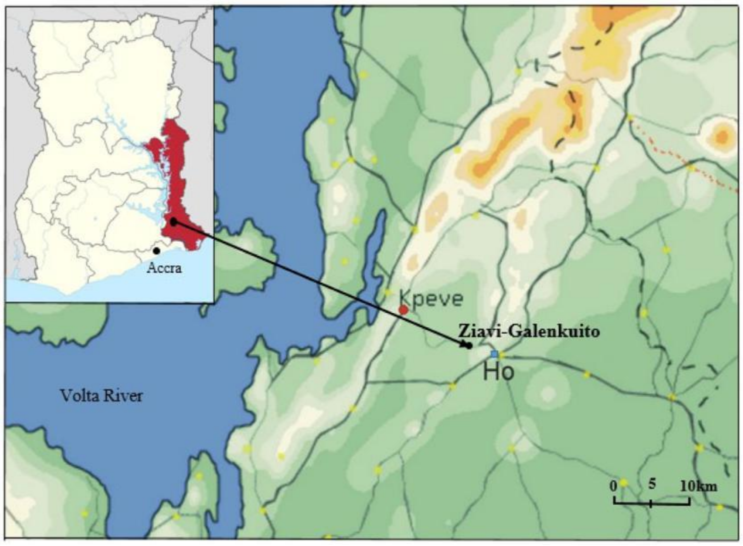


Fig. 2. Location of the study area Ziavi–Galenkuito in Ghana

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Although there are several archaeological studies in the interior regions (Stahl, 2001; Apoh, 2009) and coastal sites (DeCorse, 1992, 1996) of Ghana, research on European settlement sites were generally on historical archaeology with no reference to soil analysis.

Conversely, there are many studies conducted on the effects of past settlement activities on the chemical signatures of soils in America, Europe, and Asia (Lehmann et al., 2003; Hejcman et al., 2013a, 2013b; Šmejda et al., 2017; Fenger–Nielsen et al., 2019). Most of the authors reported nutrient-rich soils compared with surroundings non–affected by settlement activities. We hypothesize similar conclusions at Ziavi– Galenkuito, a former German and British settlement from the late 19th to mid–20th century CE in the Volta Region of Ghana (part of former German–Togoland territory; Fig. 1). We performed a multi-element analysis of AfDE soil from the Ziavi–Galenkuito site to determine the extent of enrichment by anthropogenic elements due to human settlement activities. Using the Energy dispersed portable X-Ray Fluorescence spectrometer (pXRF), we determined the total concentrations of elements and plant–available concentrations by the Mehlich III extraction (Mehlich, 1984) followed by inductively coupled plasma– mass spectrometry (ICP–MS). Previously plant-available concentrations of elements (Mehlich III extraction) was successfully used to evaluate the intensity of ancient settlement activities on agricultural and forest soils in Central Europe by Hejcman et al. (2011, 2013a, 2013b), but there are no such studies in Sub–Saharan Africa so far.

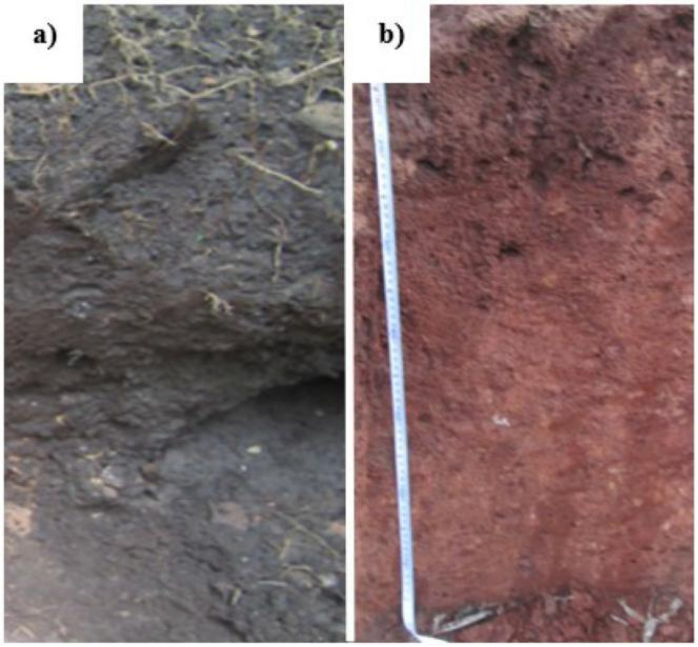

Fig. 3. (a) African Dark Earth soil (AfDE) from Ziavi–Galenkuito site and (b) the control soil (Ferric Acrisol). The two soils are 40 m apart. The depth of AfDE extends to 40 cm.

We tried to answer the following research questions: (a) Which elements are considered anthropogenic and indicators of settlement activities in the studied site?; (b) At what level can past settlement activities affect the concentrations of elements and other chemical properties in comparison to surrounding soil unaffected by settlement activities on the same geological substrate?; (c) To what extent are comparable patterns obtained by the analysis of total and plant-available concentrations of selected elements, and which method is more suitable for geoarchaeological purposes?; and (d) Can less than a hundred years of past settlement activities result in the formation of AfDE soil with a substantial accumulation of anthropogenic elements?

Materials and methods

Study site

Ziavi–Galenkuito (henceforth settlement site; Fig. 2; 6°40′49.8” N, 0°27′50.62E”) is located within the Ho–Ziavi community, about 4 km west of Ho, the capital of Volta Region and about 200 km NE of Accra, capital of Ghana. It covers an area of approximately 4 ha of the Kabakaba hills with an altitude of 457 m a. s. l. The whole area has a temperature ranging from 21 °C in winter (April to October) to 32 °C in summer (November to March). The annual precipitation of the area ranges from 900 to 1300 mm and located on metasedimentary/Voltaian bedrock (Mul et al., 2015).

The tropical climatic condition of the area is influenced by the SW Monsoon from the south Atlantic and dry NE trade winds. The study area is surrounded by mixed vegetation of guinea woodland and moist semi-deciduous forest (Dogbey, 2015). The soil in the settlement site is Acrisol/Forest Ochrosol observed from immediate surrounding (control) soil with the same geology (Adjei–Gyapong and Asiamah, 2002; Mul et al., 2015) but visually black only in the settled area (Fig. 3).

Fig. 4. Site map of Ziavi–Galenkuito showing locations of excavated units (Locus A, B, C, and D), relicts of building foundations (BF1, BF2, and BF3), and control site.

Historical background

According to documented oral accounts by the indigenous people of the area, the Germans built a plantation and settled there in the 1880s until they were conquered by the British during the 1st World War in 1914 (Apoh, 2009, 2016; Dogbey, 2015). The British then resided on the site from 1914 and left in the 1950s after Ghana gained independence in 1957 (Apoh, 2009, 2016). In total, the settlement of the Germans and the British amounted to approximately 70 years. The German first constructed buildings and were later used by the British. Material culture and ethnographic evidence suggested that there was only one family in the settlement site during the British settlement (Apoh, 2009, 2016; Dogbey, 2015). As an indigenous community, potteries confirmed from ethnographic evidence were for storing and drinking herbal medicine and palm wine commonly practiced among contemporary Ziavi indigenes (Dogbey, 2015). After the departure of the British, the Forestry Authority took custody of the site contributing to the preservation of the site from human encroachment and other illegal activities (Dogbey, 2015).

Archaeological excavation and sampling design

Archaeological excavations were conducted on the site by Wazi Apoh and his students from the University of Ghana in 2014, 2015, and 2016 seasons. The excavations were conducted based on a judgmental sampling technique (Shennan, 1992) to choose specific areas to excavate in other to maximize the recovery of artifacts.

Specific sampling design was applied to cover the variability of soils in the settlement site and the surrounding control site (Fig. 4). Soil samples were taken by soil probe from the upper 0–10, 10–20, and 20–40 cm layers after removal of surface litters. We sampled four excavated units (Locus A, B, C, and D). Again, we sampled three representative rooms of the relicts of building foundations; main building foundation (BF1) and two other building foundations (BF2 and BF3) visually identified by their collapsed stone demarcations. Soil samples were also collected from areas within the settlement site but outside building foundations and away from Locus A–D; Proxy. Additionally, we collected soil samples as control from the surroundings, visually devoid of anthropogenic activities, located 40 m away from the settlement site. In each layer of all the sampled locations, we collected three soil samples for analysis. In total, 81 soil samples were collected. We sampled the arable and part of the subsoil layers as they represent the layers of settlements before the abandonment of the site.

Analytical procedure

All 81 soil samples were air-dried, oven-dried at 40 °C for 24 h, and sieved. The homogenous fraction b2–mm was analyzed. Of each soil sample, we analyzed 10 g to determine the percentage particle size. The particle size distribution of the soil samples was determined using 2 mm (‘very coarse’), 1 mm (coarse), and 0.5 mm (medium) sieves (sieve analysis) and compared.

Total P, K, Ca, Mn, Fe, Al, Si, Cu, Zn, Sr, and Rb concentrations were determined with pXRF in soil Geochem mode (Delta Professional manufactured by Olympus) as they were above the detection limit. The pXRF is used to obtain the total or near-total concentration of elements in the soil matrix (see Canti and Huisman, 2015 for application of pXRF spectrometer). Every data reading performed for 1 min; the first 30 s using a beam generated by 10 kV and the remaining 30 s with a 40 kV beam. Each sample was tested three times with the final value as an arithmetic average of the three results. The quality of pXRF results was successfully tested by the company

BAS Rudice Ltd. (https://www.bas.cz) on 55 reference materials (e.g., SRM 2709a, 2710a, 2711a, OREAS 161, 164, 166, RTC 405, 408). The concentration of some elements was not determined in all samples as it was below the limit of detection. In only two cases, the concentration of K was below the detection limit– missing values replaced by half of the detection limit.

Fig. 5. Relicts of former settlement Ziavi–Galenkuito after its abandonment; (a) main building foundation showing cemented floor (photo by Michael O. Asare), (b) still preserved German excavated well used as a source of water for the settlement, (c) incomplete European ceramic pot and (d) upper 10 cm of an excavated unit with an incomplete vessel.

However, the concentration of Mg, S, Cl, Mo, Co, Ni, Cd, Sn, Ti, Ag, Tl, Au, Th, and Hg in all samples were omitted from further analysis as they were either not detected or above the limit of detection only in few cases. We determined the concentration of organic C and total N using the Skalar Primacs SNC–100 analyzer (Skalar, Netherland). The pH (H2O) of all soil samples was obtained from a 1:1 ratio (soil–water) using Voltcraft PH–100 ATC pH meter (pH 212) produced by I & CS spol s r.o., Czech Republic.

The pXRF results may be influenced by matrix effects, e.g., density, porosity, and grain size of analyzed materials (Kalnicky and Singhvi, 2001). However, the reliability of data obtained by pXRF was assessed by randomly selecting five homogenized soil samples. These samples were also measured to determine the total P, K, Ca, Mn, Fe, Al, Cu, Zn, and Sr concentration in an independent accredited laboratory where extractions of elements in Aqua regia extract (International Organization for Standardization USEPA 3052) determined by inductively coupled plasma mass spectrometry– (ICP–MS, Agilent 7700×). The compared elements were consistent with both methodologies except for Rb and Si (not fully soluble in Aqua regia). The plant–available

(Mehlich III extraction) P, K, Ca, S, Fe, Cu, and Zn concentrations were determined in all the soil samples using the same ICP–MS as in the case of the total elements.

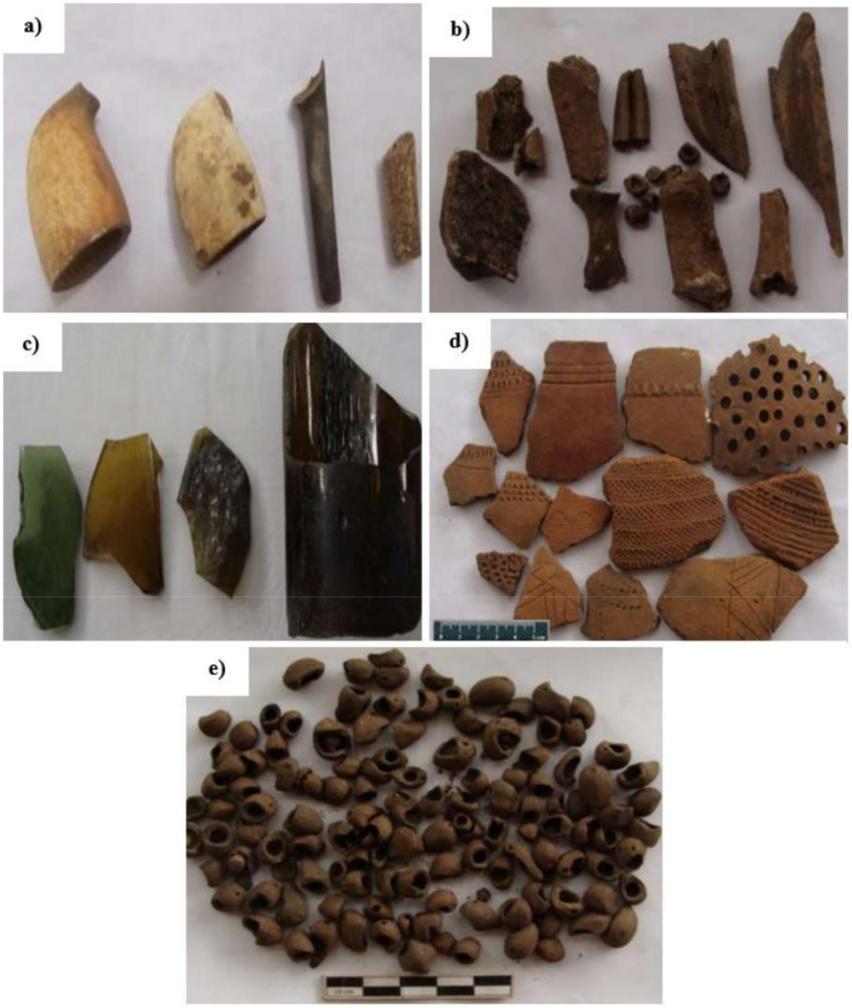

Fig. 6. (a) Broken smoking pipes, (b) bones, (c) broken bottles, (d) pottery fragments, and (e) burnt palm kernel shells unearthed during excavation and field survey.

Data analysis

There was relatively homogeneity of variance among data for all analyzed soil samples. To evaluate the differences in particle size, pH, as well as elemental composition between analyzed soil samples, we used one–way ANOVA. We used ANOVA as there was the normality of data using the Shapiro–Wilk W test of normality. In the case of significant ANOVA, we applied post–hoc comparison using the Tukey HSD test to identify significant differences between the soil particle sizes, pH, and concentration of elements among the soil layers in all sampled locations. To evaluate the relationship between the contents of different elements, as well as between elements obtained from the pXRF, Mehlich III, and Aqua regia ICP–MS data, we used Pearson's correlation. We performed all statistical analyses using the STATISTICA 13.3 program (www.statistica.oi).

Table 1 Particle size distribution (mean percentage ± S.D.) and description of 0–10, 10–20, and 20–40 cm soil layers. The F and p–values– obtained by one–way ANOVA. Using the Tukey HSD post hoc test, sampled locations with the same letter were not significantly different.

Sample location	**Soil layers [cm]**	**Soil particle size [%]**				**Color** [a]	**Texture** [b]	**Consistency**	**Other characteristics**
		≥ 2 mm	< 2-1 mm	< 1-0.5 mm	< 0.5 mm				
Locus A	0-10	11 ± 0.1a	23.4 ± 0.3a	28.9 ± 0.1b	36.6 ± 0.2b	7.5YR 2.5/1	Clay loam + artefacts	Firm, slightly sticky + plastic	St. black + few angular friable particles
	10-20	7.8 ± 0.6bc	26.3 ± 1.3a	30.4 ± 0.8a	35.5 ± 0.3b	7.5YR 2.5/1	Clay loam + artefacts	Firm, slightly sticky + plastic	St. black + few angular friable particles
	20-40	4.4 ± 0.2b	26.6 ± 0.9b	31.9 ± 0.3a	37.2 ± 0.5c	7.5YR 2.5/1	Clay loam + many artefacts	Firm, slightly sticky + plastic	St. black + very few angular friable particles
Locus B	0-10	10.5 ± 0.3a	23.7 ± 0.6a	30.4 ± 0.3a	35.3 ± 0.2a	7.5YR 2.5/1	Clay loam + artefacts	Firm, slightly sticky + plastic	St. black + few angular friable particles
	10-20	8.4 ± 0.1b	26.1 ± 0.8a	30.6 ± 0.4a	34.9 ± 0.7b	7.5YR 2.5/1	Clay loam + artefacts	Firm, slightly sticky + plastic	St. black+ few angular friable particles
	20-40	4.7 ± 0.2b	27.5 ± 0.3ab	31.8 ± 0.4a	36 ± 0.7c	7.5YR 2.5/1	Clay loam + many artefacts	Firm, slightly sticky + plastic	St. black + very few angular friable particles
Locus C	0-10	10 ± 0.1a	23.7 ± 0.3a	30.6 ± 0.5a	35.7 ± 0.6a	7.5YR 2.5/1	Clay loam + artefacts	Firm, slightly sticky + plastic	St. black + few angular friable particles
	10-20	8.4 ± 0.5ab	25.6 ± 1a	30.7 ± 0.5a	35.1 ± 0.2b	7.5YR 2.5/1	Clay loam + artefacts	Firm, slightly sticky + plastic	St. black + few angular friable particles
	20-40	6.7 ± 0.2a	27.2 ± 0.5b	30.4 ± 0.6ab	35.7 ± 1.1ab	7.5YR 2.5/1	Clay loam + relatively many artefacts	Firm, slightly sticky + plastic	St. black + few angular friable particles
Locus D	0-10	10.6 ± 0.4a	24.2 ± 0.2a	31.4 ± 0.4a	33.8 ± 0.7a	7.5YR 2.5/1	Clay loam + artefacts	Firm, slightly sticky + plastic	St black + few angular friable particles
	10-20	8.1 ± 0.1bc	25.9 ± 1.1a	30.5 ± 0.8a	35.5 ± 0.3b	7.5YR 2.5/1	Clay loam + artefacts	Firm, slightly sticky + plastic	St black + few angular friable particles
	20-40	8.2 ± 0.2a	26.6 ± 0.2b	29.3 ± 0.1b	35.9 ± 0.1c	7.5YR 2.5/1	Clay loam + relatively many artefacts	Firm, slightly sticky + plastic	St black + few angular friable particles
BF1	0-10	9.9 ± 0.1a	26 ± 0.1ab	31 ± 0.1a	32.8 ± 0.5ac	7.5YR 3/1	Clay loam + very few artefacts	Slightly firm, slightly sticky + plastic	Black + common few angular friable
	10-20	9.8 ± 0.3a	27.8 ± 0.6ab	30.6 ± 0.8a	32.5 ± 0.4a	7.5YR 3/1	Clay loam + very few artefacts	Slightly firm, slightly sticky + plastic	Black + common few angular friable
	20-40	4.1 ± 0.3b	29.3 ± 0.9a	31.9 ± 0.7a	34 ± 0.6a	7.5YR 3/1	Clay loam + very few artefacts	Slightly friable, Slightly firm, slightly sticky + plastic	Black + common very few angular friable

Table 1 *(continued)*

Sample location	**Soil layer [cm]**	**Soil particle size [%]**				**Color** [a]	**Texture** [b]	**Consistency**	**Other characteristics**
		≥ 2 mm	< 2-1 mm	< 1-0.5 mm	< 0.5 mm				
BF2	0-10	10.5 ± 0.1a	25.3 ± 0.5ab	29.8 ± 0.5ab	34.4 ± 0.1ac	7.5YR 2.5/1	Clay loam + very few artefacts	Firm, slightly sticky + plastic	Black + common few angular friable
	10-20	9.5 ± 0.5a	25.5 ± 0.5a	30.6 ± 0.4a	34.3 ± 0.2b	7.5YR 2.5/1	Clay loam + very few artefacts	Firm, slightly sticky + plastic	Black + common few angular friable
	20-40	4.6 ± 0.5b	28.9 ± 1a	31.9 ± 0.7a	34.6 ± 0.2a	7.5YR 2.5/1	Clay loam + very few artefacts	Slightly friable, Slightly firm, slightly sticky + plastic	Black + common very few angular friable
BF3	0-10	10 ± 0.1a	25.2 ± 0.3ab	30.6 ± 0.3a	34.2 ± 0.3ac	7.5YR 2.5/1	Clay loam + very few artefacts	Firm, slightly sticky + plastic	Black + common few angular friable
	10-20	9.2 ± 0.2a	25.8 ± 0.05a	30.6 ± 0.4a	34.3 ± 0.1b	7.5YR 2.5/1	Clay loam + very few artefacts	Firm, slightly sticky + plastic	Black + common few angular friable
	20-40	4.6 ± 0.5b	28.5 ± 1.1a	32.3 ± 0.9a	34.6 ± 0.2a	7.5YR 3/1	Clay loam + very few artefacts	Firm, slightly sticky + plastic	Black + common very few angular friable
Proxy	0-10	9.4 ± 0.4a	24.5 ± 0.4a	31.4 ± 0.7a	34.6 ± 0.5a	7.5YR 3/1	Clay loam + few artefacts	Firm, slightly sticky + plastic	Black + few angular friable particles
	10-20	9.3 ± 0.3a	27.5 ± 0.6ab	30.7 ± 0.6a	32.5 ± 0.3a	7.5YR 3/1	Clay loam + few artefacts	Firm, slightly sticky + plastic	Black + few angular friable particles
	20-40	4.7 ± 0.3b	29.6 ± 1.2a	31.5 ± 1.2a	34.4 ± 0.3a	7.5YR 3/1	Clay loam + few artefacts	Slightly friable, firm, slightly sticky + plastic	Black + very few angular friable particles
Control	0-10	9.3 ± 0.1a	29 ± 0.4b	30.7 ± 0.5a	30.9 ± 0.4c	7.5YR 3/3	Clay loam	Friable, slightly sticky + slightly plastic	Dark brown + few angular particles
	10-20	9 ± 0.3a	28.9 ± 0.3ab	30.6 ± 0.6a	31.3 ± 0.9a	7.5YR 4/3	Clay loam	Friable, slightly sticky+ slightly plastic	Brown + few angular particles
	20-40	4.4 ± 0.5b	29.8 ± 0.7a	31.9 ± 0.5a	33.5 ± 0.4a	7.5YR 4/6	Clay loam	Firm, sticky + plastic	St brown + very few angular particles
Mean		**7.9**	**26.8**	**30.9**	**34.3**				
Position (F & p-values)	0-10	2.6 0.05	48 < 0.001	6.7 0.001	49.9 < 0.001				
	10-20	8.9 < 0.001	8.1 < 0.001	0.06 1.00	30.2 < 0.001				
	20-40	37 < 0.001	7.5 < 0.001	5.6 0.00	15.4 < 0.001				
Interaction (F & p-values)		0.4 0.9	7.5 0.001	0.99 0.4	27.5 0.00				

Abbreviations; Locus A, B, C, and D – excavated units, BF – Building Foundation and Proxy (soil outside building foundations and excavated Units).
Munsell Soil Color Chart. according to Jahn et al. (2006), St–strong.

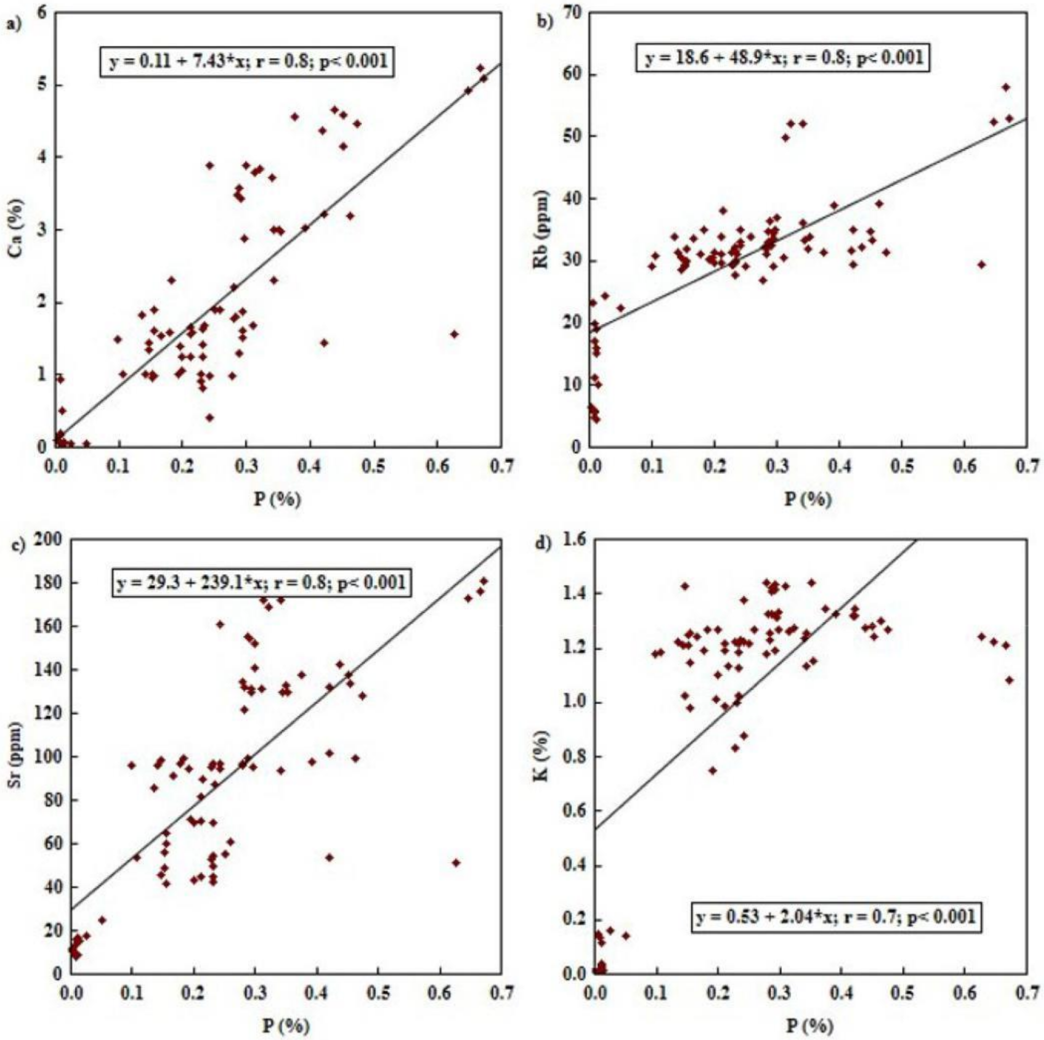

Fig. 7. Relationship between total P and total Ca (a), Rb (b), Sr (c), and K (d) concentrations.

Results

3.1. Field observation

Collapsed concrete building foundations and dug well are still visible at the settlement site (Fig. 5a and b). Materials identified from field survey and excavated units included organic (charcoal pieces, partly burnt palm kernel shells n = 171 and bones n = 24) and inorganic (incomplete vessel n = 1, European ceramics n = 29, broken glasses n = 151, smoking pipes n = 3, pottery fragments n = 422 and metallic objects n = 41) wastes (Figs. 5c, d and 6).

3.2. Particle size distribution and description of soil

There was a significant difference ($p < .05$) between the sizes of all soil particles in 0–10 and 20–40 cm in all sampled locations (Table 1). We recorded no difference in the fraction of medium size particles, in the 10–20 cm layers. There was no difference between the fractions of all the particle sizes of the control, BF1–BF3, and 'Proxy' in the 20–40 cm layers. In all soil samples, the proportion of soil particle size fractions was 7.9 (≥ 2 mm), 26.8 (< 2–1 mm), 30.9 (< 1–0.5 mm), and 34.3% (< 0.5 mm). We recorded a high proportion of fine soil particles in Locus A–D, especially in the 20–40 cm layer compared to all the other sampled locations. According to Guidelines for Soil Description, the soil texture in the settlement site and the control was clay loam with relatively sticky and plastic particles (Jahn et al., 2006; Table 1). The soil color was dark brown to strong–brown in the control and black too strong–black in the settlement site (Table 1).

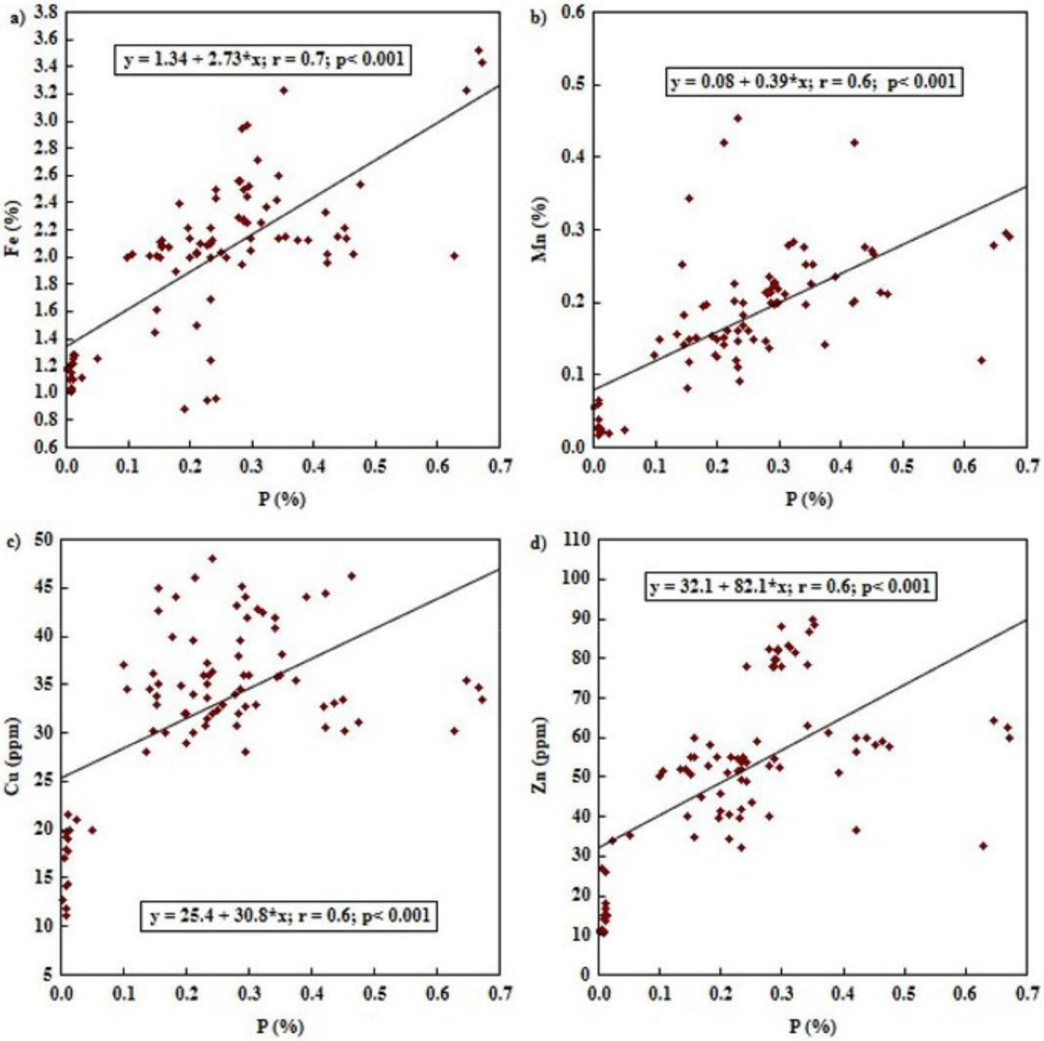

Fig. 8. Relationship between total P and total Fe (a), Mn (b), Cu (c), and Zn (d) concentrations.

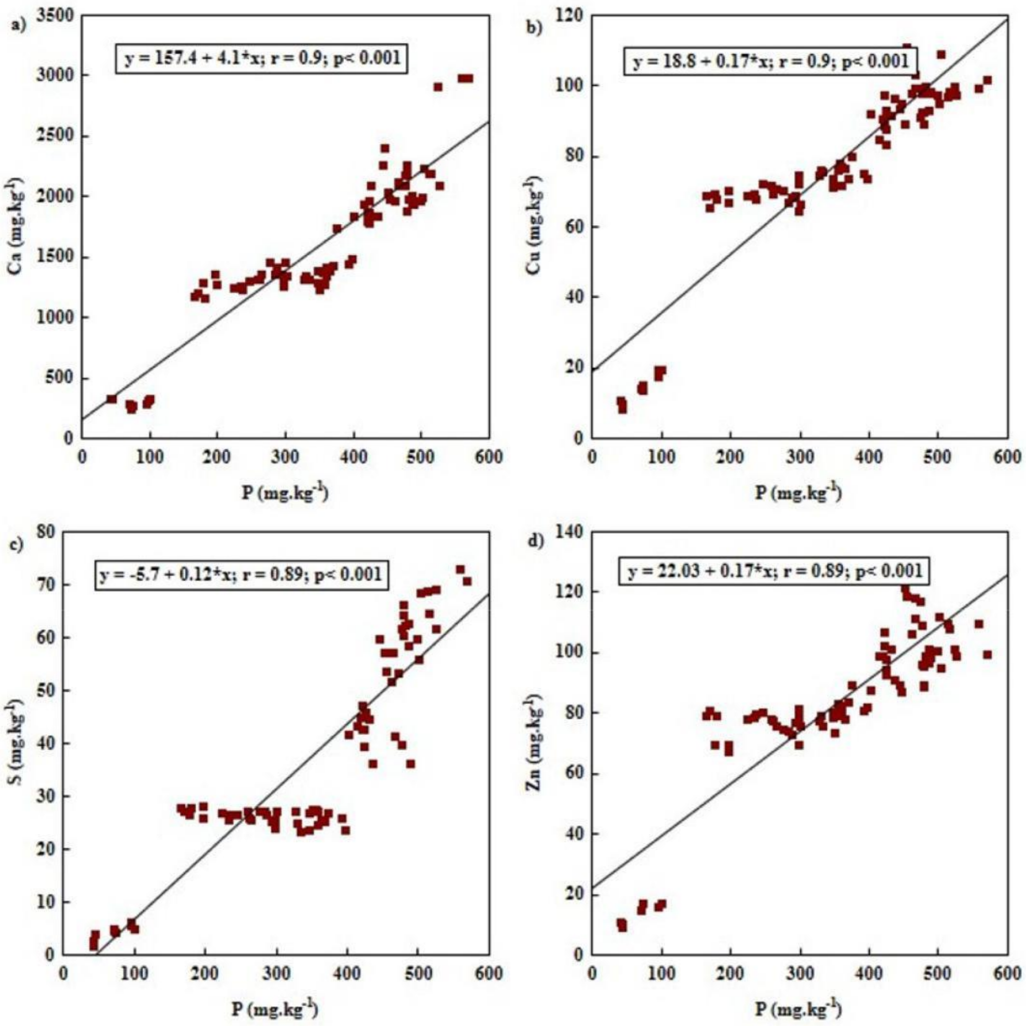

Fig. 9. Relationship between plant-available P and plant–available Ca (a), Cu (b), S (c), and Zn (d) concentrations.

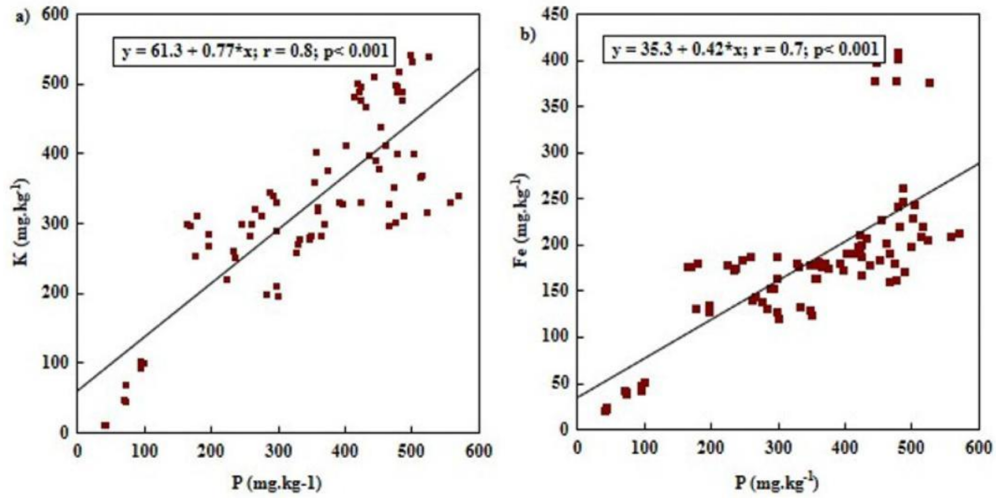

Fig. 10. Relationship between plant-available P and plant–available K (a), and Fe (b) concentrations.

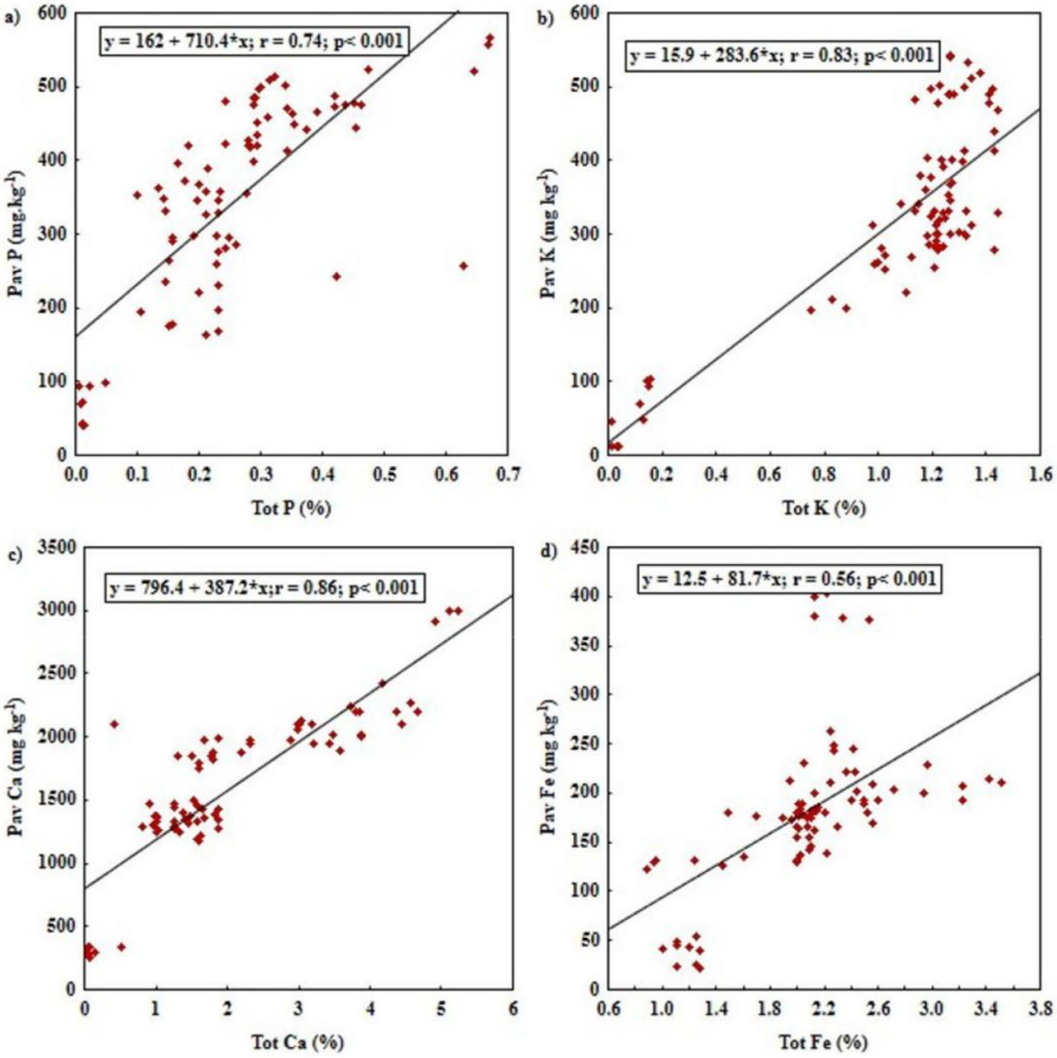

Fig. 11. Relationship between total (Tot) and plant–available (Pav) P (a), K (b), Ca (c), and Fe (d) concentrations

3.3. Soil chemical analysis

Statistical descriptions of obtained data for pH and all analyzed elements are in Figs. 7–11 and Tables 2 and 3. Slightly acidic to neutral soil reactions were recorded in the settlement site compared to moderately acidic in the control site. There was significantly larger pH, concentrations of organic C, total N, P, K, Ca, Fe, Cu, Zn, Sr, and Rb in the 0–10, 10–20, and 20–40 cm soil layers from all sampled locations of the settlement site compared to the control (Table 2). Except for the 20–40 cm layer, there was a significant difference between the other soil layers of the control and settlement site in the total Mn concentration. There was a significantly larger C/N ratio and Si ($p < .001$) concentrations in the control and vice versa in the settlement site in all the sampled layers (Table 2). Except for the concentration of Si, the largest total elements concentration in each sampled layer was in Locus A–D followed by BF1–BF3, Proxy, and the lowest in control. We recorded no pattern of accumulation of elements in all the analyzed layers except for concentrations of total P, Ca, Cu, Rb, and Sr, which mostly accumulated in the 20–40 cm layer of the settlement site.

There were significantly larger ($p < .001$) concentrations of plant-available P, K, Ca, S, Fe, Cu, and Zn in all analyzed layers in the settlement site compared to the control (Table 3). There was less variability among the concentrations of studied plant-available elements in all the sampled layers of the settlement site. The largest concentrations of plant-available elements in each soil layer were in Locus A–D compared to the respective layers of BF1–BF3 and the control. We recorded a relatively similar pattern of accumulation of plant-available elements in BF1–BF3 and Proxy.

Significantly positive correlations between total P and K, Ca, Mn, Sr, Fe, Zn, Rb, Cu were recorded (from $r = 6$ to $r = 8$; $p < .001$; Figs. 7 and 8). There were strong correlations between plant-available P and K, Ca, Sr, Fe, Zn, Rb, Cu ($r > 0.8$, $p < .001$; Figs. 9 and 10). We recorded significant correlations between total and plant–available P and K, Ca, Fe, Zn, and Cu ($r = 0.6$–0.87; $p < .001$, Figs. 11 and 12).

3.4. Validity of XRF data

The results obtained from the comparison of pXRF and Aqua regia ICP–MS data revealed a strong linear correlations among total concentration of P ($r = 0.99$, $p < .001$), K ($r = 0.96$, $p = .007$), Ca ($r = 0.99$, $p < .001$), Fe ($r = 0.97$, $p = .005$), Mn ($r = 0.99$, $p < .001$), Cu ($r = 0.99$, $p < .001$), Zn ($r = 0.98$, $p < .001$), Sr ($r = 0.99$, $p < .001$) and Al ($r = 0.99$, $p < .001$). Based on the comparison of elemental concentrations obtained by both methods, pXRF data were of adequate precision for this study (Figs. 13–15, Supplementary material).

Discussion

Even though the settlement lasted for approximately 70 years, there is a change in soil color from brown in control to black and substantial accumulation of C, N, P, K, Ca, S, Mn, Fe, Cu, Zn, Sr, and Rb due to past human activities. The changes are well visible despite the abandonment of the site for more than 60 years. The particle size and ferric properties of the soil are characteristics of Acrisol (FAO, 2015; Dowuona et al., 2009). The proximity of BF1 to the control explains the approximately similar proportion of soil particle size in all the analyzed soil layers. Additionally, the relatively similar proportion of soil particle sizes in the 20–40 cm layer of BF1–BF3 and the control further confirm that both sites have the same soil. The large proportion of fine soil particles (b0.5 mm) in the settlement site contributed to the retention and lesser leaching of studied elements (Acosta et al., 2011). The black color of the soil in the settlement site was probably due to burning and cooking observed from the homogenously mixed high number of charcoal pieces and partly burnt palm kernel shells (WinklerPrins, 2014; Solomon et al., 2016). It can also result from burnt buildings/structures and organic waste decomposition (Lehmann et al., 2003). Moreover, Sulfur readily reacts with Fe during the decomposition of organic matter and may also have contributed to the black color of the soil (Walker, 1968), indicated by the large concentrations of plant-available S, Fe, and total Fe in the settlement site. The reduced soil acidity in the settlement site relates to the large concentrations of total and plant–available Ca, organic waste (Hejcman et al., 2011), and ashy deposits in the excavated units. The highest pH range (6.1–6.9) recorded in the excavated units also contributed to the retention of the studied elements. The excavated units indicate midden pits evident from the partly burnt palm kernel shells, pottery fragments, many animal bones, pieces of charcoal, and ashy deposits in the 20–40 cm soil layer (Hirst, 2017; Howard, 2017). The midden pits also had the largest concentrations of both total and plant–available elements, especially in Locus A and B compared to all sampled locations.

The increased concentrations of organic C and total N in the settlement site compared to the control indicate organic waste deposition, manuring, and tools/houses manufacture or destruction (Deotare and Joshi, 1981; Bogaard et al., 2007). The higher organic matter stock indicated by elevated concentrations of organic C, N, plant-available elements, higher soil pH, as well as decomposed animal residues (bones) in the settlement site compared to the control, are typical features of Archaeological Dark Earth soils (Courty et al., 1990; Nicosia et al., 2012).

Large organic C concentration in the settlement site may contribute to higher CEC responsible for lesser leaching of studied elements (Glaser et al., 2001; Lehmann et al., 2003; Glaser, 2007). The lower C/N ratio recorded in the settlement site indicates biomass ash, excrement, and biosolids depositions, which denote high mineralization and nutrient supply to crops (Kanokporn, 2015).

The concentration of total P was increased by 0.16 to 0.65% in the settlement site representing approximately 2–5.2 times enrichment compared to the control. The concentration of plant-available P increased by 4.2–13.3 times in the settlement site. The varying total and plant–available P concentrations in the settlement site, indicate the intensity of deposition of biomass ash (Kofman, 2016), domestic waste including excrements and animal bones which contains 6.07–10.75% of P (Holliday and Gartner, 2007; von Oheimb et al., 2008). Moreover, the persistence of P due to its high affinity to bind with Fe/Al oxides in anthropic soil makes it a suitable indicator of settlement activities (Costa et al., 2013). Together with the relatively homogenous distribution in the concentration of total (Mn, S, Fe, Zn, K, Rb, Ca and Cu) and plant– available (Mn, Fe, Zn, K, Ca, and Cu), and their significantly positive correlation with total and plant–available P, they represent indicators of past settlement activities (Figs. 7–10, and Tables 2 and 3).

Although K in the soil is highly mobile and readily available for plant–root uptake and deficient in most soils (Hengl et al., 2017), we recorded an increased concentration of total K ranging from 0.8 to 1.44% in the settlement site compared to the control. However, the K concentration in this study is much higher in comparison to recorded values from other past settlement sites. For example, 0.11 to 0.61% of K concentration compared to a background value of 0.33% was reported by Fleisher and Sulas (2015) in a 15th–16th Century AD Swahili settlement of Songo Mnara, Tanzania. Larger K concentration in the settlement site relates to the shorter period after the abandonment of the site to date, leading to lesser K leaching.

Furthermore, plant-available K was 4–8.2 times enriched in the settlement site compared to the control. Increase K concentration in past settlements sites are due to its accumulation in food and crop processing residues, organic waste (Pogue, 1988), and biomass ash which contain approximately 2 to 7% of K (Entwistle et al., 1998; Misarti et al., 2011; Kofman, 2016). The increased total Ca concentration ranging from 0.9 to 5.02% in the settlement site represents 2.2–9.6 times enrichment compared to the control. The plant–available Ca concentration was also enriched by 4.3–8.2 times in the settlement site. The deposition of biomass ash containing from 5 to 45% of Ca, organic waste especially from cooking (Gaskin, 2002; Kofman, 2016; Simniškytė–Strimaitienė et al., 2017) and still visible daub houses built with loam/clay materials resulted in this enrichment. Additionally, increased Ca concentration also resulted from accumulation in animal bones containing from 22.2 to 24.5% Ca (Henss et al., 2013; Buddhachat et al., 2016).

Table 2. Mean pH, organic C, C/N ratio, and total concentration (± S.D.) of elements in 0–10, 10–20, and 20–40 cm soil layers in all sampled locations. The F and p–values– obtained by one–way ANOVA. Using the Tukey HSD post hoc test, sampled locations with the same letter were not significantly different.

Sample location	**Soil layer [cm]**	**pH [H_2O]**	**Org. C [%]**	**N_{tot} [%]**	**C/N Ratio**	**P [%]**	**K [%]**	**Ca [%]**	**Mn [%]**	**Fe [%]**	**Al [%])**	**Si [%]**	**Cu [ppm]**	**Zn [ppm]**	**Rb [ppm]**	**Sr [ppm]**
Locus A	0-10	6.3 ± 0.1a	4.17 ± 0.8a	0.31 ± 0.04a	16 ± 0.5a	0.42 ± 0.05b	1.31 ± 0.03ad	4.46 ± 0.01b	0.18 ± 0.04a	2.33 ± 0.2a	4.04 ± 0.4a	16.4 ± 0.1a	33 ± 3.0ab	59.5 ± 3.5a	31.5 ± 2.5a	133 ± 15b
	10-20	6.6 ± 0.4a	4.33 ± 0.4a	0.34 ± 0.03a	15 ± 0.6a	0.45 ± 0.02b	1.46 ± 0.01ab	4.46 ± 0.1b	0.27 ± 0.02a	2.43 ± 0.1a	4.02 ± 0.4a	16.4 ± 0.1a	32 ± 1.0abd	59 ± 2.0ab	33.5 ± 1.5a	138 ± 10d
	20-40	6.9 ± 0.0a	5 ± 0.09cd	0.32 ± 0.01bc	13.8 ± 0.4a	0.66 ± 0.01c	1.17 ± 0.07a	5.09 ± 0.1d	0.29 ± 0.008a	3.39 ± 0.1ab	4.7 ± 0.1ab	14.1 ± 0.1bc	34.6 ± 1a	62.2 ± 2.2e	54.4 ± 3.1d	176.6 ± 4.3cd
Locus B	0-10	6.3 ± 0.1a	4.39 ± 0.2a	0.24 ± 0.01a	14 ± 0.5ab	0.28 ± 0.02a	1.32 ± 0.04ad	3.56 ± 0.4b	0.21 ± 0.009a	2.20 ± 0.1a	4.31 ± 0.1a	16.4 ± 0.4a	36.7 ± 4ab	81.3 ± 4.7b	35.4 ± 0.9ad	151.3 ± 8.1c
	10-20	6.5 ± 0.1a	4.69 ± 0.2a	0.31 ± 0.02a	15 ± 0.1a	0.29 ± 0.02a	1.41 ± 0.03ab	3.49 ± 0.3b	0.22 ± 0.01a	2.27 ± 0.1a	4.35 ± 0.1a	16.5 ± 0.4a	36.7 ± 4.1ab	79 ± 2.1b	33 ± 1.6a	154.7 ± 4.4c
	20-40	6.8 ± 0.1a	4.8 ± 0.1cd	0.31 ± 0.01bc	15.2 ± 0.3a	0.33 ± 0.01ab	1.26 ± 0.02a	3.79 ± 0.06c	0.29 ± 0.003a	2.34 ± 0.08a	4.2 ± 0.1ab	15.2 ± 0.6ab	42.1 ± 1bc	80.7 ± 2.1d	51.3 ± 1.2c	170.9 ± 1.9cd
Locus C	0-10	6.1 ± 0.1a	3.55 ± 0.3a	0.22 ± 0.01a	16.2 ± 0.5a	0.26 ± 0.06a	1.21 ± 0.05a	1.68 ± 0.8ab	0.19 ± 0.01a	2.95 ± 0.08a	4.22 ± 0.4a	16.9 ± 0.7a	44.7 ± 2.4b	56.7 ± 5.7a	34.6 ± 1.2a	96.7 ± 2.0a
	10-20	6 ± 0.02a	3.47 ± 0.1a	0.25 ± 0.01a	14 ± 0.1a	0.29 ± 0.04a	1.32 ± 0.01a	1.68 ± 0.8ad	0.21 ± 0.01a	2.52 ± 0.06a	4.06 ± 0.5a	17 ± 0.6a	44 ± 1.6ac	53.3 ± 3.6a	34.2 ± 0.8a	97 ± 2.1a
	20-40	6.5 ± 0.2a	3.6 ± 0.2a	0.23 ± 0.02a	15.7 ± 0.5a	0.43 ± 0.03ab	1.32 ± 0.02a	3.15 ± 0.1ab	0.29 ± 0.1a	2.03 ± 0.08a	4.5 ± 0.2b	16.4 ± 0.3a	44.9 ± 1.2b	55.5 ± 3.9a	37.6 ± 2.4b	99.6 ± 1.7a
Locus D	0-10	6.7 ± 0.4a	3.69 ± 0.3a	0.24 ± 0.01a	15.2 ± 0.2a	0.29 ± 0.004a	1.23 ± 0.02a	1.73 ± 0.09ab	0.19 ± 0.04a	2.44 ± 0.4a	4.13 ± 0.1a	16.4 ± 0.5a	33 ± 4.1ab	86 ± 8.6b	30.7 ± 1.2a	128 ± 4.4b
	10-20	6.4 ± 0.2a	3.98 ± 0.2a	0.25 ± 0.01a	16 ± 1.4a	0.32 ± 0.04a	1.43 ± 0.1ab	1.78 ± 0.1ad	0.22 ± 0.01a	2.74 ± 0.4a	4.23 ± 0.08a	16.7 ± 0.4a	32.2 ± 5ab	82.3 ± 4.1b	32.1 ± 0.9a	132 ± 7.7b
	20-40	6.7 ± 0.1a	4.05 ± 0.1b	0.3 ± 0.01bc	14.7 ± 0.4a	0.34 ± 0.02ab	1.28 ± 0.1a	2.99 ± 0.01ab	0.24 ± 0.01a	2.5 ± 0.6a	4.5 ± 0.04b	15.2 ± 0.2a	38.6 ± 1ab	88.3 ± 1.5c	33 ± 0.9a	131 ± 2.1b
BF1	0-10	5.6 ± 0.1a	3.4 ± 0.2a	0.2 ± 0.001a	16.9 ± 0.3ac	0.19 ± 0.05a	1.22 ± 0.06a	1.6 ± 0.5ab	0.14 ± 0.00a	2.05 ± 0.05a	3.5 ± 0.5a	17.5 ± 0.5a	37.7 ± 6.4ab	58 ± 2.6a	32 ± 2a	62 ± 2.6d
	10-20	5.6 ± 0.1a	3 ± 0.04b	0.22 ± 0.00a	13.9 ± 0.6a	0.2 ± 0.04a	1.23 ± 0.01a	1.1 ± 0.1ac	0.15 ± 0.03a	2.14 ± 0.06a	3.7 ± 0.2a	17 ± 0.1a	35.7 ± 1.6ab	53.4 ± 1.8a	30.3 ± 1a	54.7 ± 1.6f
	20-40	5.7 ± 0.1a	2.8 ± 0.01b	0.19 ± 0.00a	13.3 ± 0.1a	0.16 ± 0.06a	1.17 ± 0.04a	0.94 ± 0.1ad	0.11 ± 0.06a	2.0 ± 0.01a	3.9 ± 0.1a	17.3 ± 0.6ac	34.2 ± 1a	51.2 ± 0.7a	29.9 ± 0.7a	50.8 ± 2.6g
BF2	0-10	5.7 ± 0.2a	3.4 ± 0.2a	0.21 ± 0.05a	16.2 ± 1.1a	0.17 ± 0.01a	1.24 ± 0.02a	1.54 ± 0.1ab	0.15 ± 0.002a	2.07 ± 0.01a	4 ± 0.2a	17.1 ± 0.1a	30 ± 2a	47.5 ± 3.7a	33 ± 0.6a	82.3 ±10.9a
	10-20	5.5 ± 0.1a	3 ± 0.03b	0.21 ± 0.01a	14.4 ± 0.4a	0.21 ± 0.03a	1.0 ± 0.02b	1.35± 0.05 a	0.14 ± 0.001a	2.11 ± 0.02a	3.4 ± 0.1b	16.9 ± 0.1a	31.1±1.1abd	40.7 ± 1.2abc	31 ± 0.5a	70.6 ± 1.6e
	20-40	5.5 ± 0.2a	3 ± 0.03a	0.22 ± 0.01a	13.8 ± 0.4a	0.2 ± 0.04a	1.04 ± 0.05a	1.21 ± 0.2ad	0.13 ± 0.001a	2.04 ± 0.02a	3.5 ± 0.3a	17.5 ± 0.1ac	29.9 ± 0.9d	40.3 ± 0.8f	30 ± 3.5a	43.7 ± 1.7ef

Table 2 (*continued*)

Sample location	**Soil layer [cm]**	**pH [H_2O]**	**Org. C [%]**	**N $_{tot}$ [%]**	**C/N Ratio**	**P [%]**	**K [%]**	**Ca [%]**	**Mn [%]**	**Fe [%]**	**Al [%])**	**Si [%]**	**Cu [ppm]**	**Zn [ppm]**	**Rb [ppm]**	**Sr [ppm]**
BF3	0-10	5.7 ± 0.1a	3.4 ± 0.2a	0.21 ± 0.01a	16.2 ±1.1a	0.22 ± 0.01a	1.19 ± 0.1ac	1.64 ± 0.1ab	0.14 ± 0.01a	1.91 ± 0.01a	3.5 ± 0.2a	17.2 ± 0.06a	38.7 ± 6.4ab	53.7 ± 2.3a	34.3 ± 3.5a	86.3 ± 4a
	10-.20	5.8 ± 0.1a	3 ± 0.03b	0.22 ± 0.01a	13.7 ± 0.7a	0.43 ± 0.1b	1.26 ± 0.1a	1.64 ± 0.5a	0.16 ± 0.04a	2.02 ± 0.01a	3.4 ± 0.1b	16.7 ± 0.2a	31 ± 1.1abd	37.4 ± 5abc	29.3 ± 0.1a	53.3 ± 1.7f
	20-40	5.9 ± 0.1a	2.9 ± 0.1b	0.22 ± 0.01a	13.6 ± 0.5a	0.2 ± 0.03a	1.13 ± 0.1a	1.6 ± 0.1d	0.42 ± 0.04a	1.95 ± 0.2a	3.5 ± 0.4a	17.2 ± 0.4ac	39.8 ± 2.7bc	33.7 ± 1.4g	29.1 ± 1.1a	44 ± 1.7ef
Proxy	0-10	5.6 ± 0.1a	3.39 ± 0.2a	0.21 ± 0.01a	16.2 ±1.1a	0.19 ± 0.08a	1.18 ± 0.1ac	1.36 ± 0.3a	0.16 ± 0.03a	1.99 ± 0.2a	3.7 ± 0.4a	16.2 ± 0.4a	37 ± 3ab	47.7 ± 6.8a	29 ± 2ac	96.7 ± 0.4a
	10-20	5.5 ± 0.1a	3.42 ± 0.1a	0.21 ± 0.02a	16.6 ± 1a	0.17 ± 0.05a	1.29 ± 0.1a	1.23 ± 0.2a	0.3 ± 0.1a	2.06 ± 0.1a	3.93 ± 0.1a	16.7 ± 0.6a	34.8 ± 1ab	50.9 ± 1.3a	30.8 ± 1.9a	97.1 ± 1.1a
	20-40	5.6 ± 0.1a	3.32 ± 0.1a	0.22 ± 0.05a	15.3 ± 0.3a	0.22 ± 0.02a	0.82 ± 0.1a	0.97 ± 0.04a	0.19 ± 0.03a	1.93 ± 0.0a	3.61 ± 0.4a	16.4 ± 0.6a	35.8 ± 0.8a	54.5 ± 0.6a	30.7 ± 1.5a	94.7 ± 0.6a
Control	0-10	4.4 ± 0.2b	2.3 ± 0.1b	0.12 ± 0.00b	19.7 ± 1.3d	0.02 ± 0.00c	0.14 ± 0.01c	0.07 ± 0.00c	0.03 ± 0.01b	1.19 ± 0.07b	2.3 ± 0.7b	19.8 ± 0.2b	19 ± 1.5c	27.2 ± 8.4c	17.4 ± 2e	21.8 ± 4.6e
	10-20	4.2 ± 0.1b	2 ± 0.002c	0.1 ± 0.02b	19.9 ± 1.1b	0.01 ± 0.00c	0.02 ± 0.01c	0.15 ± 0.02e	0.03 ± 0.01b	1.13 ± 0.1b	3.9 ± 0.2a	21.4 ± 0.5b	19.7 ± 1.3e	15.8 ± 1.6d	15.8 ±0.8b	13.9 ± 0.8g
	20-40	4.4 ± 0.2b	0.99 ±0.04e	0.05 ± 0.00d	20.9 ± 2.2b	0.01 ± 0.00d	0.016 ± 0.0b	0.28 ± 0.03e	0.03 ± 0.01a	1.15 ± 0.07c	4.1 ± 0.1a	22.5 ± 0.5d	12.8 ± 1.3d	11.4 ± 1.1h	5.5 ± 0.7e	9.3 ± 1.2h
Position (F & p-values)	0-10	40.6	10.1	21.4	11.3	19.4	296.9	24.3	12.3	4.3	14.2	20.7	10.6	24	16.3	182
		< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0	< 0.001	< 0.001	0.003	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
	10-20	67.4	251	71.1	19.9	16.6	427.9	113.9	9.4	42.6	16.7	60.4	72.7	329.8	52	1952
		< 0.001	0	< 0.001	< 0.001	< 0.001	0	< 0.001	< 0.001	< 0.001	<0.001	<0.001	<0.001	0	<0.001	0
	20-40	74.5	516.7	201.4	19.6	123	137.5	243.1	1.9	34.4	15.2	107	191	599.4	322.4	2653
		0.001	0	0	< 0.001	< 0.001	0.001	0	0.125	< 0.001	< 0.001	< 0.001	0	0	0	0
Interaction		103.2	54.7	77.7	22.9	34	15.5	84.2	5.2	18.1	9.2	48.8	41.7	82	20.8	170
(F & p-values)		<0.001	< 0.001	< 0.001	<0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

Sample locations abbreviations; Locus A, B, C, and D - excavated units, BF - Main Building Foundation and Proxy (soil outside building foundations and excavated Units).

The concentration of total Mn was increased in the settlement site by 0.08 to 0.27% in comparison to the control, representing 3.5–10 times enrichment. The increased concentration of Mn is associated with the accumulation in biomass ash containing 1 to 3% of Mn (Vassilev et al., Table 2 2013; Kofman, 2016), excrements, organic waste (Mescouto et al., 2011), and a product of burning (Aston et al., 1998). Total Fe concentration also increased by approximately 2.5–14 times in the settlement site compared to the control. The plant–available Fe concentration was 5.8–9.5 times enriched in the settlement site in comparison to the control. Iron is relatively abundant in organic materials such as livestock manure and many cultivated soils with average concentrations ranging from 2 to 4% (Cornell and Schwertmann, 2003).

The concentration of total Cu and Zn in the settlement site was within the threshold value of agricultural soils (Alloway, 2008) with an increase of 2.4–3.5 and 3–7.6 times in the settlement site in comparison to the control. The plant–available Cu and Zn concentrations were 6.1–9.8 (for Cu) and approximately 6–10 (for Zn) times enriched in the settlement site. Generally, increased concentrations of Cu and Zn are associated with agricultural activities (Klimek, 2002), evident from the mango plantation by the British (Dogbey, 2015). The increased concentration of Zn and Cu also relate to their accumulation in biomass ash which contains from 0.2 to 0.9% of Zn and approximately 0.02% of Cu, organic waste, and excrements deposition (Nielsen and Kristiansen, 2014; Campos et al., 2016; Kofman, 2016; Souza et al., 2016).

There was clear enrichment of total Sr and Rb in the settlement site, and they correlate well with total P. We conclude that Sr and Rb trace elements are relevant in identifying past human activities. The concentration of total Sr increased by 4.4–14.2 times in the settlement site compared to the control.

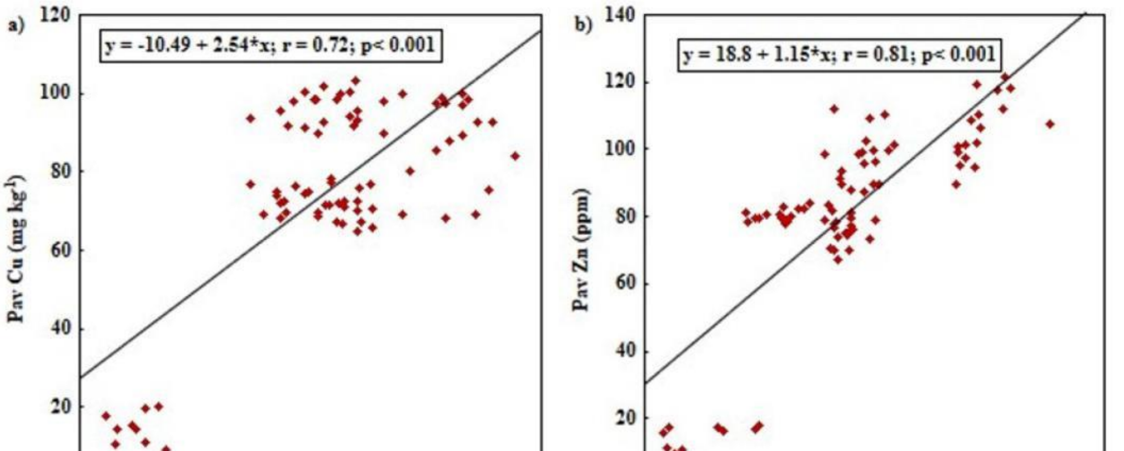

Fig. 12. Relationship between total (Tot) and plant–available (Pav) Cu (a), and Zn (b) concentrations.

Table 3. Concentration (Mean ± S.D.) of selected plant-available elements in the 0–10, 10–20, and 20–40 cm soil layers. The F and p–values were obtained by one–way ANOVA. Using the Tukey HSD post hoc test, sampled locations with the same letter were not significantly different.

Sample location	**Soil layer [cm]**	**P [mg kg^{-1}]**	**K [mg kg^{-1}]**	**Ca [mg kg^{-1}]**	**S [mg kg^{-1}]**	**Fe [mg kg^{-1}]**	**Cu [mg kg^{-1}]**	**Zn [mg kg^{-1}]**
Locus A	0-10	480 ± 40.8d	517 ± 23b	2191 ± 49.5bd	61.2 ± 1.1c	278 ± 1.5c	96.8 ± 2.5c	95 ± 4.8b
	10-20	466 ± 18.6b	428 ± 53.8b	2297 ± 45c	67.4 ± 3.3d	404 ± 5.3d	92.6 ± 2.8b	91 ± 4.4b
	20-40	549 ± 23.7d	331 ± 10.7bc	2971 ± 49.5d	71.2 ± 1.9d	210 ± 3.6c	101 ± 1.1b	104 ± 5.6b
Locus B	0-10	492 ± 19.8d	531 ± 11.5b	1996 ± 16.2b	59.7 ± 3.2c	218 ± 15.9b	97.8 ± 2.5c	104 ± 6.9b
	10-20	482 ± 4.8b	488 ± 4.9b	1952 ± 57.8b	60.8 ± 2.2d	251 ± 10.1c	97.2 ± 3.4b	96 ± 5.9b
	20-40	508 ± 5.5c	379 ± 17.9c	2212 ± 24.6b	67.5 ± 2.2d	226 ± 18c	102 ± 6.6b	105 ± 8.1b
Locus C	0-10	419 ± 5.3bc	483 ± 6.5bc	2011 ± 80.6b	44.2 ± 1.7b	192 ± 1.7b	86.2 ± 2.7b	100 ± 2.1b
	10-20	418 ± 17.7b	381 ± 42.7b	1857 ± 15.2b	39.4 ± 2.8b	180 ± 11.6b	92.5 ± 4.5b	91 ± 2.7b
	20-40	475 ± 10.6b	304 ± 6.7b	2061 ± 98.6bc	39.3 ± 2.6b	166 ± 6.1b	97.1 ± 3.7b	107 ± 7.1b
Locus D	0-10	419 ± 1.9bc	496 ± 5.6b	1829 ± 42.6bc	45.2 ± 2.2b	205 ± 7.5b	94.2 ± 3.4c	101 ± 6.3b
	10-20	447 ± 16.1b	440 ± 27.8b	1938 ± 83.1b	50.2 ± 4.6c	214 ± 13.1	101 ± 9.9b	109 ± 9c
	20-40	461 ± 10.6b	354 ± 25.1c	2084 ± 27bc	56.2 ± 2.1c	187 ± 5b	94.9 ± 7.4b	119 ± 2.3c
BF1	0-10	291 ± 5.3c	340 ± 19cd	1382 ± 17.6a	26 ± 0.6a	158 ± 5.8a	70.1 ± 2c	77 ± 2.8b
	10-20	266 ± 7.9c	311 ± 15.1a	1391 ± 72.9a	26.5 ± 0.8a	142 ± 3a	70.6 ± 0.7a	96 ± 1.5a
	20-40	189 ± 10.9f	270 ± 5.5b	1318 ± 46.9c	27.1 ± 1.1a	133 ± 3.4a	69.3 ± 1.7a	69 ± 1.4a
BF2	0-10	348 ± 17.8a	304.1 ± 20.8ac	1444 ± 34.3a	25.1 ± 1.1a	178 ± 3.6a	75 ± 1.7c	82 ± 2.8b
	10-20	333 ± 10.3a	270 ± 6.2a	1359 ± 15.8c	26.5 ± 1a	180 ± 1.3b	75.2 ± 1.1a	80 ± 1.5a
	20-40	229 ± 7.1e	245 ± 8.3bd	1258 ± 50.6c	26.5 ± 0.5a	177 ± 2.3b	70.0 ± 0.5a	79 ± 0.9a
BF3	0-10	370 ± 18.6a	326 ± 7.4cd	1411 ±28.9a	26.2 ± 1.3a	182 ± 2.4a	75 ± 2.5c	81 ± 1.2b
	10-20	266 ± 26.8c	291 ± 7a	1305 ± 22c	26.1 ± 1.6a	188 ± 2.5b	73.1 ± 1.6a	81 ± 1.7a
	20-40	170 ± 7.4f	304 ± 11.2b	1194 ± 45.3c	28 ± 0.3a	179 ± 2.4b	67.7 ± 1.5a	80 ± 1.1a
Proxy	0-10	361 ± 10.1a	380 ± 21.7a	1470 ± 241.7a	27.8 ± 0.3a	166 ± 5.8a	78.4 ± 1.7a	85 ± 3.6a
	10-20	342 ± 8.9a	281 ± 2.6a	1289 ± 38.9a	25.1 ± 2.3a	131 ± 4.9a	73 ± 2.3a	77 ± 2.6a
	20-40	293 ± 9.2a	202± 7.5a	1398 ± 57.9a	26.9 ± 1a	128 ± 5.5a	66 ± 1.3a	74 ± 3.2a
Control	0-10	95.3 ± 2.3e	99.5 ± 17.6e	318 ± 17.6e	5.8 ± 0.5d	49 ± 4.5d	19.2 ± 1.2d	16.9 ± 0.7c
	10-20	70.6 ± 1.4d	53.6 ± 13.1c	278 ± 20.1d	4.8 ± 0.4e	41.8 ± 2.2e	14.8 ± 0.7c	16.8 ± 1d
	20-40	41.3 ± 1.2g	11.9 ± 0.7e	339 ± 2.9e	2.9 ± 1.2e	23.9 ± 2d	10.2 ± 1.2c	10.5 ± 0.6d
Position (F& p-values)	0-10	139 < 0.001	329.1 0.00	88.3 < 0.001	337.8 0.00	397.9 0.00	264.7 < 0.001	107 < 0.001
	10-20	242.4 < 0.001	74.2 < 0.001	285.2 0.00	191.3 < 0.001	540.7 0.00	120.9 < 0.001	112.3 < 0.001
	20-40	767 0.00	168.6 < 0.001	812.2 0.00	550.8 0.00	208.9 < 0.001	182.1 < 0.001	161.1 < 0.001
Interaction (F & p-values)		76 < 0.001	33.9 < 0.001	125.4 < 0.001	315.5 < 0.001	44.1 < 0.001	249.6 < 0.001	166.4 < 0.001

Sample locations abbreviations; Locus A, B, C, and D – excavated units, BF– Building Foundation and Proxy (soil outside building foundations and excavated Units).

Moreover, total Rb concentration increased by 23.6 to 48.9 ppm representing 5.3–10 times in the settlement site. Increased Sr and Rb concentrations in past settlement sites indicate their accumulation in wood ash and manure (Neilsen and Kristiansen 2014; Oroian et al., 2015).

There was an increased concentration of total Al in the 0–10 cm soil layer of the settlement site compared to the control probably due to their accumulation in biomass ash which contains from 2 to 4% of Al (Pitman, 2006; Dibdiakova et al., 2015). However, the total concentration of Al in the control soil reflects its natural origin. The lowest concentration of total Si in the settlement site relates to an increased proportion of other elements and a less fraction of sand particles (Acosta et al., 2011), consistent with the building foundations where Si concentration was higher than the excavated units and proxy for similar reasons.

Increased fertility of the soil in the settlement site is indicated by enrichment by both total and plant–available elements (Hejcman et al., 2013a, 2013b; Solomon et al., 2016). Archaeological dark earth soils may contain 2–3 times enrichment by P, K, Ca, Mn, Cu, and Zn in (Glaser et al., 2001; Lehmann et al., 2003; Glaser, 2007). However, the real surprise in this study is the extraordinary enrichment in the concentrations of total and plant–available elements in a shorter duration on a tropical soil. The chemical signatures obtained in the settlement soil predominately relate to the European settlements evident from discovered relics and artefacts.

Meanwhile, the pattern for total and plant–available elements in this study was not the same. Plant–available elements are dependent on total element concentration and other soil chemical properties, such as pH, and the presence of Al/Fe oxides. For example, at N pH 7.5, plant-available P can quickly react with Ca and Mg to form less soluble compounds (Jensen, 2010). These complicate the estimation of enrichment factors of the plant–available concentration of elements in the field.

In this study, plant–available and the total concentration of elements significantly positively correlated, indicating that both analytical methods are suitable to estimate the enrichment factor of P, K, Ca, Fe, Cu, and Zn in deserted settlements in geoarchaeological studies. The significant relationship among these elements is associated with the pH range in all the soil layers suitable to retain relatively similar concentration of the studied elements. We suggest that in Acrisols, both analytical methods can provide suitable outcomes for the studied elements. However, in similar analyses conducted on Luvic Cambisol in the Czech Republic, except for total and plant–available Ca, total and plant–available P and K were not well correlated (Asare et al., unpublished). Again, there is a long laboratory protocol in the extraction of plant-available elements. Analysis of the total element concentration is much suitable for geoarchaeological purposes as the enrichment factor is easy to calculate in the field.

The higher concentrations of elements in the settlement site compared to the control resulting from past human settlement inputs demonstrated by different analytical approaches and identified organic/ inorganic materials. The studied site thus represents nutrient-rich AfDE soil.

Conclusions

Less than 100 years of past settlement activities contributed to a changed soil color from brown to black mainly from the addition of charcoal, reduced acidity, and substantially increased concentrations of organic C, total N, P, K, Ca, Mn, Fe, Cu, Zn, Sr, Rb and plant– available P, K, Ca, S, Fe, Cu, and Zn leading to the development of AfDE soil. The accumulation and retention of the elements resulted from the deposition of organic waste, excrements, biomass ash, increased pH, the high proportion of fine soil particles, and charcoal inclusion in the soil.

Together with P, total Ca, K, Mn, Rb, Cu, Zn, and Sr, as well as plant-available, Ca, K, Mn, Cu, and Zn are indicators of past human settlement activities.

Although there was variability in the concentrations of studied elements in the settlement soil layers, there was a substantially higher concentration in the soil layers when compared to their respective control layers indicating that elemental analysis of the upper soil layer is adequate to identify past human settlement activities.

The concentrations of total and plant–available P, K, Ca, Fe, Cu, and Zn were well correlated, thus both analytical approaches are suitable for geoarchaeological purposes. However, the pattern recorded using the concentration of plant-available elements is affected by some soil chemical properties making it hard for straightforward conclusions without a detailed analysis of soil properties, hardly performed by geoarchaeologists in the field.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

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SUPPLEMENTARY MATERIAL

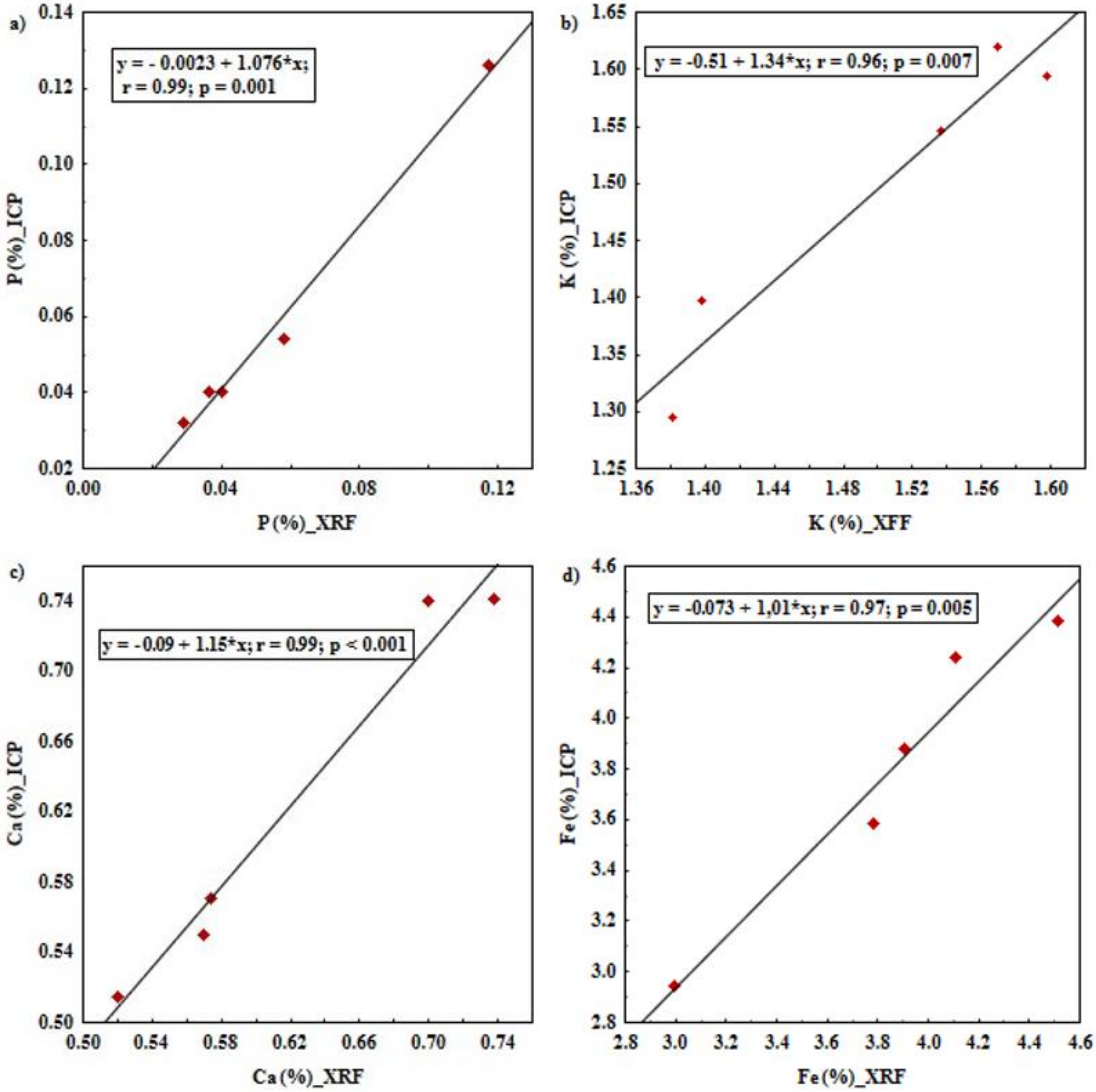

Fig. 13 Scatterplot correlation between pXRF and *Aqua regia* ICP data of P (a), K (b), Ca (c), and Fe (d) contents

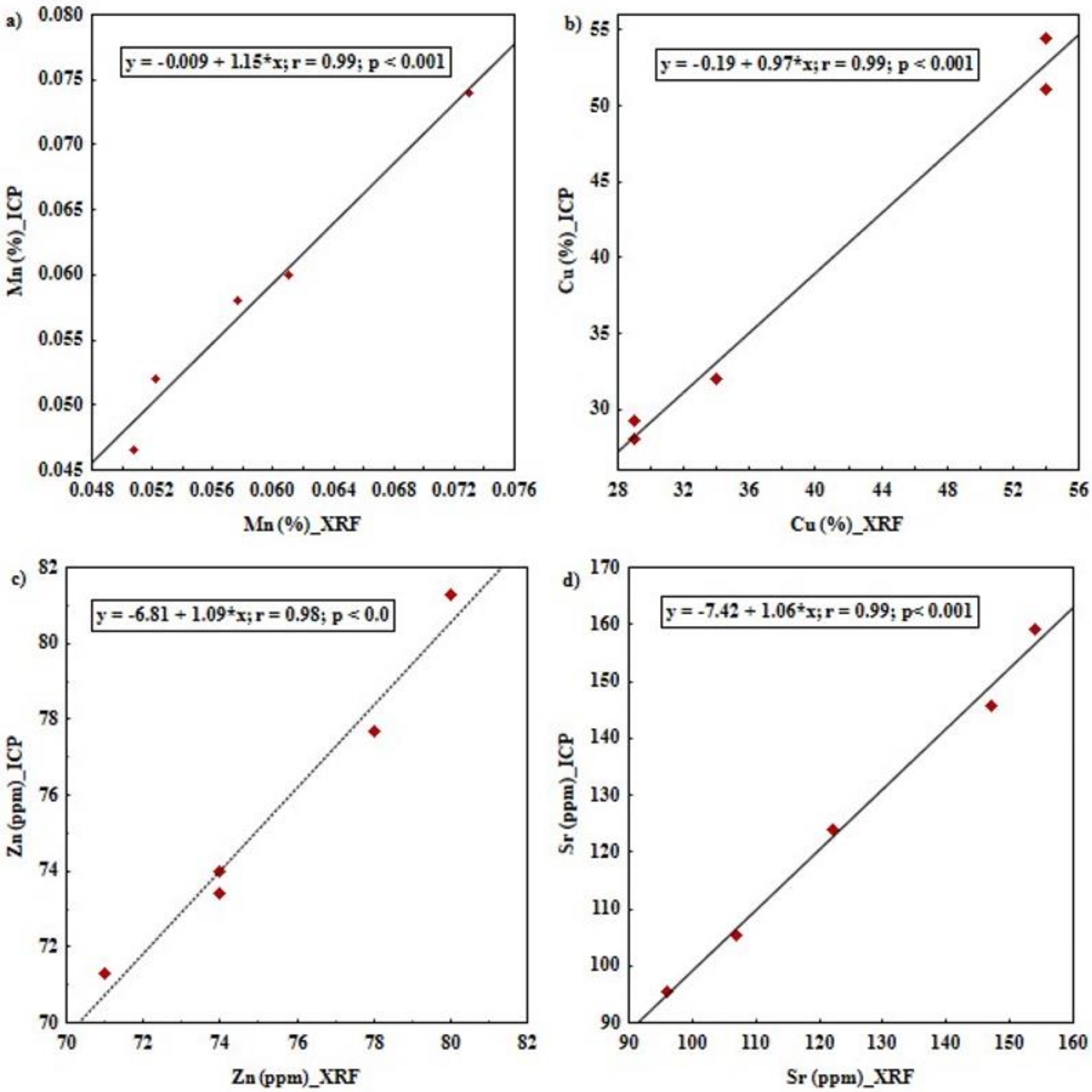

Fig. 14 Scatterplot correlation between pXRF and *Aqua regia* ICP data of Mn (a), Cu (b). Zn (c), and Sr (d) contents

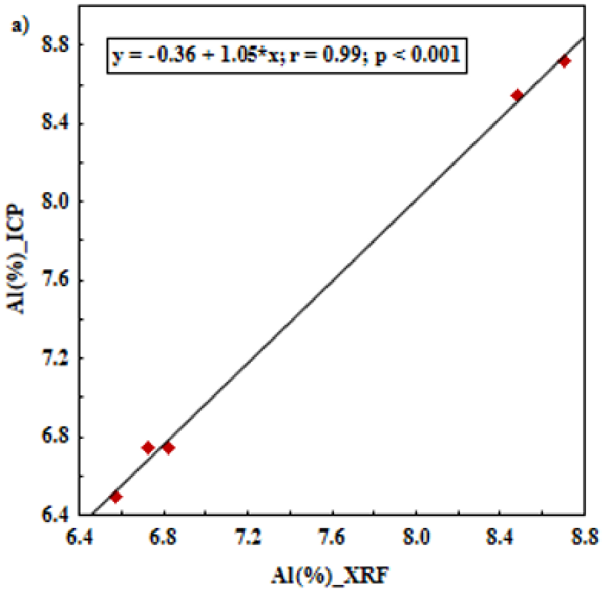

Fig. 15 Scatterplot correlation between pXRF and *Aqua regia* ICP data of Al contents

CHAPTER 4

Tracing the past from the analysis of Cu, Zn, Mn, Sr, and Rb in Archaeological Dark Earth soils from the tropics and temperate zone

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ABSTRACT

The analysis of minor/microelements in anthropogenic soils resulting from past settlement activities in different environmental conditions and geographical regions is not well-known. The study aimed to determine whether minor/microelements are suitable proxy indicators of past human activities of Archaeological Dark Earth (ADE) soils from two past hilltop settlements Ziavi-Galenkuito in Ghana and Dřevíč hillfort, Czech Republic. Total and plant-available (Mehlich 3) contents of minor/microelements were determined using portable X-Ray Fluorescence spectrometry and Inductively coupled plasma mass spectrometry, respectively. The black color of the soils from Ziavi-Galenkuito and Dřevíč hillfort contrasted the brownish Ferric Acrisol and greyish Luvic Cambisol control, respectively. The contents of total and plant-available Cu, Zn, Mn, Sr, and total Rb was substantially higher in both sites compared to their control of the same geological substrates. The highest total and plant-available Mn content in Ziavi-Galenkuito may indicate specific intensive settlement activities in a comparatively shorter duration. The highest total Cu, Zn, Sr, and Rb content in the soil from Dřevíč hillfort compared to Ziavi-Galenkuito related to longevity and intensity of the past human activities. Total Cu, Zn, Mn, and Sr can well reflect past human activities from different geographical regions according to their significant correlations from both studied sites. Except for Mn and Sr, total and plant-available content of Cu and Zn were not well correlated. Except for Mn and Sr, total and plant-available content of Cu and Zn were not well correlated. In the calculation of enrichment factors in ADE soils for geoarchaeological purposes, total Mn, Cu, Zn, and Sr are more suitable. Enrichment by minor/microelements can be reliable enough in predicting past human activities in ADE soils of different geology and climatic conditions, even after hundreds of years.

Introduction

Minor/microelement is a category of trace elements present in small amounts in soils (Bunt, 1988). However, contents of such elements (e.g., Cu, Zn, Se, Mn, Fe, and Mo) in the soil can substantially increase as a result of past human activities, ranging from food preparation, middening, manuring, craftwork, and agriculture (Wiedner et al., 2015; Devos et al., 2018; Wouters et al., 2019). For instance, Entwistle et al. (1998, 2000) identified high contents of Sr and Th as reliable indicators of crofts (small backyard farms) in former settlement sites in Scotland. The high contents of Ba and Mn at Piedras Negras, Guatemala, were found to be associated with areas with organic wastes disposition (Parnell et al., 2002).

Minor/microelements in archaeological soils were studied together with other major soil elements. (Ottaway and Matthews, 1988; Bintliff et al., 1992; Šmejda et al., 2017). However, due to the persistent effects of some major elements (e.g., P and Ca) in archaeological localities, they are mostly used in tracing past human activities. Several studies about minor elements in archaeological soils related to mining and metallurgy, and their resultant soil contamination (Hillman et al., 2015; Homsher et al., 2016). The analysis of micro-elements in archaeological soils, however, can offer useful insights into the history of human activities.

However, interpreting the patterns of elemental contents in archaeological soils is challenging, owing to the effects of post-depositional soil processes as well as the complexity of site-use history (Ottaway and Matthews, 1988; Wilson et al., 2009). A host of natural and modern anthropogenic processes may influence the contents of so-called ‘anthropogenic elements’ (elemental loadings from human activities) in soils. Furthermore, background variation linked to the differences in geology, soils, hydrology, and changes in climatic conditions can result in patterns of elemental content disconnected from past anthropogenic activities. Post-depositional soil-forming processes such as podzolization, gleying, and leaching may influence the retention and distribution of anthropogenic element loadings in the soil (Ottaway and Matthews, 1988; Pierce et al., 1998). Several studies reported the leaching of macro elements such as P, Ca, and Mg in archaeological localities (Ottaway and Matthews, 1988; Pierce et al., 1998). Therefore, it is necessary to emphasize the use of other elements (e.g., micro/minor elements) to assess their suitability as indicators of past settlement activities in archaeological localities.

Moreover, materials imported to a site often become mixed, following site abandonment, re-use of structures, the decay of buildings, and later anthropogenic additions such as pesticides, weedicides, lime, fertilizers, and atmospheric deposition can alter the soil by the loading of some elements. For example, Pb discharge through lead gasoline in the Czech Republic from the 1930s to 2000 increased the content in the soil (Janovský et al., 2020). Moreover, there are potentials for the development of secondary elemental patterns linked to previous site activity, but not directly reflecting the geochemistry of the inputs to soils. Such patterns develop when past human activity alters the physicochemical and biological soil properties, which affect the retention and distribution of natural and anthropogenic elements loadings.

Despite the complex nature of soil geochemical loadings, different studies to validate the use of multi-element analysis of soil in archaeological contexts exist (Šmejda et al., 2017; Horák et al., 2018; Janovský et al., 2020). Ethnographic studies have also provided much data, which confirmed that soils and floor layers from different activity areas often have recognizable chemical signatures (Terry et al., 2004; Wilson et al., 2005). Other studies compared modern soils unaffected by past human activities with ancient anthropogenically affected soils (Wiedner et al., 2015; Solomon et al., 2016). The resultant chemical signatures reflected both similarities and discrepancies in the geochemical patterns of studied soils. According to our knowledge, what is still not well-known is the tracing of past settlement activities from the analyses of both total and plant-available minor/microelements in Archaeological Dark Earth (ADE) soils from different regions using multi analytical approaches.

ADE soil is mostly a nutrient-rich dark layer of anthrosol resulting mainly from deliberate or unintentional human activities including organic wastes deposition with charcoal inclusion (FAO, 2020; WinklerPrins, 2014; Solomon et al., 2016). Most studies on ADE soils were previously limited to visual descriptions of different organic and inorganic inclusions (Runge, 1973; Mücher et al., 1990; van Smeerdijk et al., 1995) and micromorphological analysis (Macphail et al., 1990). These studies determined the variability of the position in local catena's, parent materials, and broader landscape locations (Glaser et al., 2003; Woods et al., 2009). However, there are no studies that emphasize on the enrichment of only both total and plant-available minor/microelements in ADE soils originating from different geographical locations.

Therefore, we performed a multi-element analysis of ADE soils from different geographical regions using the portable X-ray fluorescence spectrometer (pXRF) in determining the total element contents and Mehlich 3 extraction using inductively coupled plasma mass spectrometry (ICP-MS) for the contents of plant-available (Pav) element. In this study, we adopted these methodologies as successfully used in the analyses of chemical signatures in agricultural, forest, and even archaeological soils (Hejcman et al., 2011, 2012). Such analyses offer relevant data in making reliable inferences on the effects of anthropogenic elements in past settlement sites with different environmental conditions and analytical approaches.

Therefore, this study aimed to evaluate through the analysis of ADE soils the extent to which minor/microelements contents reflect past human activities in settlement sites from the tropical African region and temperate zone in central Europe compared to the control of the same geology. The study further answers the question, to what extent are the comparable patterns obtained by the analyses of plant-available and total contents of elements (minor/microelements), and which method is more suitable for geoarchaeological purposes?

2. Regional setting

2.1. Environmental conditions

The studied sites were both former hilltop settlements. Ziavi-Galenkuito (Fig.1a; map reference 6°37'60" N, 0°25'60" E) is approximately 4 km west of Ho, the capital of the Volta Region, and 200 km NE of Accra, the capital of Ghana. The former mound settlement covers an area of 4 ha of the Kabakaba hill with an altitude of 234 m asl. The temperature ranges from 21 to 32 °C in the wet/rainy and dry/harmattan seasons. The average annual precipitation ranges from 900 to 1300 mm. The site is on a metasedimentary/Voltaian geology (Mul et al., 2015). The tropical climatic condition of the area is influenced by the SW Monsoon from the south Atlantic and dry NE trade winds. The vegetation of the study area is guinea woodland and moist semi-deciduous forest. The soil was previously brownish Ferric Acrisol, visually observed from the surrounding control site of the same geology without past settlement activities (FAO, 2020; Mul et al., 2015). However, the soil color in the study site has turned black (Fig. 2a) resulting from past settlement activities with relatively high homogenous pieces of charcoal.

Dřevíč was formerly a fortified hillfort settlement (Fig. 1b; map reference 50˚14'51''N, 13˚49'33'' E), located 1 km SE of Kozojedy village in Rakovník district and 50 km west of Prague, Czech

Republic. The size of the fortified area is 11 ha with an altitude of 464 m asl. The mean annual temperature and precipitation are 7.1 ^{o}C and 634 mm, respectively. The site is on a Marlstone geology. The soil in the Dřevíč hillfort was originally greyish Luvic Cambisol, observed from control (Tok, Mšec 167) 6 km SE from the Dřevíč hillfort of the same geology (Chytrý, 2012; Czech Geological Survey, 2019).

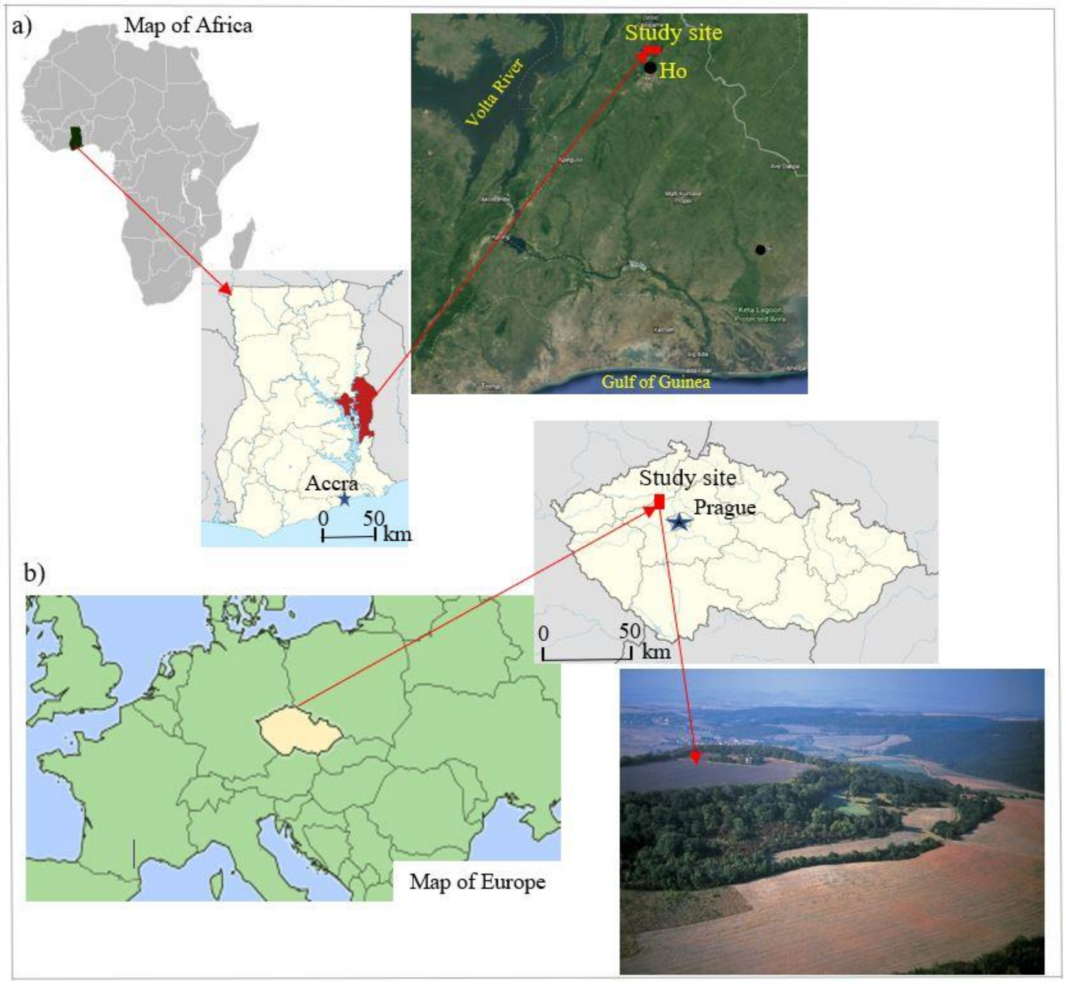

Fig. 1. Location of the study sites (a) Ziavi-Galenkuito in Ghana and (b) Dřevíč hillfort in the Czech Republic (aerial view of the internal area of the hillfort characterized by Archaeological Dark Earth soil and surrounded with a valley of woody species) (Photo by Zdeně Smrž).

The immediate surrounding soil to the hillfort is reddish-brown colored Modal Cambisol in valleys developed on older red sandstone sediments (Czech Geological Survey, 2019) of different elemental compositions. The dark color of soil from the internal area of the Dřevíč hillfort (Fig. 2b) was due to settlement from different archaeological timelines (Profantová et al., 2012).

2.2. Site history

Ziavi-Galenkuito site was settled first by the Germans in 1884 until the British conquered them during World War 1 in 1914 (Apoh, 2009; Dogbey, 2015). The British then resided afterward and left after Ghana gained independence in 1957. The archaeological excavation conducted in 2016 resulted in the discovery of materials such as pottery and bottle fragments, broken glasses, metal objects, smoking pipes, European ceramics, burnt palm kernel shells, and bones of animals (Dogbey, 2015). There are still some visible relics of dug wells and collapsed building foundations.

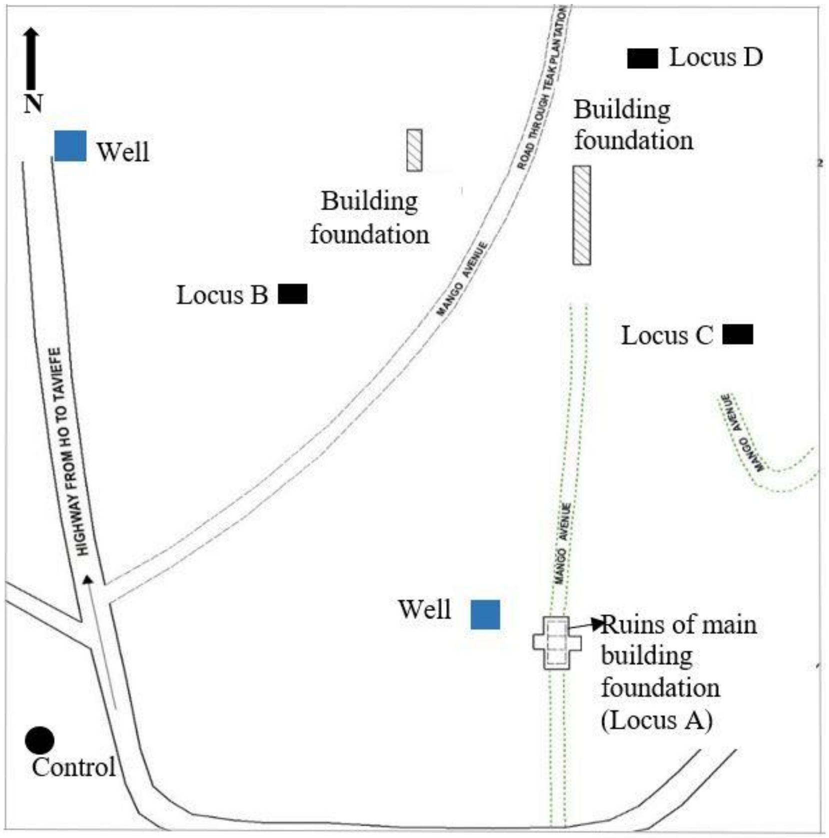

Fig. 2. Site map at Ziavi-Galenkuito, showing the sampled locations (Locus A-D and control). The control site is located 40 m from the past settlement site. Locus B, C, and D are outside the ruins of building foundations (modified from Dogbey, 2015).

The buildings were first constructed by the Germans and later used by the British, and finally abandoned in 1957. The strategic location of Ziavi-Galenkuito on a hill overlooks the valley on surrounding lowland villages and the Ho Township. After the British left, the Forestry Authority in Ho took control of the site from further human activities, contributing to the well-preserved site. Dřevíč hillfort existed from 8 - 13th century AD. Written evidence indicates that Dřevíč belongs among the most important strongholds in Bohemia during the 11th and 12th centuries. Dřevíč hillfort has records of Neolithic, Late Bronze Age (Knoviz culture, 1300 -750 BC), and Early Iron Age Hallstatt period up to the early 13th century AD settlements. Previous human activities in this site are supported by discovered artifacts such as stone battle axes, split tools, pottery fragments, S-shaped earrings, and coins from the 10th and 11th centuries AD, and the graveyard (Profantová et al., 2012). In the 12th century, it was a center of Dřevíč province (Kabát et al., 1971; Čtverák, 2003). In 2005, an archaeological discovery bought to light a solidus byzantine coin, an imperial coin of Constantine VII (913 – 959 AD), Romanus I (920 – 944 AD), and Christopher (921 – 931

AD) (Profantová, 2009). The stronghold includes a St. Wenceslas church mentioned in medieval sources. In 1950, an exploratory trench provided evidence for an early medieval cemetery.

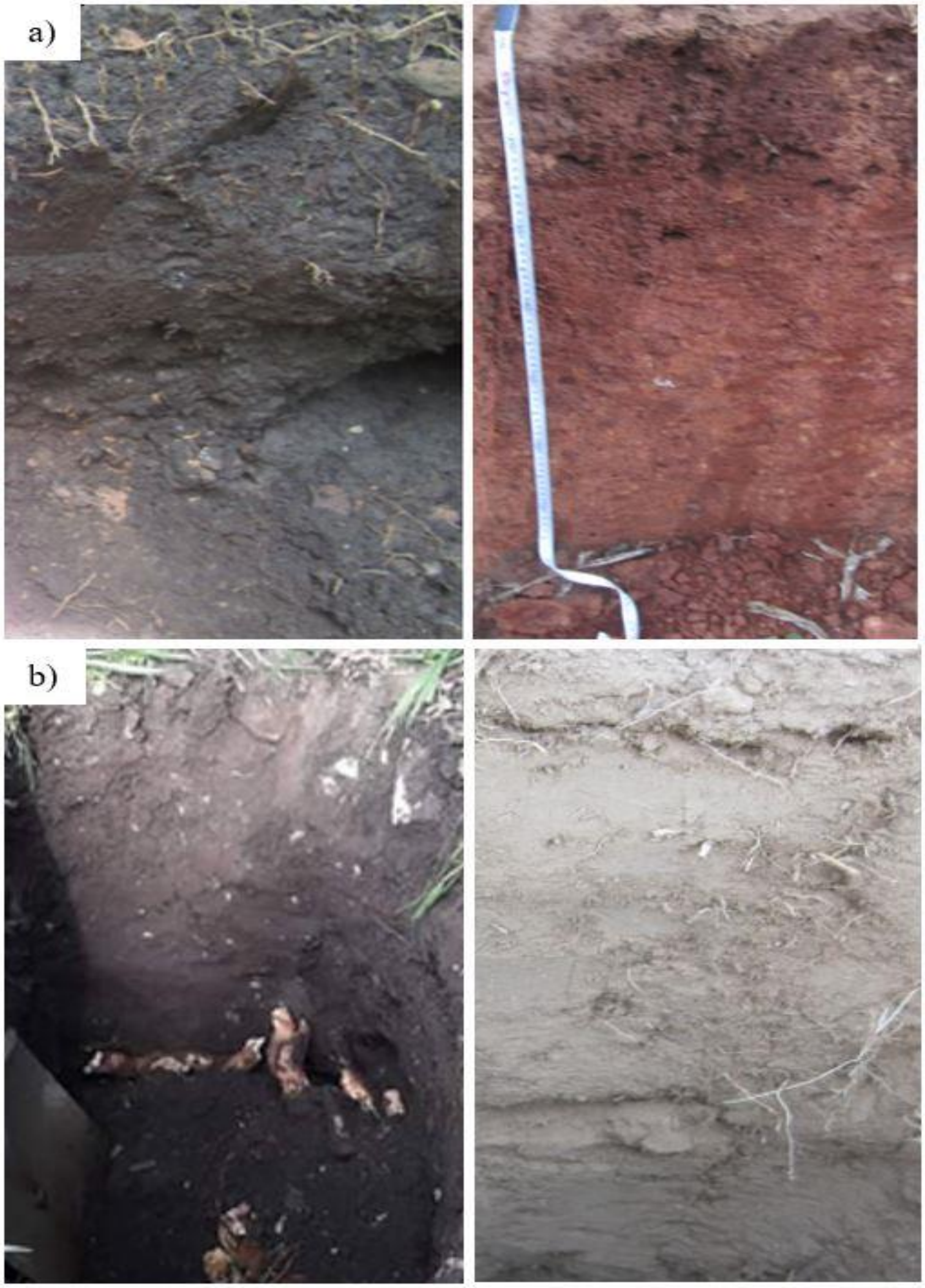

Fig. 3. Representative photos of Archaeological dark earth soils from (a) Ziavi-Galenkuito, and control (right) and (b) Dřevíč hillfort and control (right). The depths are ≥ 40 cm in all the trenches.

The graves yielded 15 to 16 mm diameter rings (Bubeník, 1988), and a bronze bracelet. It could be of Belobrdo Culture origin (second half of the tenth century). According to Bubeník (1988), the rings may be as early as the 10th century AD; this means that either there was a continuity of burial activities or two cemeteries were superimposed over each other. Some gravestones are well-known from the later phase of the burial ground from the 12 – 13th century AD.

3. Materials and methods

3.1. Sampling Design

A specific sampling design to cover the variability of soils in the study sites and their surrounding control sites was adopted. The Ziavi-Galenkuito settlement was divided into four quadrants by a judgmental approach (Etikan and Bala, 2017, Fig. 2). The first quadrant (Locus A) represents soil samples inside the ruins of the main building foundation; the remaining quadrants (Locus B, C, and D) were outside the ruins of the building foundations. We randomly collected five mixed soil samples from each quadrant. Moreover, five mixed soil samples were randomly collected as control from the surrounding unaffected by settlement activities, located about 40 m away from the study site.

In the case of Dřevíč hillfort, soil samples were collected only from the internal area and compared with the control. We randomly collected five mixed soil samples from each quarter (Q 1 – Q 4) of the four stratified designs. Additionally, we randomly collected five mixed soil samples as control from the surrounding.

Each mixed sample contained three sub-samples taken by soil probe (Purchhauer type, core-diameter: 3 cm) from the upper 10 cm soil layers to obtain a representative sample without extreme values to ensure a more reliable generalization of the results. In total, we collected 50 mixed soil samples as representative samples for further analysis.

Analytical procedure

All the soil samples were air-dried and subsequently, oven-dried at 40 °C for 24 hours. The samples were ground in a porcelain mortar and homogenized by passing through a 2 mm sieve after the removal of living roots.

The particle size distribution of the soils was done after FAO (2008) by sieve analysis. For each soil sample, 10g were sieved through 2, 1, 0.5, 0.25, 0.1, 0.05, and 0.002 mm sieves and compared. The total Cu, Zn, Mn, Sr, and Rb content was determined with portable–ED-XRF (energy (pXRF) analyzer Delta Professional by Olympus InnovX (Waltham, MA, USA). These elements were in all cases above the detection limits in the soils from both study sites. The pXRF was in the soil Geochem mode for all the measurements. The pXRF is used to determine the total or near-total content of elements in the matrix (Canti and Huisman, 2015; Šmejda et al., 2018). Operationally, all the measurements were performed over 1 minute, with 30s of a 10-kV beam and 30s of a 40-kV beam, and each sample was measured in three replicates and averaged. The quality of pXRF results was also successfully tested by the company BAS Rudice Ltd. (https://www.bas.cz) on 55 reference materials (e.g., SRM 2709a, 2710a, 2711a, OREAS 161, 164, 166, RTC 405, 408). The contents of some elements (e.g., Mo, Co, Ni, Se, Sb, Cd, Sn, Ti, Ag, Tl, Au, Hg, and Th) were omitted from further analysis as they were not detected or above the detection limit in a few cases. Three replicates of Pav (Mehlich 3 extraction; Mehlich 1984) Cu, Zn, Mn, Sr, and Rb contents were further determined by ICP-MS (Agilent 7700x, Agilent Technologies Inc., Santa Clara, CA, USA). The pH (H_2O) of all soil samples was obtained from a 1:1 ratio (soil-water) using Voltcraft PH-100 ATC pH meter (pH 212; I & CS spol. s r.o., Czech Republic) in two replicates.

Verification of pXRF data

The pXRF results are influenced by matrix effects such as density, porosity, and grain size of analyzed materials (Kalnicky and Singhvi, 2001; Newlander et al., 2015). However, the reliability of the data obtained by pXRF was assessed by randomly selecting 10 dried and homogenized soil samples (< 2 mm) each from Ziavi-Galenkuito and Dřevíč hillfort (*n* = 2 from each sampled location). These samples were also analyzed to determine the total content of Cu, Zn, Mn, Sr, and Rb in an independent accredited laboratory where extraction of elements in *Aqua regia* extract (3ml HCl and 1ml HNO3; International Organization for Standardization USEPA 3052) again was determined by ICP-MS.

Data Analysis

There was relative homogeneity of variance among the obtained data in all the analyzed soil samples. Data on soil particle size distribution, pH, and contents of elements tested by the Kolmogorov-Smirnov test of normality met assumptions for the use of parametric tests. One-way ANOVA followed by *posthoc* comparison using Turkey (HSD) test was applied to identify significant differences between the fractions soil particle size, pH, and content of elements. For an evaluation of the quality of pXRF measurement, we applied correlation and regression analysis of obtained data by pXRF and *Aqua regia* ICP-MS. The relationship between the content of the studied elements was determined by correlation and regression analysis (Pearson's correlation). We performed all statistical analyses using STATISTICA 13.4
(www.statistica.io).

Results

Soil description and particle size distribution

Anthropogenic soils from the two past settlement sites were characterized by black color (7.5YR 3/1) in contrast to a strong-brown (7.5YR 4/6) control in Ziavi-Galenkuito and grey (7.5YR 7/1) in Dřevíč hillfort (Table 1). The soils in Ziavi-Galenkuito are clayey-loam and sandy-loam in Dřevíč hillfort, similar to their respective controls with inputs of mostly pottery fragments in the settlement sites. Overall, the clay loam texture of the soil in Ziavi-Galenkuito reflected by 48.3% sand, 16.7% silt, and 22.9% clay (Table 2). In Dřevíč hillfort, 73.9% sand, 12% silt, and 13.7% clay was recorded, indicating sandy loam texture.

There was a significant effect of settlement activities on the grain size of soils from the two sites compared to their respective control (Table 2). In Ziavi-Galenkuito, the fraction of silt (< 0.05 - 0.002 mm) and clay (< 0.002) were higher in comparison with the different fractions of sand (≥ 2 to 0.05 mm). Coarse particles (< 1 – 0.5 mm) dominated in the soil from Dřevíč hillfort. However, there was a higher proportion of fine sand (< 0.1 – 0.005 mm), silt, and clay in both sites compared to their respective control. The fractions of grain size in some sampling locations were relatively similar to the controls in both sites.

Table 1 Morphological description of the upper 10 cm layers of ADE soil from Ziavi-Galenkuito and Dřevíč hillfort with their respective controls.

Site/Soil	color [a] (moist)	Texture [b]	Structure	Consistency	Skeleton grains (> 2 mm)	Pedological features	Roots
			Ziavi-Galenkuito				
ADE	Black (7.5YR 3/1)	Clay loam + pottery fragments + pieces of charcoal	Moderate medium + medium subangular blocky	Firm, slightly sticky + plastic	Very few angular	Very few, few irregular, soft and hard, red and black Fe-Mn nodules	Medium, moderate
Control	Strong brown (7.5YR 4/6)	Clay loam	Weak-moderate, fine + coarse subangular blocky	Friable., slightly Sticky + plastic	Very few friable angular	Common fine and very fine irregular soft Mn nodules	Very few
			Dřevíč hillfort				
ADE	Black (7.5YR 3/1)	Sandy loam + pottery fragment + pieces of charcoal	Moderate medium + coarse sub-rounded blocky	Firm, slightly sticky + plastic	Very few subrounded	Common fine and very fine irregular Soft Mn nodules	High
Control	Grey (7.5YR 7/1)	Sandy loam	Moderate medium + coarse spherical blocky	Firm, slightly sticky + slightly plastic	Mostly sub-rounded	Common fine and very fine irregular soft Mn nodules	Moderate

[a] – Munsell Soil Color Chart, [b] – according to Jahn et al. (2006)

Table 2 The particle size distribution of soil (% mean ± SD) from Ziavi-Galenkuito and Dřevíč hillfort. One-way ANOVA was used to obtain the p-values. Using the Tukey HSD post hoc test, mean values with the same letters were significantly not different.

Ziavi-Galenkuito								
Sampling location	Sand (%)						Silt (%)	Clay (%)
	≥ 2	< 2 - 1	< 1 - 0.5	< 0.5 - 0.25	< 0.25 - 0.1	< 0.1 - 0.05	< 0.05 - 0.002	< 0.002
	Mm							
Quadrant A (Locus A)	7.2 ± 0.4^{a}	8.1 ± 0.2^{a}	9.1 ± 0.4^{a}	12.1 ± 0.7^{b}	11.3 ± 0.5^{ab}	12 ± 0.2^{a}	16.1 ± 0.4^{a}	23 ± 0.7^{b}
Quadrant B (Locus B)	7.1 ± 0.4^{a}	8.6 ± 0.4^{a}	9.2 ± 0.2^{a}	10.1 ± 0.4^{a}	12.4 ± 0.7^{b}	12 ± 0.4^{a}	17.2 ± 0.5^{ac}	23.2 ± 0.5^{b}
Quadrant C (Locus C)	7 ± 0.3^{a}	7.5 ± 0.4^{a}	9 ± 0.6^{a}	10.1 ± 0.3^{a}	12.2 ± 0.2^{b}	11.9 ± 0.5^{a}	19.2 ± 0.5^{b}	23.1 ± 0.5^{b}
Quadrant D (Locus D)	7.1 ± 0.1^{a}	8.4 ± 0.2^{a}	9 ± 0.1^{a}	10.5 ± 0.1^{ab}	10.5 ± 0.5^{a}	14.1 ± 0.1^{b}	17.1 ± 0.2^{ac}	23 ± 1^{b}
Control	9.4 ± 0.1^{b}	10.1 ± 0.4^{b}	10.4 ± 0.4^{b}	10.3 ± 0.5^{a}	10.2 ± 0.4^{a}	11.5 ± 0.2^{a}	16 ± 0.2^{a}	21.4 ± 0.4^{a}
Mean	7.6 ± 1	8.5 ± 0.9	9.3 ± 0.5	10.6 ± 0.8	11. 3 ± 0.9	12.3 ± 1	16.7 ± 1.5	22.9 ± 0.8
p-value	<0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.003

Dřevíč hillfort								
Sampling location	Sand (%)						Silt (%)	Clay (%)
	≥ 2	< 2 - 1	< 1 - 0.5	< 0.5- 0.25	<0.25 - 0.1	< 0.1 - 0.05	< 0.05 - 0.002	< 0.002
	mm							
1st Quarter (Q 1)	10 ± 0.2^{a}	19.5 ± 0.4^{ab}	21.1 ± 0.4ab	10.2 ± 0.4b	7.1 ± 0.5^{b}	5.3 ± 0.1^{ab}	11.9 ± 0.4^{b}	14.2 ± 0.4^{b}
2nd Quarter (Q 2)	11.1 ± 0.3^{ab}	18.8 ± 0.1^{a}	20.4 ± 0.2a	10.2 ± 0.3^{b}	7 ± 0.2^{b}	6.2 ± 0.1^{b}	12.6 ± 0.4^{b}	13.6 ± 0.1^{b}
3rd Quarter (Q 3)	10 ± 0.1^{a}	19 ± 0.3^{a}	20.4 ± 0.1a	10.4 ± 0.2^{b}	7.2 ± 0.4^{b}	6.5 ± 0.1^{b}	12.5 ± 0.2^{b}	14 ± 0.4^{b}
4th Quarter (Q 4)	10 ± 0.3^{a}	18.3 ± 0.1^{a}	20.1 ± 0.2a	10.1 ± 0.3^{ab}	7 ± 0.2^{b}	7 ± 0.2^{b}	12.6 ± 0.3^{b}	14.8 ± 0.2^{b}
Control	12.2 ± 0.3^{b}	22.9 ± 0.3^{b}	22.1 ± 0.3b	9.4 ± 0.3^{a}	5.9 ± 0.2^{a}	4.1 ± 0.2^{a}	10.4 ± 0.1^{a}	12 ± 0.2^{a}
Mean	10.7 ± 0.9	19.7 ± 1.8	20.8 ± 0.8	10.1 ± 0.4	6.8 ± 0.5	5.8 ± 1.1	12 ± 0.9	13.7 ± 1.1
p-value	<0.001	< 0.001	< 0.001	0.003	<0.001	< 0.001	< 0.001	< 0.001

Analytical accuracy and precision

Data for Cu, Zn, Mn, and Sr were compared, except for Rb, which was not fully soluble in *Aqua regia*. The results from the comparison of data obtained by pXRF and *Aqua regia* ICP-MS revealed a strong linear correlation among the elements ($r > 0.9$, $p < 0.001$ for all the elements from both study sites; Table 3).

Soil chemical properties

The statistical descriptions of obtained data for pH and all analyzed elements from both study sites are given in Tables 4 and 5 and Figs. 4 - 6.

The pH and total contents of Cu, Zn, Mn, Sr, and Rb were significantly higher in the two past settlement sites in comparison to their respective controls (Figs. 4 and 5). A relatively neutral soil reaction from both study sites contrasted to their moderately acidic control (Figs. 4a and 5a). There were significantly higher pH and total content of Zn and Rb in soils from Dřevíč hillfort in comparison to Ziavi-Galenkuito and vice versa in the case of Mn (Figs. 6a, c, f, and 6d). There was no significant difference in the content of total Cu and Sr in both sites, with a marginal increase in Dřevíč hillfort compared to Ziavi-Galenkuito (Figs. 6b and e).

Significantly higher contents of Pav Cu, Zn, Mn, Sr, and Rb were in the soils from Ziavi-Galenkuito and Dřevíč hillfort in comparison to their respective control (Table 4). Except for the content of Rb ($r = 0.38$, $p = 0.059$), there was a significant correlation between the contents of total Cu, Zn, Mn, and Sr ($r = 0.42 – 0.9$, $p < 0.05$) in the soils from Ziavi-Galenkuito and Dřevíč hillfort (Fig. 7). In contrast to Cu ($r = 0.29$, $p = 0.061$) and Zn ($r = 0.24$, $p = 0.087$), there was a significant correlation between total and plant-available Sr ($r = 0.84$, $p < 0.001$) and Mn ($r = 0.83$, $p < 0.001$) (Fig. 8).

Table 3 The relationship (Pearson’s correlation) between the total content of obtained data by pXRF and Aqua regia ICP-MS.

	Ziavi-Galenkuito				**Dřevíč hillfort**			
Parameters	Cu	Zn	Mn	Sr	Cu	Zn	Mn	Sr
Regression equation	y = - 6.5 + 1.2*	y = 4.9 + 0.95*	y = 2.9 + 0.9*	y = 13.3 + 0.9*	y = 1.4 + 0.9*x	y = - 6.1 + 1.1*	y = 3.4 + 1.2*	y = 2.7 + 0.9*
Correlation coefficient (*r*)	0.94	0.99	0.99	0.99	0.94	0.93	0.99	0.99
p-value	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001

Table 4 The basic statistical description of obtained data for pH and total content of micro-elements from Ziavi-Galenkuito and Dřevíč hillfort

			Ziavi-Galenkuito									**Dřevíč hillfort**					
Sampling location	No. of samples		pH [H_2O]	Cu [ppm]	Zn [ppm]	Mn [pm]	Sr [ppm]	Rb [ppm]	Sampling location	No of samples		pH [H_2O]	Cu [ppm]	Zn [ppm]	Mn [ppm]	Sr [ppm]	Rb [ppm]
Quadrant A (Locus A)	5	Min.	5.4	27	40	1273	68	27	1st Quarter (Q 1)	5	Min	6.4	36	106	608	138	102
		Median	5.6	37	50	1473	70	29			Median	6.5	41	106	609	138	104
		Mean	5.6	34.7	47.7	1566.3	70	29			Mean	6.5	40.3	106.7	616.6	138.3	103.7
		Max	5.7	40	53	1953	68	31			Max	6.6	44	108	633	139	105
Quadrant B (Locus B)	5	Min.	6	42	49	1676	33	94	2nd Quarter (Q 2)	5	Min	6.4	40	118	625	118	113
		Median	6.1	44	58	1976	35	97			Median	6.6	46	120	644	120	114.3
		Mean	6.1	44.7	56.7	1876	35	96.7			Mean	6.6	45.3	119.7	639.7	119.7	115
		Max	6.3	48	63	1976	36	99			Max	6.7	50	121	650	121	115
Quadrant C (Locus C)	5	Min.	6.3	28	78	1363	122	29	3rd Quarter (Q 3)	5	Min	6.5	37	111	743	112	113
		Median	6.8	32	82	1963	131	31			Median	6.6	40	114	747	114	117
		Mean	6.7	32.6	86	1896.3	128.3	29			Mean	6.6	40	116	751	114.7	116.7
		Max	7.1	38	98	2363	132	32			Max	6.6	43	123	763	118	120
Quadrant D (Locus D)	5	Min.	5.4	33	55	1181	60	30	4th Quarter (Q 4)	5	Min	6.3	32	92	569	112	117
		Median	5.6	35	59	1481	61	32			Median	6.5	35	97	595	114	118
		Mean	5.6	37.6	58	1381	62	30			Mean	6.5	34	96	586.3	114	118.3
		Max	5.7	45	60	1481	65	34			Max	6.6	35	99	595	116	120
Control	5	Min.	4.3	19	14	191	13	19	Control	5	Min	5.2	19	46	353	82	77
		Median	4.5	20	27	229	16	22			Median	5.4	28	79	398	91	77
		Mean	4.5	22.4	31.2	312	17.4	21.8			Mean	5.4	26	70	392	88	77.6
		Max	4.6	32	55	654	25	25			Max	6	32	91	414	92	79

Table 5 Content (mean ± SD) of plant-available available Cu, Zn, Mn, and Sr in the Ziavi-Galenkuito and Dřevíč hillfort past settlement sites. One-way ANOVA was used to obtain p-values. Using the Tukey HSD post hoc test, mean values with the same letters were significantly not different.

Ziavi-Galenkuito					**Dřevíč hillfort**				
Sampling location	Cu [mg kg^{-1}]	Zn [mg kg^{-1}]	Mn [mg kg^{-1}]	Sr [mg kg^{-1}]	Sampling location	Cu [mg kg^{-1}]	Zn [mg kg^{-1}]	Mn [mg kg^{-1}]	Sr [mg kg^{-1}]
Quadrant A (Locus A)	78.4 ± 1.7^{a}	85.4 ± 3.6^{a}	642 ± 16.8^{a}	46.7 ± 1.3^{a}	1st Quarter (Q 1)	36.3 ± 0.9^{a}	63.6 ± 1.8^{a}	443 ± 16^{a}	57.3 ± 1.1^{a}
Quadrant B (Locus B)	86.2 ± 2.7^{b}	100.2 ± 2.1^{b}	707 ± 13.2^{b}	29.6 ± 0.8^{b}	2nd Quarter (Q 2)	39.3 ± 1.2^{a}	69.7 ± 3^{a}	452 ± 21^{a}	64.3 ± 2.4^{b}
Quadrant C (Locus C)	97.8 ± 2.5^{c}	104.1 ± 6.9^{b}	614 ± 13.4^{c}	86.1 ± 1.9^{c}	3rd Quarter (Q 3)	30.7 ± 0.6^{b}	78.5 ± 3.7^{b}	374 ± 9.3^{b}	56.9 ± 1.7^{a}
Quadrant D (Locus D)	75 ± 1.7^{a}	81.7 ± 2.8^{a}	699 ± 9.8^{d}	49.4 ± 1.1^{a}	4th Quarter (Q 4)	31 ± 3.2^{b}	99.1 ± 8.1^{c}	449 ± 14^{a}	56.6 ± 1.8^{a}
Control	19.2 ± 1.2^{d}	16.9 ± 0.7^{c}	86.5 ± 3.9^{e}	10.1 ± 0.2^{d}	Control	15.8 ± 1.1^{c}	29.1 ± 1.9^{d}	105 ± 2.9^{c}	28.2 ± 0.9^{c}
p-value	< 0.001	< 0.001	< 0.001	< 0.001	*p*-value	< 0.001	< 0.001	< 0.001	< 0.001

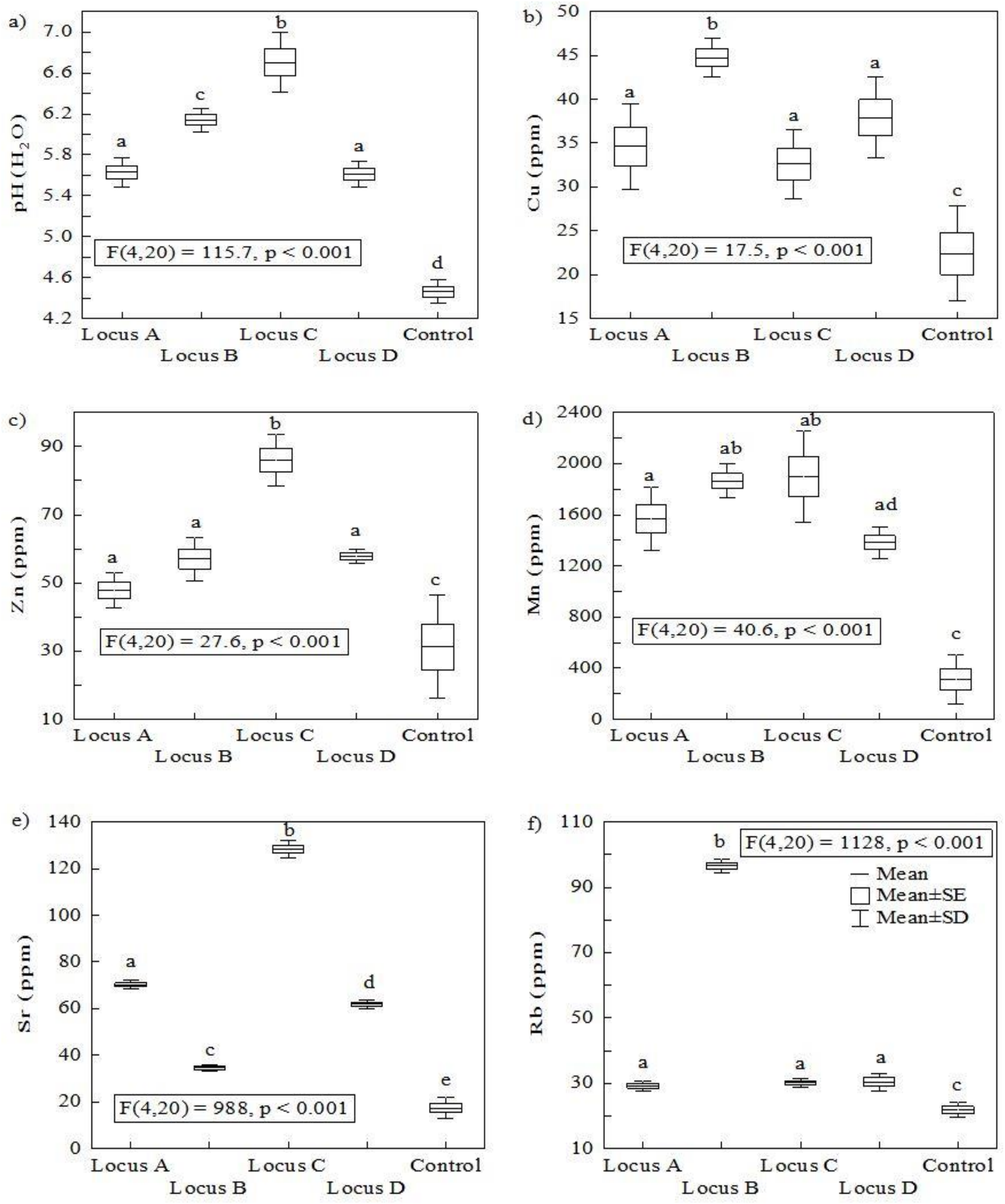

Fig. 4. Mean (a) pH and total content of (b) Cu, (c) Zn, (d) Mn, (e) Sr, and (f) Rb in the sampled locations in the Ziavi-Galenkuito site. The F and p-values were obtained by one-way ANOVA. Using the Tukey HSD post hoc test, mean values with the same letters were significantly not different. Locus A represents soil samples inside the ruins of the main building foundation. Locus B, C, and D are soil samples outside building foundations.

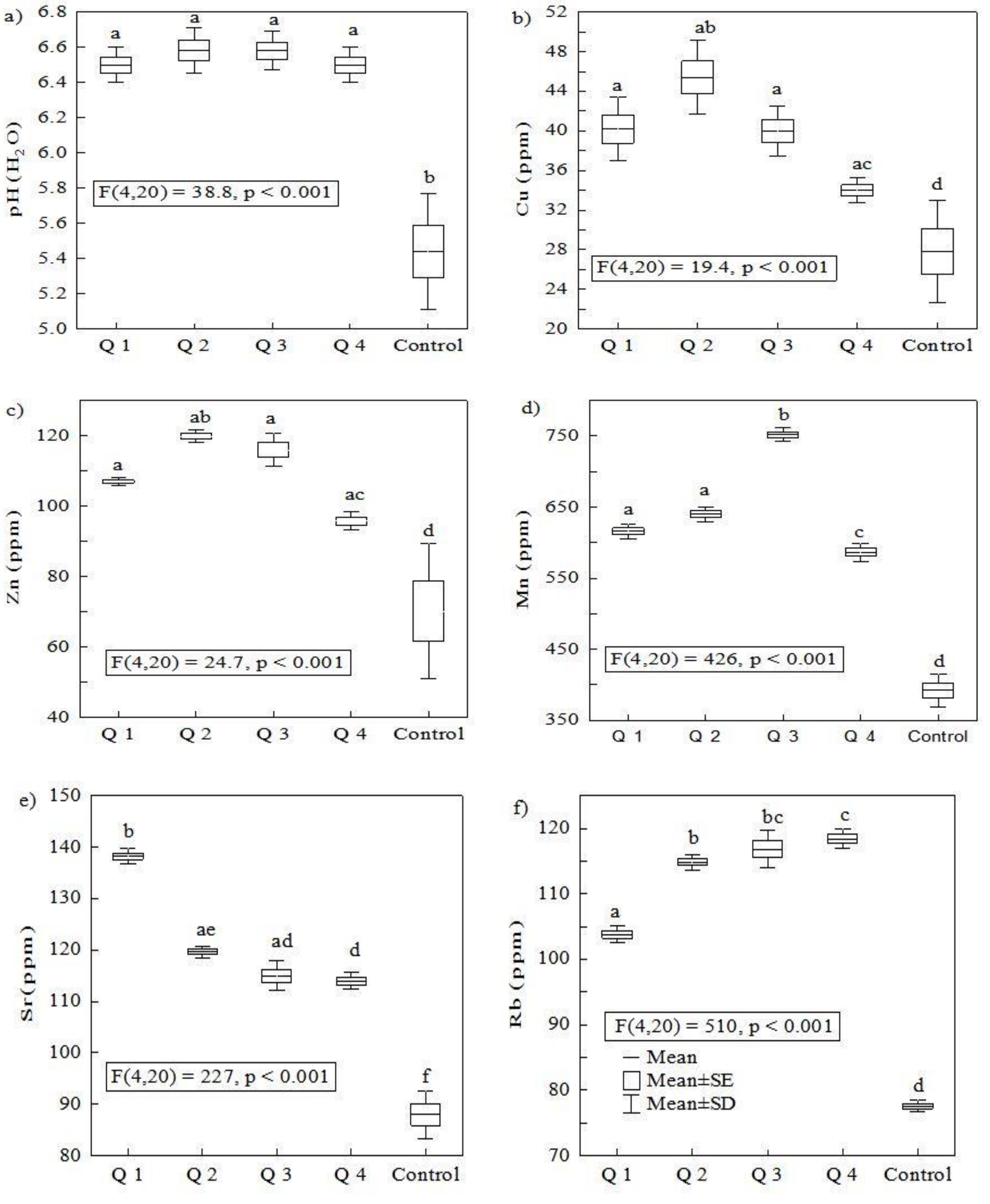

Fig. 5. Mean (a) pH (H_2O) and total content of (b) Cu, (c) Zn, (d) Mn, (e) Sr, and (f) Rb in the sampled locations in Dřevíč hillfort. The F and p-values were obtained by one-way ANOVA. Using the Tukey HSD post hoc test, mean values with the same letters were significantly not different.

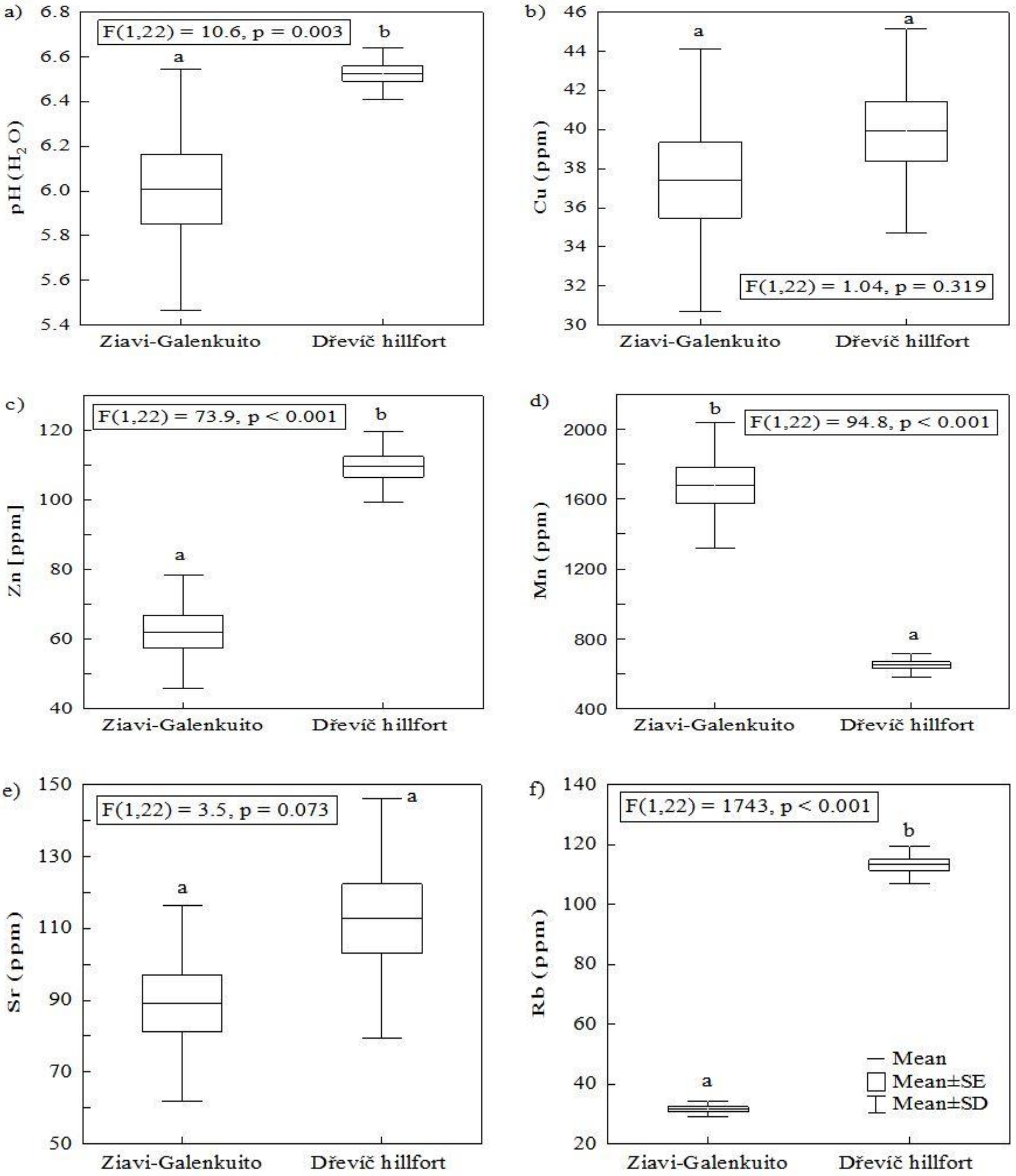

Fig. 6. Mean (a) pH and total content of (b) Cu, (c) Zn, (d) Mn, (e) Sr, and (f) Rb in the ADE soils from Ziavi-Galenkuito and Dřevíč hillfort. The F and p-values were obtained by one-way ANOVA. Using the Tukey HSD post hoc test, mean values with the same letters were significantly not different.

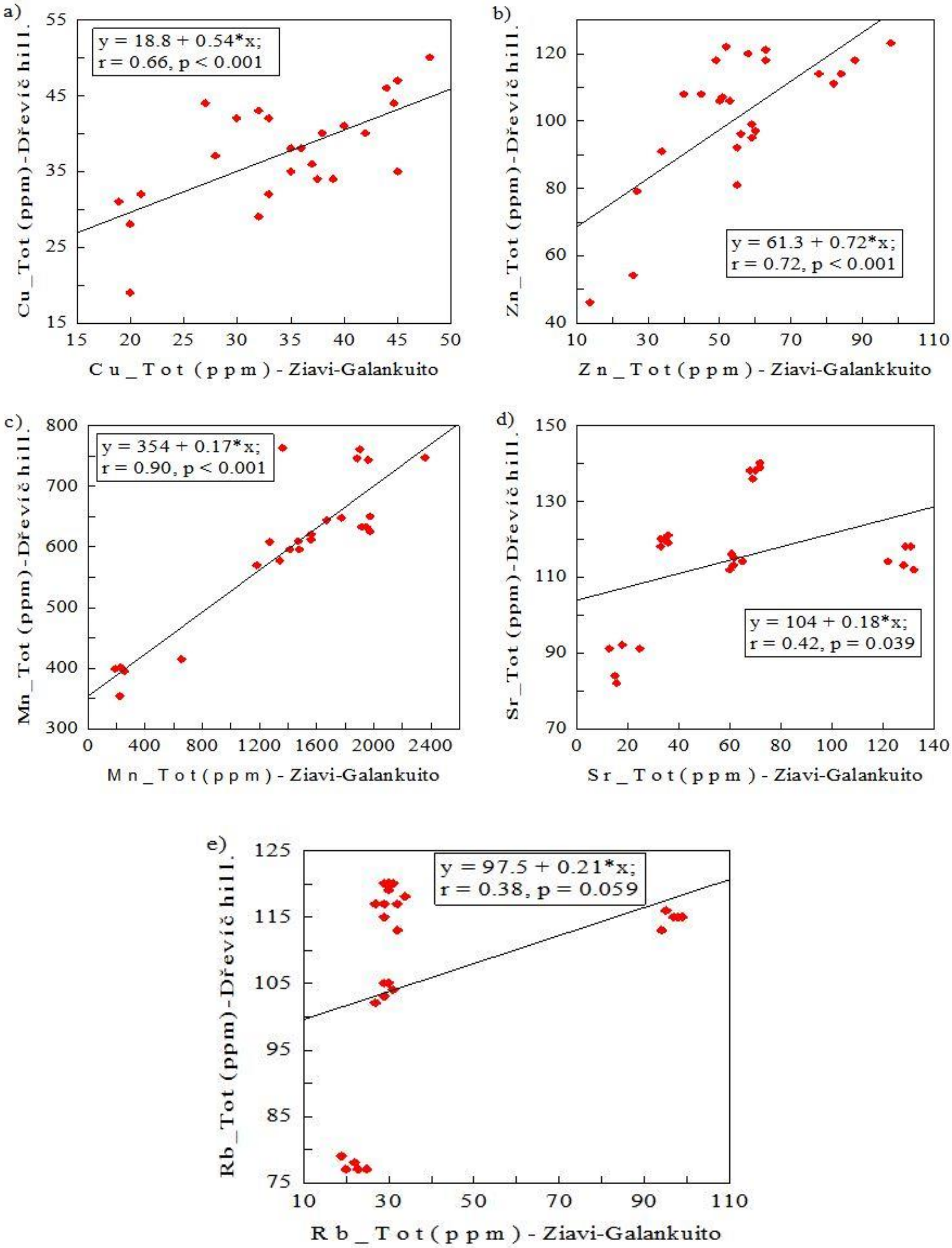

Fig. 7. Relationship between total content of (a) Cu, (b) Zn, (c) Mn, (d) Sr, and (e) Rb in the soils from Ziavi-Galankuito and Dřevíč hillfort (Dřevíč hill.).

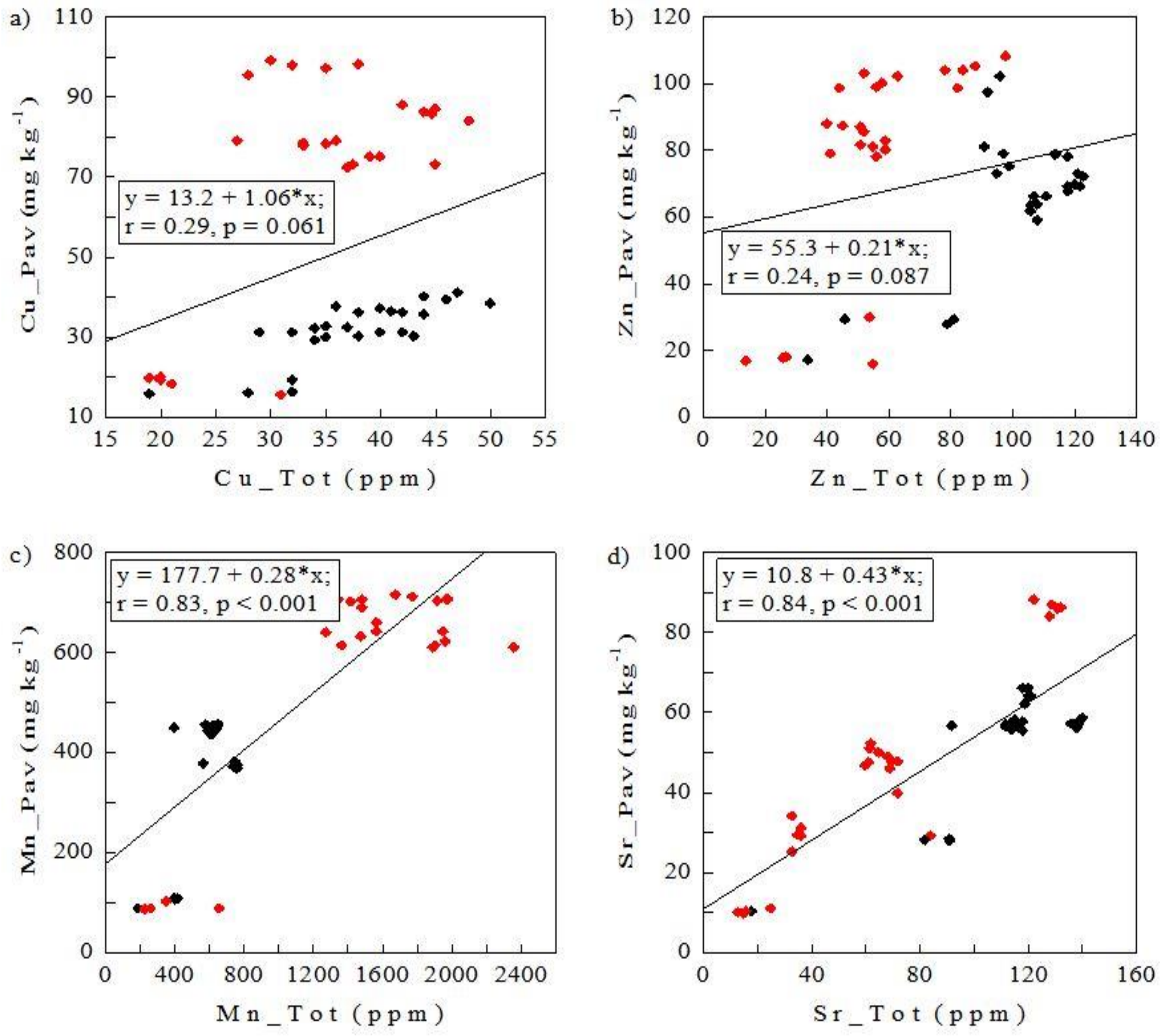

Fig. 8. Relationship between total (Tot) and plant-available (Pav) contents of (a) Cu, (b) Zn, (c) Mn, and (d) Sr. The red and black marks indicate values from Ziavi-Galenkuito and Dřevíč hillfort, respectively.

Discussion

Although settlement activities have stopped after the abandonment of the studied sites, the black color of soils, increased soil reactions (pH), and high contents of the total (Mn, Cu, Zn, Sr, and Rb) and Pav (Mn, Cu, Zn, and Sr) elements are well-preserved. Even with the influence of different climatic conditions, the total Mn, Cu, Zn, and Sr can reflect past human activities in both the tropics and temperate zone. The strict adherence to protocols involved in the analytical approaches resulted in the strong correlation between the pXRF and *Aqua regia* ICP-MS of the tested elements (Table 3), indicating that pXRF data were adequate precision (Asare et al., 2020).

The relatively higher fraction of fine particles, silt, and clay (< 0.25 mm - < 0.002 mm) in the past settlement sites in comparison to their control, also contributed to the retention and lesser leaching of the studied elements (Acosta et al., 2011). Together with the soil texture and other pedological features, the relatively similar grain sizes show that the settlement sites and their respective control are on the same local geology (Jahn et al., 2006; FAO, 2008). The reduced soil acidity in the two settlement sites also contributed to the retention of the studied elements. Inside the ruins of the main building foundation (Locus A) and Locus D in the Ziavi-Galenkuito site, the slightly acidic soil contributed to the comparatively low content of Pav Cu, Zn, and total Mn in comparison to other sampled locations (Fig. 4). The neutral reaction in the soils from Dřevíč hillfort can also attest to the high content of total Zn and Rb in comparison to Ziavi-Galenkuito (Fig. 6c and f). Conversely, in acidic soils, there is depletion of elements (Haynes and Swift, 1986; Fodor and Szabó, 2004).

The lower content of total (Zn and Mn) and plant-available (Cu and Zn) elements in Ziavi-Galenkuito were in Locus A compared to Locus B and C, an area with probably no or little deposition of organic wastes. Conversely, the higher content of total (Cu and Mn) and Pav (Cu and Zn) elements in Locus B and C compared to other sampled locations were areas with high numbers of pottery fragments, burnt palm kernels, and pieces of charcoal. In Dřevíč hillfort, the comparatively homogenous contents of the elements in all the quarters resulted from the regular plowing of the site for arable purposes.

The total content of Cu was 10 to 22 ppm higher in the Ziavi-Galenkuito site in comparison to the control, representing 1.6 - 2.2 times enrichment in the sampled locations. The content of Pav Cu was 3.9 - 5.1 times higher in the Ziavi-Galenkuito site compared to the control. In Dřevíč hillfort, the content of total Cu increased from 7 to 20 ppm representing and 1.3 – 1.8 times enrichment, compared to the control. The plant-available Cu content was 2 - 2.8 times higher in Dřevíč hillfort in comparison to control. The contents of the total Cu in both sites were not significantly different. Generally, Cu content relates to agricultural activities (da Costa, 1999; Klimek, 2002), disposition of excrement (Campos et al., 2016), and biomass ashes, which contain approximately 200 ppm. Hejcman et al. (2011, 2012) recorded Cu accumulation *via* deposition of biomass ashes in ancient settlements in the Czech Republic. In archeological localities, Cu also accumulates in locations of a high density of pottery fragments (Souza et al., 2016). The Cu contents in both sites do not suggest any form of mining and metallurgy with up to 2000 ppm Cu (Bastrygina et al., 2017).

The total Zn content due to past settlement activities in Ziavi-Galenkuito was 20 to 55 ppm representing 1.8 - 3 times enrichment in comparison to the control. Plant-available Zn content was approximately 4.8 to 6.2 times higher in Ziavi-Galenkuito compared to control. An increased total Zn content from 20 to 40 ppm was in the soil from Dřevíč hillfort representing from 1.3 - 1.7 times enrichment in comparison to the control. Plant-available Zn content was approximately 2.2 to 3.4 times higher in Dřevíč hillfort compared to control. However, there was a higher content of total Zn in Dřevíč hillfort than Ziavi-Galenkuito (45% enrichment). Anthropogenic loadings of Zn in archaeological localities result from agricultural activities (Klimek, 2002), biomass ashes (Nielsen and Kristiansen, 2014; Kofman, 2016), organic wastes deposition, excrement, and localities with a high amount of potteries (Souza et al., 2016).

There was an increased total Mn content from 1252 to 1747 ppm in all sampled locations of Ziavi-Galenkuito, which represents from 4.4 - 6.1 times enrichment compared to control. Moreover, the plant-available Mn content was from 7.1 - 8.2 times higher in Ziavi-Galenkuito in comparison to the control. In Dřevíč hillfort, an increased total Zn content from 197 to 349 ppm represent approximately 1.5 - 2 times enrichment in comparison to control. Plant-available Mn content was approximately 3.6 - 4.3 times higher in Dřevíč hillfort in comparison to control. Meanwhile, there was an increase of 120% in the total estimated Mn content in Ziavi-Galenkuito in comparison to Dřevíč hillfort. The high enrichment of Mn content in the Ziavi-Galenkuito site may result from the deposition of excrement and organic wastes (Parnell et al., 2002; Mescouto et al., 2011; Vassilev, 2013). The enrichment by Mn in the settlement sites relates to the disposition of biomass ashes containing approximately 10000 to 30000 ppm Mn

(Brais, 2015; Kofman, 2016). Considering the higher enrichment in a shorter duration of settlement activities in Ziavi-Galenkuito compared to Dřevíč hillfort, these activities were probably very intensive, and wastes deposition was done only within the small settlement area. However, the high pH of the soil in Dřevíč hillfort and the long period of abandonment probably contributed to Mn mobility, thus consistent with its content (Dabkowska-Naskret and Jaworska, 2013).

The total content of Sr was 19 to 115 ppm higher in Ziavi-Galenkuito, which is 2 - 7.5 times enrichment in comparison to the control. Available Sr content was 2.9 - 8.5 times higher in Ziavi-Galenkuito compared to control. In Dřevíč hillfort, the total Sr content was 24 to 47 ppm higher, representing 1.3 - 1.6 times increase in comparison to the control. The accumulation of Sr is related to the manuring of fields (Entwistle et al., 1998, 2000), deposition of bones (Lengfelder et al., 2018), and biomass ashes (Wedepohl and Simon, 2010; Oroian et al., 2015). Wood ashes from common European tree species, e.g., *Fagus sylvatica*, *Picea abies*, and *Pinus spp*, contain a high content of Sr (Oroian et al., 2015; Simniškytė-Strimaitienė et al., 2017). The increased contents of total Rb from 7 to 75 ppm in Ziavi-Galenkuito and 19 to 35 ppm in Dřevíč hillfort in comparison to the respective control probably resulted from similar activities as in Sr accumulation. The increased total Rb content in Ziavi-Galenkuito and Dřevíč hillfort was from 1.4 - 4.4 and 1.4 - 1.6 times, respectively, compared to their control.

Generally, the contents of total Cu, Zn, Sr, and Rb were higher in Dřevíč hillfort compared to Ziavi-Galenkuito. Although the intensity and duration of settlement activities play a significant role in the loadings of anthropogenic elements, the size of the settlement site is pertinent. The increased content of total Cu, Zn, Sr, and Rb in Dřevíč hillfort is as a result of the longevity and intensity of past settlement activities resulting from different archaeological timelines.

Ziavi-Galenkuito, as a plantation site for cash crops and residence for German as well as British merchandise, contained household wastes and remains of local and foreign trade goods. Similarly, Dřevíč hillfort, an administrative capital at the time of the hillfort with a high number of human interactions and activities, resulted in the accumulation of a high amount of organic wastes. The enrichment by total and Pav Cu, Zn, Mn, and Sr contents together with total Rb were so substantial in the past settlement sites compared to the control sites without settlement activities, which represent anthropogenic loadings from past human activities. Even though the study sites present different climatic conditions, the relationship between the total content of Cu, Zn, Mn, and Sr was significantly correlated (Fig. 7). Together with the high element content in the settlement sites, total Cu, Zn, Mn, and Sr can well indicate past human activities in different geographical regions due to their significant positive correlations.

The higher content of studied Pav elements in both sites compared to their control indicate that past settlement activities resulted in available nutrients for the growth of plants. Thus, the ADE soils are suitable for arable land use. The pattern of recorded plant-available elements was different from the total (Fig. 8). According to the results of this study, the total contents of Cu and Zn are more suitable for geoarchaeological purposes. The calculation of enrichment factors of these elements in the field can be easy. For Pav Mn, the content is dependent not only on the total Mn content in the soil but also on other soil chemical properties such as pH and the presence of oxides. These complicate the estimation of the enrichment factors of Pav elements, including Mn and Sr. Such data interpretation is very complicated. Therefore, the total element contents are more suitable in calculating enrichment factors for geoarchaeological purposes.

Conclusions

The result of this comparative study indicated increased total and Pav contents of Cu, Zn, Mn, and Sr together with total Rb in the past settlement sites from different geographical positions compared to their respective controls. The increased contents of these elements were consistent with all the sampled locations of the studied sites compared to their control of the same geology.

The level of accumulation of these elements relates to the size of the settlements, longevity, and intensity of settlement activities.

The anthropogenic accumulation of the Cu, Zn, Mn, Sr, and Rb in the settlement sites resulted mainly from organic wastes, biomass ashes, and excrement dispositions. Moreover, retention of the elements resulted from the high fraction of fine grain sand, silt, and clay, with optimum pH values from both study sites. Furthermore, the total content of Cu, Zn, Mn, and Sr in both studied sites well correlated and can be used to indicate past human activities in different geographical regions.

Comparing the contents of total and Pav (Mehlich 3) elements, the analysis of total element content is more suitable for geoarchaeological purposes as enrichment factors are easy to calculate. In the case of Cu and Zn, total and Pav contents are not well correlated, as each method revealed different patterns. The patterns recorded using Pav contents of elements are affected by some soil chemical properties. Hence, difficult to draw straightforward inferences without a detailed analysis of soil properties, which may be hard to perform by geoarchaeologists in the field.

In conclusion, minor/microelements are prominent indicators of settlement activities, even in different environmental conditions. The use of pXRF is a suitable method in tracing anthropogenic elements in ADE soils.

Conflict of interest

The authors declare no conflict of interest.

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CHAPTER 5

Can wood ashes of commonly planted tree species in Ghana be applied as fertilizers?

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ORIGINAL PAPER

Can Wood Ashes of Commonly Planted Tree Species in Ghana be Applied as Fertilizers?

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Abstract

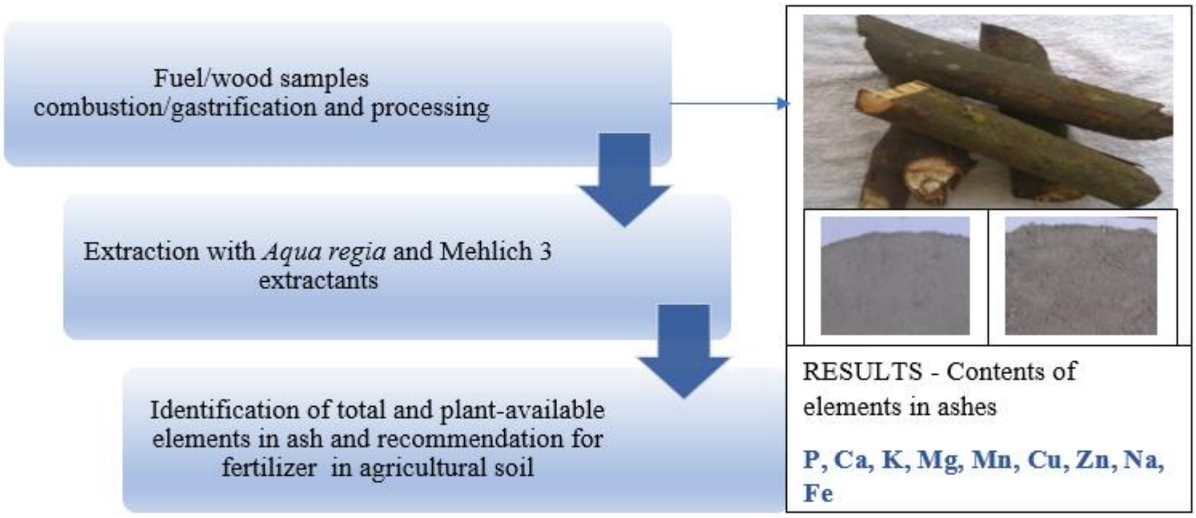
Purpose The fertilizer values of ashes from commonly used woody species in the tropics are not well-known. To determine whether ashes of *Theobroma cacao*, *Persea americana*, *Cola nitida*, *Mangifera indica*, *Citrus sinensis*, *Prunus dulcis*, and *Senna siamea* are suitable fertilizers, we studied the contents of total and plant-available elements.

Methods Ashes of dry wood samples burnt at 500 °C were digested in Aqua-regia and Mehlich-3 extractants to determine the contents of total and plant-available elements, respectively, with inductively coupled plasma-mass spectrometry.

Results Ash yields ranged from 3.1 to 7.1% with pH (H_2O) of 7.8–12.9. The ashes contained high P, Ca, K, Mg, S, Fe, Na, Mn, Cu, and Zn contents, with significant effects among the species. Total element content ranged from (g kg^{-1}) 2–49 P, 19–218 Ca, 64–325 K, 48–95 Mg, 0.4–16 Fe, 3.6–29 Na, (mg kg^{-1}) 143–798 Mn, 52–81 Cu, and 188–312 Zn. Available plant elements ranged from (mg kg^{-1}) 22–512 P, 37,491–88,303 K, 2948–19,713 Ca, 13,719–29,001 Mg, 75–168 Mn, 40–74 Cu, 44–91 Zn, 1.5–383 Fe, and 836–6937 Na. The releasability (proportion of plant-available elements from the total) ranged from 0.08 to 92.8%. The relatively high releasability (25.4–80.4%) of Ca, K, Mg, Mn, Cu, and Zn in the ashes of the over-all species can supplement low nutrient availability for plants. The low releasability of P (1.1%) of the overall species explains its persistence in soils applied with ashes.

Conclusion The high yield of the ashes and pH support their ideal use, especially for very acidic soils. Ashes of the studied species are suitable fertilizers for soils according to the availability and releasability of macro (P, Ca, K, Mg, S) and microelements (Mn, Cu, Zn, Fe, Na). Total and plant-available Ni, Pb, As, and Cd contents in the ashes were below permissible limits in soils. Thus, the studied ashes are especially suitable for soils with high acidity and low fertility.

Graphical abstract



Keywords Macro-element · Microelement · *Mangifera indica* · Releasability · *Theobroma cacao*

Statement of novelty

The fertilizer value of ashes of most tropical tree species is not well-known. From pieces of literature, the detection of the total element contents in ashes may provide less information about ash utilization in agricultural soils. For this reason, we determined both total and plant-available elements and their releasability to fill the gap in the extent of elemental accumulation of wood ashes of selected species.

Introduction

Biomass and particularly wood ashes were produced by humans since the first use of fire in the Paleolithic. It is well established that places with the deposition of wood ashes have increased crop production even after hundreds of years [1, 2]. Wood ashes probably have been used as fertilizers on agricultural soils since the Neolithic, and waste pits with deposited ashes can be identified according to high crop growth compared to surroundings without deposited ash, even after thousands of years [2]. In many regions, wood ashes helped to improve soil fertility and in the establishment of extraordinary fertile archaeological soils [3-5].

Wood ash has a high potential to be used as P, Ca, K, Mg, Zn, Cu, and Fe fertilizers on agricultural and forest soils, even to date. However, risk elements represent the biggest challenge in the applying of ashes on agricultural soils, particularly As and Pb, that concentrate in ashes if the burned biomass eventually are enriched by them.

It is, therefore, necessary to perform chemical analysis of ashes and to identify if risk elements do not exceed acceptable limits, which are (in mg kg^{-1}) 20 for As, 100 for Pb, 3 for Cd, 50 for Ni, 50 for Co, and 100 for Cr [6]. Also, the chemical properties of ashes from different woody species are not well known. Many elements in ashes, e.g., P, is in forms not easily accessible by plants. In addition to the total element content, it is necessary to estimate the releasability (proportion of plant-available elements from the total).

The next important parameter is the ash yield, which can range approximately from 0.8 to 12% [7-9] from the burned wood depending on the species, the proportion of bark and wood, and combustion temperature. To determine the yields of ash, the weight of wood samples before burning is vital as well as resultant ash, at specific temperatures [7, 10, 11]. Wood ashes of trees species such as aspen, alder, walnut, poplar, bird cherry, spruce, birch, hornbeam, hazel, etc., according to the study conducted by Symanowicz et al. [12] considered suitable for use in agriculture as a liming agent for soils due to their low pH, which ranged from 9.6-13.7. The application of wood ashes to soils can increase soil pH and have significant liming effect than other limes (e.g., $CaCO_3$) [13].

Determination of ash yield is essential as it enables the application of an appropriate dosage of ashes to soils [7, 8]. Most studies on the elemental composition of ashes previously were based only on the total content of elements in ashes [14-16] without any information about releasability. Woody species have different elemental compositions due to genetic variations in uptake of elements, different soils, geological backgrounds, and anthropogenic activities in the growing area. In Ghana, *Theobroma cacao, Persea americana, Cola nitida, Mangifera indica, Citrus sinensis, Prunus dulcis,* and *Senna siamea* are commonly planted trees in plantations, and the secondary product is firewood used for cooking. These species form a vital part of the socio-economic development of many households in Ghana. Thousands of people across the country produce and market the species regularly in the local, regional, and international markets. About 20% of the economically active population derives income from these products [17]. Moreover, about 75% of households in Ghana rely on biomass as a source of energy for cooking [18]. This proportion is highest among rural households, with about 89% using biomass as cooking fuel [18]. Almost all the tree species studied are grown in rural and urban areas also in small quantities (as home gardens or mixed with food crops on farmlands). Ashes of these species are commonly applied as fertilizer on agricultural soils, although their chemical properties are not well known.

Therefore, the study aimed to determine the ash yield, contents of the total, and plant-available elements in ashes of the species mentioned above. We asked, what are the differences in; (a) ash yields, (b) total, and (c) plant-available contents of macro, micro, and other elements among studied species?

We also asked, (d) how high is the releasability of elements - the proportion of elements available for plants from the total content? (e) can the studied ashes be used as fertilizers?

Material and methods

Sample collection and preparation

Samples of branches (wood and bark) of *T. cacao, P. americana, C. nitida, M. indica, C. sinensis, P. dulcis,* and *S. siamea* initially were collected during the rainy season in June 2019. *T. cola* is the only native species in Ghana among the selected species. All the selected species most often are planted in the Western and Central African countries in plantations and farmlands. Except for *T. cacao,* which thrives very well only in the lowlands of Ghana, the remaining six species are planted commonly in both lowlands and highlands (Table 1). Secondary product from plantations is firewood, obtained during the regular management of trees.

Table 1. List of selected tree species and details of their distribution in Ghana.

Scientific name	Common name	Commonly locations in Ghana	Location collected
Theobroma cacao	Cocoa	Lowlands	Esaase, Ashanti region
Persea americana	Avocado	Very common in lowlands	Koforidua, Eastern region
Cola nitida	Cola	High and lowlands	Tumu, Upper West region
Mangifera indica	Mango	High and lowlands	Ziavi, Volta region
Citrus sinensis	Orange	High and lowlands	Koforidua, Eastern region
Prunus dulcis	Almond	High and lowlands	Ejura, Ashanti region
Senna siamea	Cassia	High and lowlands	Koforidua, Eastern region

We used 50 cm long branches with a diameter from 8 to 17 cm as such firewood, most often used for cooking in Ghana. With each species, we collected four branch samples from different locations in Ghana. The branch samples were thoroughly washed in deionized water before chopping, to prevent contamination by dust or soils. Fresh samples of branches were chopped into small slides of 0.5 cm thick and then dried for three days at 50 ºC to total desiccation. We took 200 g of the dry wood with the bark of each sample and burned completely in a muffle furnace at a temperature of 500 ºC for 4 hours. The muffle furnace has a chamber dimension of 30 × 20 × 15 cm with a holding capacity of six crucibles. The obtained ash samples were collected and homogenized by passing through a 0.1-mm sieve and subsequently put into a labeled plastic bag. We prepared 28 ash samples (seven species × four replications) for subsequent laboratory analysis.

Analytical methods and sample digestion

For digestion purposes, 65% nitric acid (HNO_3) and 32% hydrochloric acid (HCl) was used. Ultrapure-deionized water (18Ω) again was used throughout the study. The glassware was soaked in 3 M HNO_3 for 12 hours, washed, and rinsed with deionized water (18Ω) to reduce the chances of interferences. All the chemical analyses were conducted under the extractor hood and a digital IR Vortex Mixer (S/N296058) used for the mixing of solutions. Inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700x, Agilent Technologies Inc., USA), further employed to determine the content of elements in the ash samples.

Of each homogenized ash sample, 2 g and a certified reference material (CRM, fly ash applied for the quality assurance of analytical data) were initially weighed and transferred into a VWR® PTFE Jar containing 60 ml of *Aqua-regia* (3ml HCl and 1ml HNO_3, International Organization for Standardization – USEPA 3052 – Microwave-assisted extraction of the *Aqua regia* soluble fraction for the determination of elements). The mixture was placed on a hot plate at 120 ºC until the volume again was reduced to 40 ml. After the heating, we transferred each solution to a conical flask and diluted it to 100 ml using Ultrapure-deionized water (18Ω). Approximately 20 ml of the diluted solution was transferred into glass test tubes for the determination of the total content of elements using ICP-MS. The total contents of macro (P, K, Ca, Mg, and S), micro (Mn, Cu, Zn, Na, and Fe), and other (such as Ni, Cr, Pb, Co, As, Cd, V, Al, and Sr) elements were pertinent in this case. These elements were above the detection limit in all cases.

Plant-available P, K, Ca, Mg, Mn, Cu, Zn, Na, Fe, Ni, Cr, Pb, Co, As, Cd, Al, and Sr, were extracted by the Mehlich-3 reagent [19]. The extractant composition is as follows: 0.2 M CH3COOH + 0.25 M NH4NO3 + 0.013 M HNO3 + 0.015 M NH4F + 0.001 M EDTA. In this case, 2 g of each homogenized ash sample subsequently was mixed with extractant in a ratio (ash: extractant; g: mL) of 1:5. The contents of the plant-available elements also were determined by the same ICP-MS. We procured all the chemicals in this study from Analytika Czechia.

Total and plant-available contents of Hg, Ag, Ti, Se, and many elements were below the limit of detection, and as such, omitted from further analysis. Plant-available S and V contents were also not detected in all cases. The pH (H_2O) of all the ash samples also was determined at a ratio of 1:1 (ash: water) using a Voltcraft PH-100 ATC pH meter (pH 212; I & CS spol. s r.o., Czech Republic). All measurements of the pH and content of the elements were in two replicates.

Operating conditions of ICP-MS

A quadrupole mass filter, a pneumatic nebulizer (MicroMist), and an octopole collision cell pressurized with helium (He) constitute the characteristic components of the ICP-MS employed in this study. The operating conditions set as follows: power = 1.40 kW, carrier argon (Ar) flow rate = 1.08 L min^{-1}, auxiliary Ar flow rate = 0.90 L min^{-1}, plasma Ar flow rate = 15.0 L min^{-1}, collision He flow rate = 7.0 mL min^{-1}, and sampling depth = 5.5 mm. The acquisition parameters were: points/peak = 1, replicates = 2, replicate read time = 10 s, integration time = 3 s, sweeps/replicate = 20, calibration mode = external calibration at 0.1, 0.5, 1.0, 5.0, 10.0 µg L^{-1}, and aspirating 20 µg L^{-1} Ge as an internal standard.

Analytical accuracy and precision

From our analysis of the CRM (BCR – 176R), we obtained the following mass fraction of the following elements: 13414 ± 261 mg kg^{-1} Fe, 1088 ± 17.4 mg kg^{-1} Cu, 16709 ± 237 mg kg^{-1} Zn, 56 ± 0.7 mg kg^{-1} As, 118 ± 2.8 mg kg^{-1} Ni, 24.5 ± 1.1 mg kg^{-1} Co, and 4954 ± 498 mg kg^{-1} Pb as against the original values of 13100 ± 500 mg kg^{-1} Fe, 1050 ± 70 mg kg^{-1} Cu, 16800 ± 400 mg kg^{-1} Zn, 54 ± 5 mg kg^{-1} As, 117 ± 6 mg kg^{-1} Ni, 26.7 ± 1.6 mg kg^{-1} Co, and 5000 ± 500 mg kg^{-1} Pb. The calculated recovery ((mean value of element/mean reference value) × 100), according to the Eurachem guide [20], was > 90% for Fe, Cu, Zn, As, Ni, Co, and Pb, respectively. Thus, the precision of the analytical measurements was adequate for this study.

Data analysis

There was homogeneity of variance among obtained data for the contents of elements in studied ashes. Data for elemental contents of ashes were tested using the Shapiro-Wilk W-test for normality and met the assumptions for the use of parametric tests. One-way ANOVA followed by *post hoc* comparison using the Turkey's *HSD* test was applied to identify significant differences among ashes of different species. To determine the relationship between the content of total and plant-available elements (P, Ca, K, Mg, Na, Mn, Fe, Cu, and Zn), Pearson's correlation was used. We performed all statistical analyses using STATISTICA 13.4 (www.statsoft.io).

Results and Discussion

Ash color, pH, and yield

Ashes from all species were grey but with a slightly different tone (Fig. 1). For example, the lightest ash was from *Citrus,* and the darkest ash from *Theobroma*.

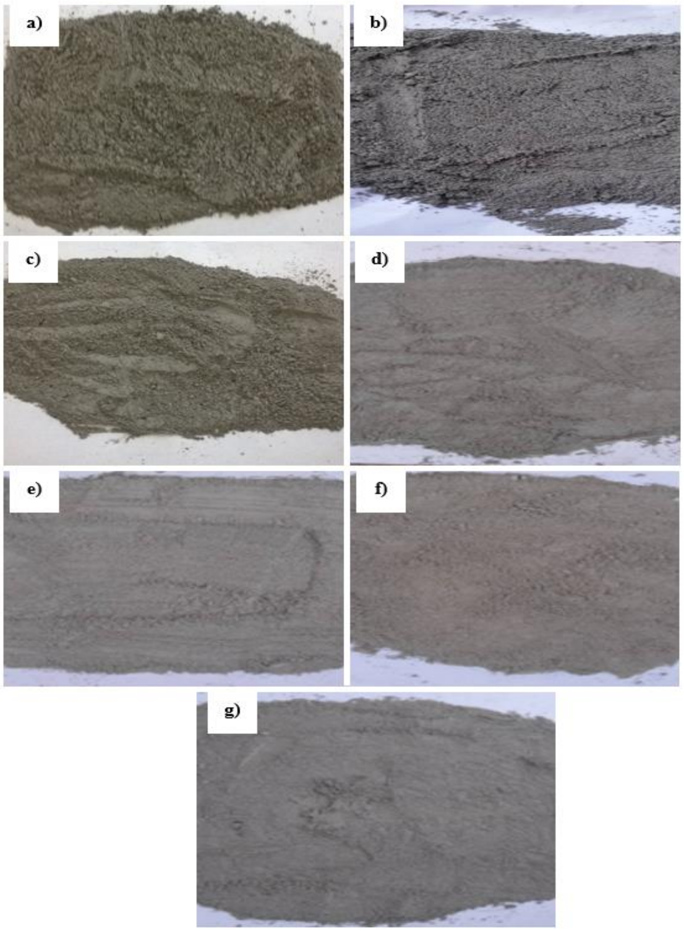


Fig. 1 The representative ash samples from (a) *Theobroma cacao*, (b) *Persea americana*, (c) *Cola nitida*, (d) *Mangifera indica*, (e) *Citrus sinensis*, (f) *Prunus dulcis*, and (g) *Senna siamea*.

However, this contrasted with some European woody species where the color of home-produced wood ashes was white in the case of *Tilia cordata* to black in *Picea abies* (unpublished data of authors). The comparatively similar color of the ashes in this study related to the relatively low temperature adopted for the burning and also all the species were broad-leaved. Sometimes black color relates to the presence of microcharcoals, indicating incomplete combustion of the wood. And this can result in the different elemental composition of ashes, but not the case of this study.

The overall pH of ashes was basic, ranging from 7.8 to 12.9 in *C. sinensis* and *T. cacao*, respectively (Table 2). The range of pH of ashes was high, indicating that ashes of different woody species have different elemental compositions. All ashes were alkaline, indicating their suitability as amendments to alleviate soil acidity.

The dry matter yield of ashes ranged from 3.1 to 7.1 % in *P. dulcis* and *T. cacao*, respectively (Table 2). The mean ash yield of the overall species was 5.1 %. Except for *P. dulcis*, the yield of ashes was higher compared to results reported by Dibdiakova et al. [11] and Kfle et al. [21]. And can be attributed to the relatively low temperature (500 °C) of combustion used in this study. Combustion temperature ≤ 600 ºC results in the decomposition of Ca and K carbonates and the subsequent decrease in ash yields [10, 11, 22]. Additionally, at > 500 °C temperature, carbonates and bicarbonates increase, while oxides become more prevalent in temperatures < 1000 °C [23]. The temperature adopted in this study was adequate in the recovery of many elements, e.g., high total and plant-available Ca, K, and Mg contents. The high contents of Ca, K, and Mg contributed to the high pH of the ashes. We used relatively small combustion temperature to simulate conditions in many households, so the ash yields and chemical properties are more similar to ashes applied on arable fields in Ghana.

Table 2. The pH (H_2O) and ash content (dry mass) of selected tree species. The *p*-values were obtained by one-way ANOVA. Using the Tukey's HSD *post hoc* test, mean values with the same letter relative to other tree species were not significantly different. The SE indicates the standard error of the mean.

Tree species	pH (H_2O)	Ash, dry basis (% wt)
Theobroma cacao	12.9	7.1 ± 0.2^{a}
Persea americana	9.1	4.8 ± 0.8^{bc}
Cola nitida	10.4	5.2 ± 0.8^{b}
Mangifera indica	10.2	5.7 ± 0.9^{bd}
Citrus sinensis	7.8	5.3 ± 0.8^{bcd}
Prunus dulcis	10.9	3.1 ± 0.3^{e}
Senna siamea	12.1	4.6 ± 0.7^{b}
Mean		5.1 ± 1.1
p-value	< 0.001	< 0.001

The dry matter yield of ashes ranged from 3.1 to 7.1 % in *Prunus* and *Theobroma*, respectively (Table 2). The mean ash yield of the overall species was 5.1 %. Except for *Prunus*, the yield of ashes was higher in comparison to results reported by Dibdiakova et al. [11] and Kfle et al. [17], and this was asa result of the relatively low temperature (500 °C) in our study. Combustion temperature 600ºC and higher results in the decomposition of Ca and K carbonates and the subsequent decrease in ash yields [10, 11, 18]. Carbonates and bicarbonates predominate in a temperature below 500 °C, with oxides in temperatures above 1000 °C [19].

The temperature adopted in this study was adequate in the recovery of many elements, e.g., high total and plant-available Ca, K, and Mg contents. The high contents of Ca, K, and Mg also contributed to the high pH of the ashes. We used relatively small combustion temperature to simulate conditions in many households, so our ash yields and chemical properties of ashes are more similar to ashes applied on arable fields in Ghana.

Elemental composition of ashes

Contents of total and plant-available macro-elements (P, Ca, K, and Mg) were above detection limits in all studied ash (Figs. 2a, b, and Table 3). Sulfur was above the detection limit only in the case of total contents (Table 3). There were significant differences in the contents of total P, Ca, K, S, and Mg among the species as well as the contents of plant-available P, Ca, K, and Mg.

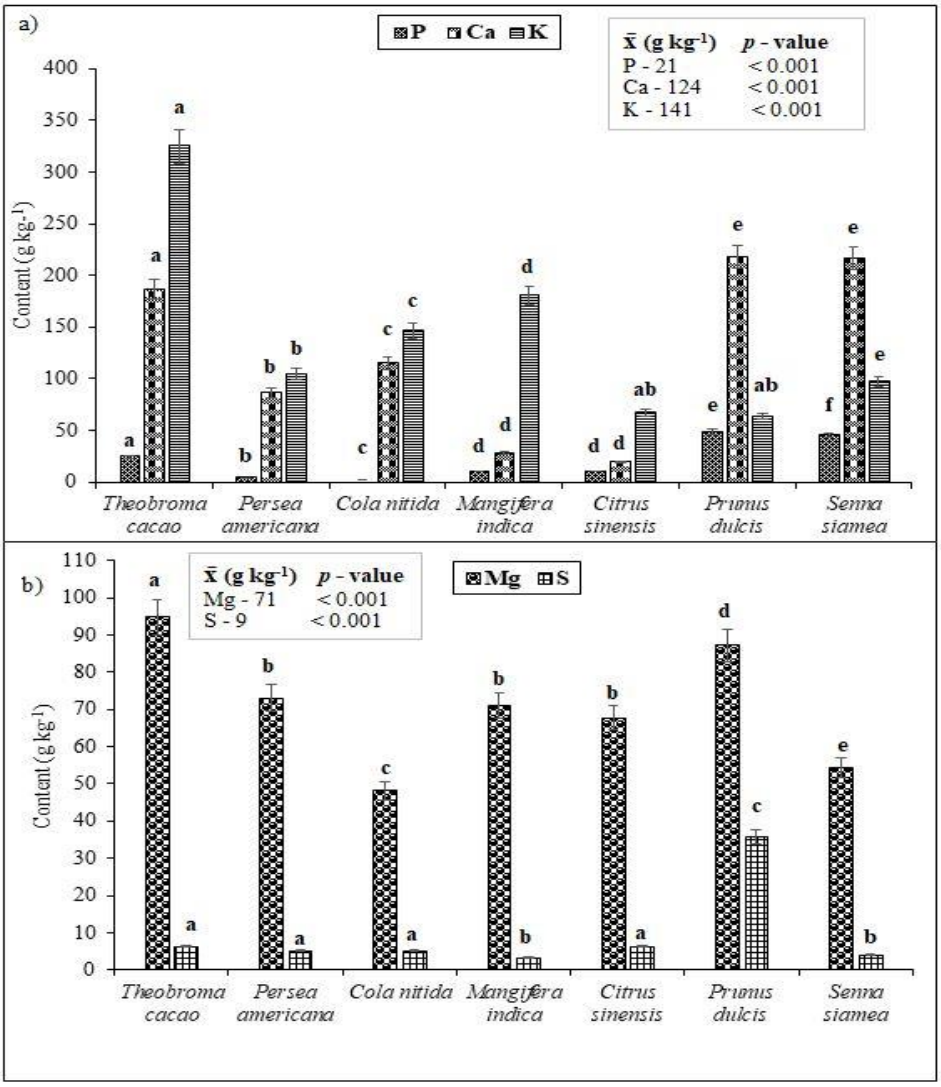


Fig. 2 Total contents (mean ± SE) of (a) P, Ca, and K and (b) Mg and S in the ashes of the studied species. The p-values were obtained by one-way ANOVA. Using the Tukey HSD *post hoc* test, mean values with the same letter relative to other tree species were not significantly different. SE indicates the standard error of the mean. The x̄ indicates the overall mean of elements of all species.

The lowest total P content (2 g kg^{-1}) was in *C. nitida* and the highest (49 g kg^{-1}) %) in *P. dulcis*. Of the overall species, the mean total P content in the ashes was 21 g kg^{-1}. The content of plant-available P ranged from 22 to 512 mg kg^{-1} in *C. nitida* and *P. dulcis*, respectively. The mean content of plant-available P content in the ashes of the overall species was 219 mg kg^{-1}. The wood ashes from our study are suitable P fertilizer in P deficient soils. The most suitable source of P was ash from *P. dulcis*, followed by ashes from *S. siamea* and *T. cacao* according to the higher P availability compared to ashes from other studied species (Table 3). The available P content was comparatively low in the ashes of *C. Nitida*, *C. sinensis*, and *P. americana*, with relatively similar releasability, among all the species. Thus, the ashes of *P. Dulcis*, *S. Siamea*, *T. Cacao*, and *M. indica* are the most suitable P fertilizers according to the availability and releasability for plants. Although *P. americana* and *C. nitida* are suitable P fertilizers for soils, the total and plant-available content was lower than the other species. Notwithstanding, unlike

C. nitida, the releasability of P for *P. americana* was the highest (1.6 %), however, with a comparatively lower total P (4.1 g kg^{-1} or 4100 mg kg^{-1}) to compensate for plant-available content recorded in the other species. The ash of *C. sinensi*, has the lowest P releasability, with a comparatively lower plant-available content – considered among the least P fertilizer for soils compared to other species, *e.g., P. dulcis, S. Siamea,* and *T. Cacao.*

The ideal availability of P in soils is mostly from pH (H_2O) 6.5-7.5 (relatively neutral to alkaline) [24]. Thus, in very acidic soils, ashes are suitable because P in the ashes can become readily available for plants.

The releasability of P ranged from 0.5 to1.6 % in *C. sinensis* and *P. americana*, with a mean value of overall species of 1.1 %. Generally, the releasability of P overall the species was only 1.1 % – the lowest value from all analyzed elements. This well explains why P signature on archaeological localities with deposition of wood ashes is very stable and long-lasting. Field studies from different regions revealed that sites with the deposition of ashes have a high total and plant-available P contents in the soils even after thousands of years of abandonment [2, 5].

Table 3. Content (mean ± SE) of plant-available macro, micro, and other elements in the ash samples of selected tree species. The p-values were obtained by one-way ANOVA. Using the Tukey HSD *post hoc* test, mean values with the same letter relative to other tree species were not significantly different. The SE indicates the standard error of the mean.

Elements	***Theobroma. cacao***	***Persea americana***	***Cola Nitida***	***Mangifera indica***	***Citrus sinensis***	***Prunus dulcis***	***Senna siamea***	**Mean**	**p-value**
Macroelements									
P [mg kg^{-1}]	265 ± 19.2^{a}	64 ± 4.4^{b}	22 ± 3^{c}	161 ± 5.2^{d}	57 ± 3.7^{b}	512 ± 9.4^{e}	449 ± 8.5^{f}	219 ± 64.5	< 0.001
Ca [mg kg^{-1}]	2948 ± 19.8^{a}	19713 ± 16.9^{b}	13610 ± 13.4^{c}	16382 ± 12.7^{d}	12923 ± 21.9^{e}	17781 ± 12^{f}	13827 ± 11.3^{g}	13883 ± 2047	< 0.001
K [mg kg^{-1}]	79086 ± 13.4^{a}	88303 ± 11.3^{b}	42394 ± 20.8^{c}	63714 ± 21.2^{d}	59671 ± 4.9^{e}	44237 ± 12.7^{f}	37491 ± 17^{g}	59271 ± 7303	< 0.001
Mg [mg kg^{-1}]	29001 ± 7.8^{a}	15239 ± 7.7^{b}	27265 ± 9.8^{c}	13719 ± 9.9^{d}	14627 ± 14.1^{e}	24381 ± 17^{f}	28478 ± 16.9^{g}	21816 ± 2640	< 0.001
Microelements									
Mn [mg kg^{-1}]	102 ± 7.1^{a}	88 ± 5.7^{b}	168 ± 12.6^{ac}	82 ± 2.1^{a}	75 ± 1.6^{ab}	105 ± 5.7^{af}	141 ± 5.8^{ad}	109 ± 12.8	< 0.001
Cu [mg kg^{-1}]	40 ± 2.3^{a}	41 ± 1.7^{a}	62 ± 5.2^{b}	64 ± 0.8^{b}	61 ± 4.7^{b}	73 ± 3^{bc}	74 ± 3.1^{c}	59 ± 5.2	< 0.001
Zn [mg kg^{-1}]	75 ± 4.1^{a}	44 ± 4.3^{b}	72 ± 6.3^{ac}	85 ± 1.3^{ad}	66 ± 2.8^{ac}	89 ± 5.7^{ad}	91 ± 5.5^{ad}	75 ± 6.1	< 0.001
Na [mg kg^{-1}]	941 ± 15.6^{a}	6937 ± 11.2^{b}	1171 ± 5.7^{c}	6178 ± 18.4^{d}	836 ± 5.9^{e}	1027 ± 12.7^{f}	1164 ± 8.5^{c}	2608 ± 1024	< 0.001
Fe [mg kg^{-1}]	1.5 ± 0.2^{a}	41 ± 4.1^{b}	383 ± 5.7^{c}	39 ± 7.1^{b}	2.8 ± 0.2^{a}	209 ± 5.7^{d}	278 ± 12.7^{e}	136 ± 58	< 0.001
Other elements									
Ni [mg kg^{-1}]	3.3 ± 0.4^{a}	1.7 ± 0.2^{b}	3.5 ± 0.2^{a}	1.2 ± 0.2^{b}	0.98 ± 0.04^{b}	4.2 ± 0.4^{a}	3.1 ± 0.1^{a}	2.6 ± 0.4	< 0.001
Cr [mg kg^{-1}]	0.2 ± 0.02^{a}	9.7 ± 1.4^{b}	3.5 ± 0.4^{cd}	4.8 ± 0.4^{cd}	3.2 ± 0.3^{cd}	1.9 ± 0.1^{ac}	4.3 ± 0.2^{cd}	3.9 ± 1.1	< 0.001
Pb [mg kg^{-1}]	3.6 ± 0.2^{a}	0.99 ± 0.1^{b}	0.7 ± 0.1^{b}	0.01 ± 0.0^{c}	0.09 ± 0.0^{c}	1.9 ± 0.2^{d}	0.2 ± 0.0^{bc}	1.1 ± 1.2	< 0.001
Co [mg kg^{-1}]	1.4 ± 0.2^{a}	0.72 ± 0.1^{b}	1.07 ± 0.02^{a}	0.52 ± 0.1^{b}	0.22 ± 0.04^{c}	1.13 ± 0.1^{a}	3.41 ± 0.2^{d}	1.2 ± 0.4	< 0.001
As [mg kg^{-1}]	0.02 ± 0.0^{a}	0.16 ± 0.01^{a}	0.01 ± 0.0^{a}	0.02 ± 0.0^{a}	0.19 ± 0.01^{a}	0.91 ± 0.1^{b}	1.32 ± 0.3^{b}	0.4 ± 0.1	< 0.001
Cd [mg kg^{-1}]	0. 01 ± 0.0^{a}	0.03 ± 0.0^{b}	0.03 ± 0.0^{b}	0.03 ± 0.0^{b}	0.01 ± 0.0^{a}	0.01 ± 0.0^{a}	0.2 ± 0.01^{c}	0.05 ± 0.02	< 0.001
Sr [mg kg^{-1}]	47 ± 5.7^{a}	106 ± 5.6^{b}	108 ± 3.8^{b}	121 ± 5.7^{b}	101 ± 11.3^{b}	55 ± 4.2^{a}	32 ± 4.1^{c}	81 ± 13.4	< 0.001
Al [mg kg^{-1}]	1.4 ± 0.2^{a}	19.5 ± 1.4^{b}	1.5 ± 0.05^{a}	4.5 ± 0.3^{c}	8.6 ± 1.3^{d}	1.9 ± 0.2^{a}	2.0 ± 0.07^{a}	5.6 ± 2.5	< 0.001

Table 4. Releasability (the content of *plant-available element / total element content × 100*) of macro, micro, and other elements of ashes from the studied tree species. The p-values were obtained by one-way ANOVA. Using the Tukey HSD *post hoc* test, mean values with the same letter relative to other tree species were not significantly different. The SE indicates the standard error of the mean.

Ash samples	**P**	**Ca**	**K**	**Mg**	**Mn**	**Cu**	**Zn**	**Na**	**Fe**	**Ni**	**Cr**	**Pb**	**Co**	**As**	**Sr**	**Al**
								[%]								
Theobroma cacao	1.1 ± 0.1^{a}	1.6 ± 0.2^{a}	24.3 ± 1.5^{a}	30.5 ± 2.3^{a}	55.6 ± 3.9^{a}	67.2 ± 4.2^{a}	38 ± 3.1^{a}	3.2 ± 0.2^{a}	0.08 ± 0.0^{a}	71.7 ± 2.2^{a}	3.7 ± 0.2^{a}	4 ± 0.6^{a}	70.7 ± 0.9^{ae}	0.9 ± 0.1^{a}	24.1 ± 1^{a}	1.8 ± 0.2^{a}
Persea. Americana	1.6 ± 0.07^{b}	22.9 ± 1.5^{b}	84.3 ± 0.7^{b}	20.9 ± 2^{b}	50.6 ± 1.4^{b}	76.1 ± 3.6^{b}	23.5 ± 4.1^{b}	75 ± 4.7^{b}	0.9 ± 0.1^{b}	42.3 ± 2.6^{b}	45.6 ± 0.9^{bc}	9 ± 0.4^{b}	74.2 ± 2.5^{a}	21 ± 1.4^{b}	24.8 ± 0.8^{a}	24.7 ± 1.2^{b}
Cola nitida	1.1 ± 0.2^{a}	11.8 ± 2^{c}	29.1 ± 2.1^{c}	56.8 ± 3.3^{c}	48.4 ± 2.4^{b}	79.1 ± 4.8^{b}	30.2 ± 4.1^{c}	14 ± 5.2^{c}	0.24 ± 0.1^{a}	36.4 ± 1.1^{c}	27.6 ± 0.5^{d}	16.1 ± 0.6^{c}	72.1 ± 2.4^{a}	0.2 ± 0.0^{c}	67.1 ± 1.1^{b}	0.8 ± 0.05^{c}
Mangifera indica	1.5 ± 0.3^{b}	58.5 ± 2.5^{d}	35.4 ± 1.4^{d}	19.3 ± 3.1^{b}	55.2 ± 2.6^{a}	84.6 ± 2.9^{c}	37.9 ± 3.6^{a}	56.1 ± 5.5^{d}	0.93 ± 0.3^{b}	$37.1\ 1.1\pm^{c}$	48.1 ± 1^{b}	1.6 ± 0.02^{d}	65 ± 0.9^{b}	2.1 ± 0.2^{a}	26.2 ± 1.4^{a}	6.4 ± 0.3^{d}
Citrus sinensis	0.5 ± 0.3^{c}	68 ± 2.2^{f}	88.5 ± 2.3^{e}	21.5 ± 2.4^{b}	52.6 ± 2.1^{ab}	85.9 ± 3.2^{cd}	32.7 ± 4^{c}	23.2 ± 5.5^{e}	0.71 ± 0.07^{b}	25.6 ± 0.8^{d}	42.4 ± 0.9^{bc}	19.1 ± 0.9^{c}	24.4 ± 0.6^{c}	1.9 ± 0.4^{a}	66.7 ± 2.9^{b}	14.5 ± 1.2^{e}
Prunus dulcis	1.1 ± 0.3^{a}	8.4 ± 2.1^{g}	69.3 ± 2^{f}	28 ± 2.8^{d}	27 ± 3^{c}	89.7 ± 3.9^{cd}	28.6 ± 3.5^{c}	8.2 ± 0.1f	3.5 ± 0.3^{c}	67.2 ± 1.8^{e}	35.6 ± 0.8^{e}	63.3 ± 1.6^{e}	36.6 ± 1.2^{d}	13.5 ± 1.1^{d}	59.1 ± 2.8^{b}	0.4 ± 0.06^{c}
Senna siamea	1 ± 0.4^{a}	6.4 ± 2^{g}	38.6 ± 2.3^{d}	5.2 ± 2.3^{e}	17.7 ± 2.7^{d}	92.8 ± 4.9^{e}	36.2 ± 3.5^{a}	7.8 ± 0.2f	3.3 ± 0.4^{c}	31.6 ± 1.3^{f}	45.9 ± 1.1^{bc}	33.8 ± 1.2^{f}	66.9 ± 2.4^{ef}	13 ± 0.9d	51.2 ± 1.9^{bc}	1.6 ± 0.1^{a}
Mean	1.1 ± 0.3	25.4 ± 10.1	52.7 ± 10.3	26 ± 5.9	43.9 ± 5.7	80.4 ± 3.3	32.4 ± 2	26.8 ± 10.4	1.4 ± 0.5	44.5 ± 6.7	35.6 ± 5.9	20.9 ± 8.1	58.5 ± 7.4	7.5 ± 3.1	45.3 ± 7.5	7.3 ± 3.4
P-value	< 0.001	< 0.001	0.001	0.001	0.001	< 0.001	< 0.001	0.001	0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

Phosphorous signature in soils is more stable than in the case of many other elements. The application of wood ash as fertilizer shows the best results in stands with visual symptoms of P deficiency, especially on N-rich drained peat soils [16]. Phosphorus is responsible for several vital plant roles, including photosynthesis, nutrient movement, transfer of energy as well as genetic characteristics. P deficiency in soil severely affects plant metabolism and yields [16]. The total P contents in most of the studied ashes were within the ranges from 8.5 to 21.9 g kg^{-1} recorded by Etiégni et al. [25], Huang et al. [26], and Górecka et al. [27] for ashes of some woody species. However, a range from 24.4 to 49 g kg^{-1} in total P was in *T. cacao, S. siamea*, and *P. dulcis*, higher than recorded values by these authors for different woody species. The lowest total Ca content (19 g kg^{-1}) among the ashes was observed in *C. sinensis* and the highest (218 g kg^{-1}) in *P. dulcis*. The mean total Ca content in ashes of the overall species was 124 g kg^{-1}. The content of plant-available Ca ranged from 2948 to 19713 mg kg^{-1} in *T. cacao* and *P. americana*, respectively. The mean content of plant-available Ca of the overall species was 13883 mg kg^{-1}. The wood ashes from the selected species of this study can be applied to Ca demanding soils according to their high levels of availability to plants among the species. The releasability of Ca ranged from 1.6 to 68 % Ca in *T. cacao* and *C. sinensis*, respectively. The mean releasability of Ca of the ashes overall species was 25.4 %. The releasability of Ca in the ashes in the overall species was higher in comparison to P and other elements (such as Fe, Al, and Pb). Ca is readily available in pH ranging from 7 - 14, as also observed in this study. However, the releasability of Ca from individual species relates to the nature of the plant. Thus, ashes from *M. indica* and *C. sinensis* are more appropriate Ca fertilizers in agricultural soil as they have relatively high releasability. Although *C. sinensis* has the highest releasable Ca, the total and plant-available Ca contents were low in this study. The comparatively low total and plant-available Ca contents in *C. sinensis* to other species attest to the fact that this species is mostly planted in moderately acidic to neutral soils with lower Ca content [28]. Wood ashes have the same liming effects as commercial lime and comparatively provide better plant growth responses than limestone because of the additional nutrients in ashes [15]. Notably, wood ashes contain a high content of Ca, which plays a part in neutralizing organic acids formed by metabolic activities of plants and a structural component of cell walls [29].

Except for comparatively lower total Ca contents in *P. americana, M. indica,* and *C. sinensis,* content recorded in the remaining species of this study was within the range (109 to 361 g kg^{-1}) reported by Etiégni et al. [25], Huang et al. [26], and Górecka et al. [27] among ashes of different woody species.

The total content of K ranged from 64 to 325 g kg^{-1} in *P. dulcis* and *T. cacao,* respectively, with mean overall species of 141 g kg^{-1}. The plant-available K content ranged from 37491 to 88303 mg kg^{-1} in *S. siamea* and *P. americana,* respectively. The mean content of plant-available K in the overall species was 59271 mg kg^{-1}. Except for the higher total content of K in *T. cocoa*, all the studied ashes were within 26 to 122.6 g kg^{-1} recorded by Etiégni et al. [25], Huang et al. [26], and Górecka et al. [27] for ashes of some woody species (e.g., *Quercus spp*., *Betula spp*., and coniferous trees). Considering the level of P in wood ash is comparatively lower than most macroelements (e.g., Ca and Mg), K content is mostly responsible for the positive impact of wood ash applied as fertilizer [16]. Increased availability of K in soil positively affects the growth of plants (volume of plants) after application of ash [30].

Hence, ashes obtained by *P. americana* and *T. cacao* are much suitable to be used as mineral K supplements in soils according to their availability to plants. The lowest releasability of K (24.3 %) was in *T. cacao,* and the highest (88.5 %) in *C. sinensis,* with a mean value overall species of 52.7 %. Based on the releasable fraction of K, ashes of *C. sinensis* (84.3 %) and *P. americana* (88.5 %) are more preferred to ashes of the other species. Generally, the high releasability of K in the ashes relates to its high mobility. Plant-available K in wood ash is relatively similar to K fertilizers [27].

Soil available K levels increase with the application of wood ash, attributed to the release of K by wood ash and also the replacement of K on soil exchange sites by Ca and other exchangeable cations released directly from wood ash into soil suspension [27]. The solubility and availability of macronutrients to plants in wood ashes are high, and K has the highest accumulation compared to Mg, Ca, and P [14]. Since K fertilizers are usually expensive, the ashes from all the studied species can be good alternative sources of mineral K fertilizers for soils with K deficiency. According to this study, high total K is consistent with high ash mass, probably indicating that ash forming material is high in K-rich plants, but this needs further detailed studies.

The lowest content for total Mg (48 g kg^{-1}) was in *C. nitida* and the highest (95 g kg^{-1}) in *T. cacao*. The mean total Mg content in the ashes of the overall species was 71 g kg^{-1}. The total Mg content in this study was comparatively higher than 16 to 26 g kg^{-1} of ashes from different tree species recorded by Etiégni et al. [25], Huang et al. [26], and Górecka et al. [27]. The content of plant-available Mg ranged from 13719 to 29001 mg kg^{-1} in *M. indica* and *T. cacao*, respectively. The mean content of plant-available Mg of the ashes in all the species was 21816 mg kg^{-1}.

The releasability of Mg ranged from 5.2 to 56.8 % in *S. siamea* and *C. nitida,* with a mean value of 26 % for overall species. Considering the high content of plant-available Mg in all the ashes, applying them to Mg deficient arable soils are suitable coupled with a relatively high releasable fraction. However, the ash of *T. cacao* and *C. nitida* is more suitable for plant uptake in Mg-deficient soils due to their comparatively high plant-available content and releasability. Magnesium is a constituent of the chlorophyll, proto chlorophyll, phytin, and pectin required in small quantities during plant metabolic processes [15].

The total S content ranged from 3.3 to 36 g kg^{-1} in *M. indica* and *P. dulcis*. The mean total S in the ashes of the overall species was 9 g kg^{-1}. The relatively low contents of total S indicate high volatility during the combustion process, especially in temperatures > 500°C [7, 11]. If wood ashes of the studied species, consequently applied to arable fields as fertilizer, S and N must be from other sources.

Notably, the total and plant-available Ca, K, and Mg contents were dominant elements in the ashes of studied species (Figs. 1a, b, and Table 3). However, plant-available K and Mg were highest in the ashes of *P. americana* and *T. cacao*, but the total content of both elements was highest in *T. cacao*. For most of the ashes, the content of total Mg was lower compared to total Ca and K. The high pH values of the ashes of this study also were attributed to the high contents of total and plant-available Ca, K, Mg, and Na in the studied ashes.

There was a significant effect of species on the contents of total and plant-available microelements (Mn, Cu, Zn, Na, and Fe; Figs. 3a, b, and Table 3).

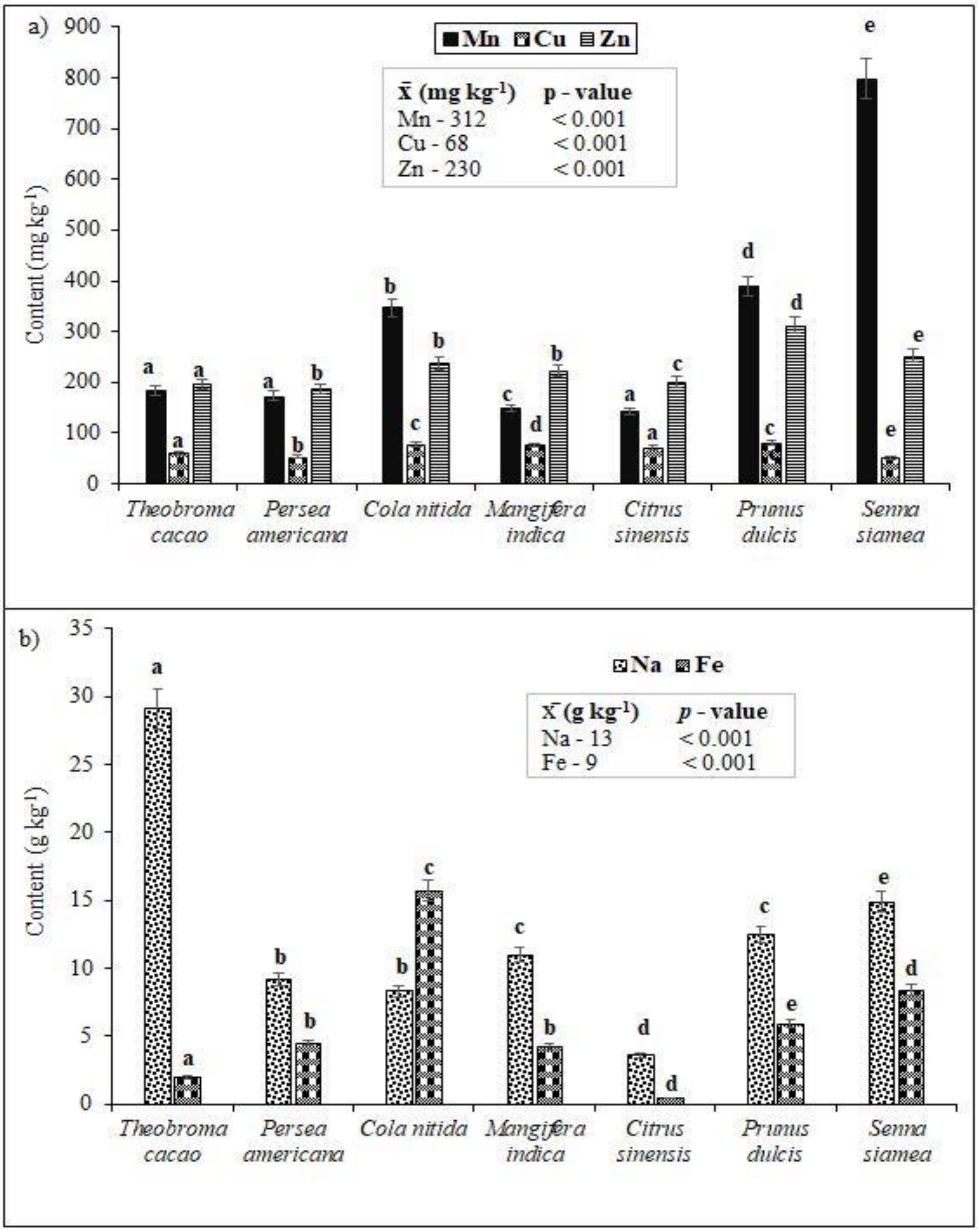


Fig. 3 Total contents (mean ± SE) of (a) Mn, Cu, and Zn and (b) Na and Fe in the ashes of the studied species. The p-values were obtained by one-way ANOVA. Using the Tukey HSD post hoc test, mean values with the same letter relative to other tree species were not significantly different. SE indicates the standard error of the mean. The $\bar{x}$ indicates the overall mean of elements of all species

The lowest content of total Mn (143 mg kg^{-1}) was in *C. sinensis* and the highest (798 mg kg^{-1}) in *S. siamea*. The mean total Mn in the ashes of the overall species was 312 mg kg^{-1}. The lowest plant-available Mn content (75 mg kg^{-1}) was in *C. sinensis*, and the highest (168 mg kg^{-1}) in *C. nitida*. The mean plant-available Mn in the ashes of the overall species was 109 mg kg^{-1}. The releasability of Mn ranged from 17.7 to 55.6% in *S. siamea* and *T. cacao*, respectively. The mean releasability of Mn in all the ashes of the overall species was 43.9%. Ash of *C. nitida* is the most suitable Mn fertilizer for Mn-deficient soils for plant uptake compared to the other ashes resulting from the plant-available content. In the case of the releasable proportion of Mn, ash of *T. cacao* is most suitable. However, over 50% Mn content of all the ashes is releasable to soils. Manganese is vital to plants as a contributor to various biological systems such as photosynthesis, respiration, and nitrogen assimilation, and also involves pollen germination, pollen tube growth, root cell elongation, and resistance to root pathogens [31].

Furthermore, the lowest content of total Cu was in *Senna* (52 mg kg^{-1}) and the highest (81 mg kg^{-1}) in *Prunus*, with mean overall species of 68 mg kg^{-1}. The plant-available Cu content ranged from 40 to 74 mg kg^{-1} in *T. cacao* and *S. siamea*, respectively. The mean plant-available Cu in the ashes of the overall species was 59 mg kg^{-1}. The releasability of Cu ranged from 67.2 to 92.8% in *T. cacao* and *S. siamea*, with a mean value overall the species 0f 80.4%. Generally, Cu has the highest releasability in the studied ashes. The lowest content (188 mg kg^{-1}) of total Zn was in *P. americana* and the highest (312 mg kg^{-1}) in *P. dulcis*, with a mean of overall the species of 230 mg kg^{-1}. The plant-available Zn content ranged from 44 to 91 mg kg^{-1} in *P. americana* and *S. siamea*, respectively. The mean plant-available Zn content in the ashes in the overall species was 75 mg kg^{-1}. The releasability of Zn ranged from 23.5 to 38% in *P. americana* and *T. cacao*. The mean releasability of Zn overall the species was 32.4%. Zinc and Cu are essential microelements that play a vital role in the physiological and metabolic processes of plants but can be harmful when they reach threshold levels [32]. The contents of total Zn and Cu in the ashes were below the world permissible limit in soils - 300 mg kg^{-1} for Zn and 100 mg kg^{-1} for Cu [6]. Although the content of Zn in the ash of *P. dulcis* was slightly higher (312 mg kg^{-1}) than this limit, however, it is suitable for fertilizer according to reported guideline values (about 1200-1500 mg kg^{-1}) for the use of biomass ashes on agricultural soils [33]. Thus, the ashes obtained from the species again are suitable fertilizers for Zn/Cu deficient soils.

The lowest content of total Na (3.6 g kg^{-1}) was in *C. sinensis* and the highest (29 g kg^{-1}) in *T. cacao*, with a mean overall species of 13 g kg^{-1}. Plant-available Na (836 mg kg^{-1}) content was lowest in *C. sinensis* and highest in *P. americana* (6937 mg kg^{-1}). The mean plant-available Na content of the ashes overall species was 2608 mg kg^{-1}. The releasability of Na ranged from 3.2 to 75% in *T. cacao* and *P. americana*, with a mean overall species of 26.8%. Sodium, considered a functional micronutrient, is required for maximal biomass growth for many plants due to its ability to replace K in osmoticium for cell enlargement and as an accompanying cation for long-distance transport [34]. Notably, total and plant-available Na contents are also responsible for the pH range recorded in our study. For example, ash of *C. sinensis* exhibited lower pH compared to all the other ashes, which can relate to its lower Na content. However, the high content of either total or plant-available Na or both significantly corresponds to the high pH in this study.

The mean total Fe content ranged from 0.4 to 16 g kg^{-1} in *C. sinensis* and *C. nitida*, respectively. The mean total Fe of the ashes overall species was 9 g kg^{-1}. The lowest plant-available Fe content was in *T. cacao* (1.5 mg kg^{-1}) and the highest in *Cola* (383 mg kg^{-1}). The mean plant-available Fe content in the ashes overall species was 136 mg kg^{-1}. The releasability of Fe ranged from 0.08 to 3.5% in *T. cacao* and *P. dulcis* with the mean value of overall species of 1.4%. The Fe content in the studied ashes varied significantly with generally low releasability. In plants, Fe plays a critical role in metabolic processes such as DNA synthesis, respiration, and photosynthesis. Moreover, many metabolic pathways often are activated by Fe and components of many vital enzymes, such as cytochromes of the electron transport chain [35].

There was a significant effect of species on the content of total Ni, Cr, Pb, Co, As, Sr, V, and Al in ashes (Figs. 4a and b). There was a significant effect of species on the content of plant-available Ni, Cr, Pb, Co, As, Cd, Sr, and Al in ashes.

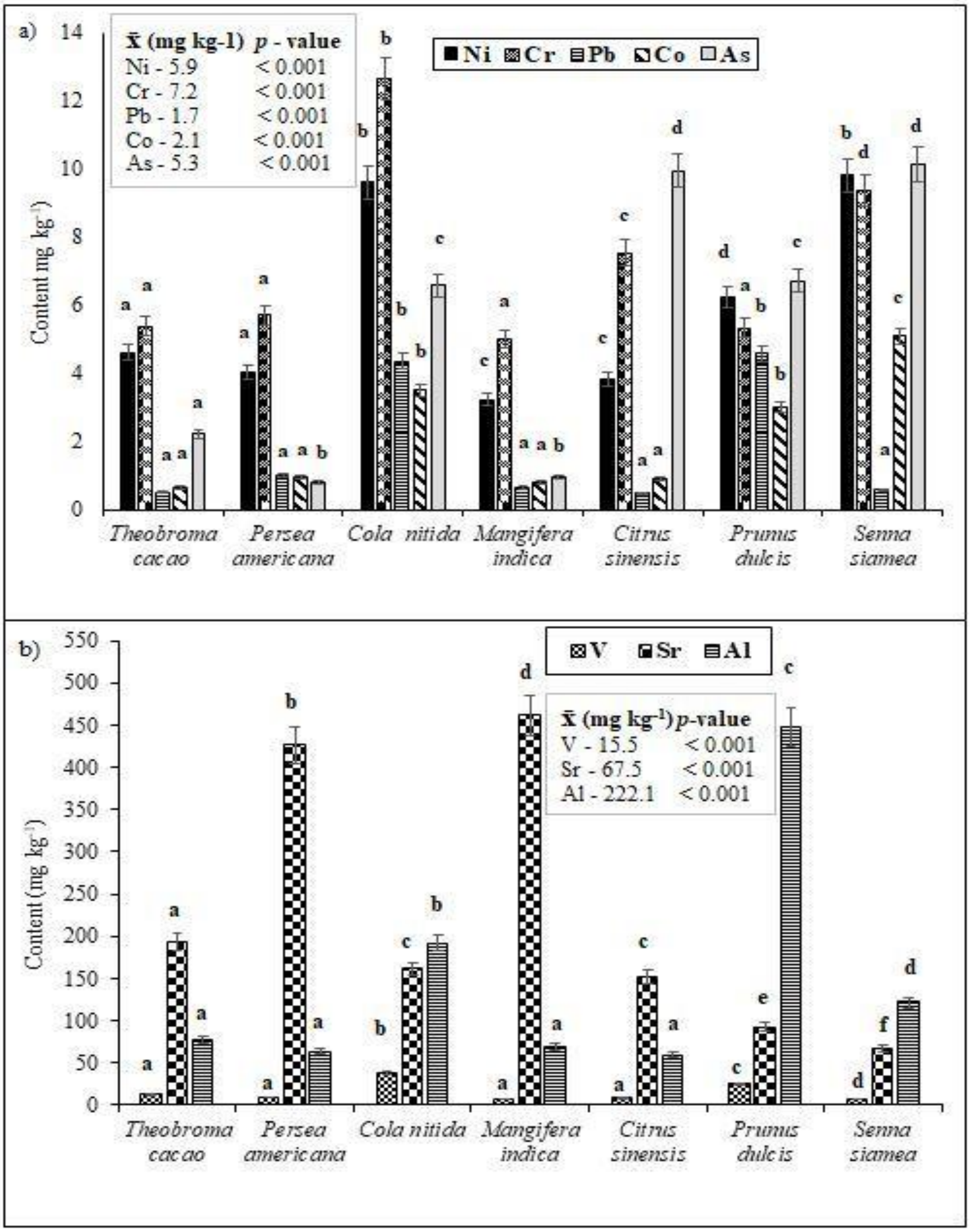


Fig. 4 Total contents (mean ± SE) of a) Ni, Cr, Pb, Co, and As and b) V, Sr, and Al in the ashes of *Theobroma cacao*, *Persea americana*, *Cola nitida*, *Mangifera indica*, *Citrus sinensis*, *Prunus dulcis*, and *Senna siamea*. The p-values obtained by one-way ANOVA. Using the Tukey HSD *post hoc* test, mean values with the same letter relative to other tree species were not significantly different. SE indicates the standard error of the mean. The x̄ indicates the overall mean of elements of all species.

The content of total Cd was above the limit of detection only in *S. siamea* (0.43 ± 0.02 mg kg^{-1}) and *C. nitida* (0.10 ± 0.0 mg kg^{-1}) ashes. The lowest content of total Ni (3.5 mg kg^{-1}) was in *M. indica* and the highest (9.8 mg kg^{-1}) in *S. siamea*. The mean total Ni content of the ashes overall species was 5.9 mg kg^{-1}. The content of plant-available Ni ranged from 0.98 to 4.2 mg kg^{-1} in *C. sinensis* and *P. dulcis.* The mean plant-available Ni content of the ashes overall species was 2.6 mg kg^{-1}. The releasability of Ni ranged from 25.6 to 71.7% in *C. sinensis* and *T. cacao.* The mean releasability of Ni was 44.5%.

The lowest content of total Cr (4.99 mg kg^{-1}) was in *M. indica* and the highest in *C. nitida* (13 mg kg^{-1}). The mean total content of the ashes' overall species was 7.2 mg kg^{-1}. Additionally, plant-available Cr content ranged from 0.2 to 9.7 mg kg^{-1} in *T. cacao* and *P. americana,* respectively. The mean plant-available Cr content in the ashes overall species was 3.9 mg kg^{-1}. The releasability of Cr ranged from 3.7 to 48.1% in *T. cacao* and *M. indica*, with the mean value of the overall species of 35.6%. The lowest content of total Pb (0.47 mg kg^{-1}) was in *C. sinensi* and the highest (4.57 mg kg^{-1}) in *P. dulcis.* Among all the ashes, the mean total content of Pb overall species was 1.7 mg kg^{-1}. The plant-available Pb content ranged from 0.01 to 3.6 mg kg^{-1} in *M. indica* and *T. cacao*. The releasabilty of Pb ranged from 4 to 33.8% in *T. cacao* and *Senna* with a mean value overall species of 20.9%.

The lowest total Co content (0.8 mg kg^{-1}) was in *T. cacao* and the highest (5.1 mg kg^{-1}) in *S. siamea*, with a mean overall species of 2.1 mg kg^{-1}. Content of plant-available Co ranged from 0.22 to 3.4 mg kg^{-1} in *C. sinensis* and *S. siamea* with mean overall species of 1.2 mg kg^{-1}. The lowest releasability of Co (24.4%) was in *C. sinensis* and the highest (74.2%) in *P. americana* with a mean value overall species of 58.5%. The total and plant-available Co were within the range, which could not affect the soil adversely when applied as fertilizer on agricultural soils as Co has both beneficial as well as harmful effects on plants. Cobalt is vital for symbiotic N fixation by legumes and a cofactor of cobalamine (Vitamin B12), which functions as nodule growth [36].

The total content of V ranged from 7.5 to 38 mg kg^{-1} in *M. indica* and *C. nitida*, respectively, with a mean overall species was 16 mg kg^{-1}. The total content of V of our studied ashes was higher than the ashes of many European woody species such as oak, birch, ash, and apple studied by Górecka et al. [27]. However, Kfle et al. [21] recorded a range from 4.9 to 39.7 mg kg^{-1} total V content in the ashes of some tropical tree species relatively similar to the obtained content of V in this study. A low supply of V results in greater plant height, leaves, flowers, and plant mass. However, at high supply, V is harmful to plants as it induces Fe deficiency, a decrease in stems, and root fresh weight [37].

Similarly, the lowest total As content (0.79 mg kg^{-1}) was in *P. americana* and the highest (10.1 mg kg^{-1}) in *S. siamea*. The mean total As of the ashes overall species was 5.3 mg kg^{-1}. Content of plant-available As ranged from 0.01 to 1.3 (mg kg^{-1}) in *C. nitida* and *S. siamea*, respectively, with a mean overall species of 0.4 mg kg^{-1}. The arsenic releasability ranged from 0.2 to 21% in *C. nitida* and *P. americana*, respectively, with a mean overall species of 7.5%.

Contents of total Ni, Cr, Pb, As, and Al in the ashes are lower compared to contents in wood ashes of previous works conducted by Etiégni et al. [25] and Huang et al. [26] as well as Górecka et al. [27], who recorded together with elements mentioned above, higher contents of Cd from the combustion of wood of 14 tree species. In soils, plants can uptake Ni, Cr, Pb, Co, As, V, and Al (potentially toxic elements), which are water-soluble or get easily solubilized by roots [38]. The total and plant-available Ni, Cr, Pb, Co, Cd, As, and Al contents were very low in comparison to permissible levels in soil and plants [6, 39, 40] to render a potential threat to soils and plants. As these elements cannot undergo an easy degradation, when their contents in the soil exceed permissible limits, they adversely affect the plant [41]. High contents of Ni, Cr, Pb, Co, As, V, and Al may lead to the decrease in some vital soil nutrients, organic matter decomposition, and enzymatic activities useful for plant metabolism leading to a decline in plant growth and subsequent death [42]. Moreover, the content of Ni, Pb, As, Al, Co, Cr, and V in the wood ashes was not high enough to contaminate agricultural soils, according to the permissible levels in uncontaminated soils [6, 40, 41].

The content of total Sr ranged from 67 to 461 mg kg^{-1} in *S. siamea* and *M. indica*, respectively, with a mean of 68 mg kg^{-1} overall species. Plant-available Sr content ranged from 32 to 121 mg kg^{-1} in *M. indica* and *S. siamea.* The mean plant-available Sr content in the ashes overall species was 81 mg kg^{-1}. The releasability of Sr ranged from 24.1 to 67.1% in *T. cacao* and *C. nitida*, respectively, with a mean value of 45.3%. Strontium may accumulate in plants [43], and higher plants cannot differentiate between Sr and Ca due to their similar divalent charge and can substitute for each other. Hence, this accounted for the generally high releasability of Sr in the ashes of this study. Wedepohl and Simon [44] and Oroian et al. [45] reported Sr accumulation in biomass ashes.

The lowest content of total Al (60 mg kg^{-1}) was in *C. sinensis* and the highest (448 mg kg^{-1}) in *P. dulcis*. Additionally, the mean total content of Al of all the species was 222 mg kg^{-1}. Plant-available Al ranged from 1.4 to 19.5 mg kg^{-}1, with the highest in *P. americana* and lowest in *T. cacao*. The mean plant-available content of Al in the ashes overall species was 5.6 mg kg^{-1}. The releasability of Al ranged from 0.4 to 24.7% in *P. dulcis* and *P, americana* with the mean value overall species of 7.3%. Although the studied wood ashes have a relatively high total content of elements, the bioavailable fractions (plant-available and releasable content from the total elements) well reflect the fertilizer values.

There was no significant correlation between total and plant-available Ca (r = - 0.25, p = 0.199), Mg (r = - 0.24, p = 0.210), and Na (r = - 0.21, p = 0.279 Table S1) overall species. In contrast, there was significant correlation between total and plant-available P (r = 0.9, p < 0.001; Fig. 5a), K (r = 0.45, p = 0.016; Fig. 5b), Mn (r = 0.65, p < 0.001; Fig. 5c), Cu (r = 0.60, p < 0.001; Fig. 5d), Zn (r = 0.61, p < 0.001; Fig. 6a), and Fe (r = 0.93, p = 0.001; Fig. 6b).

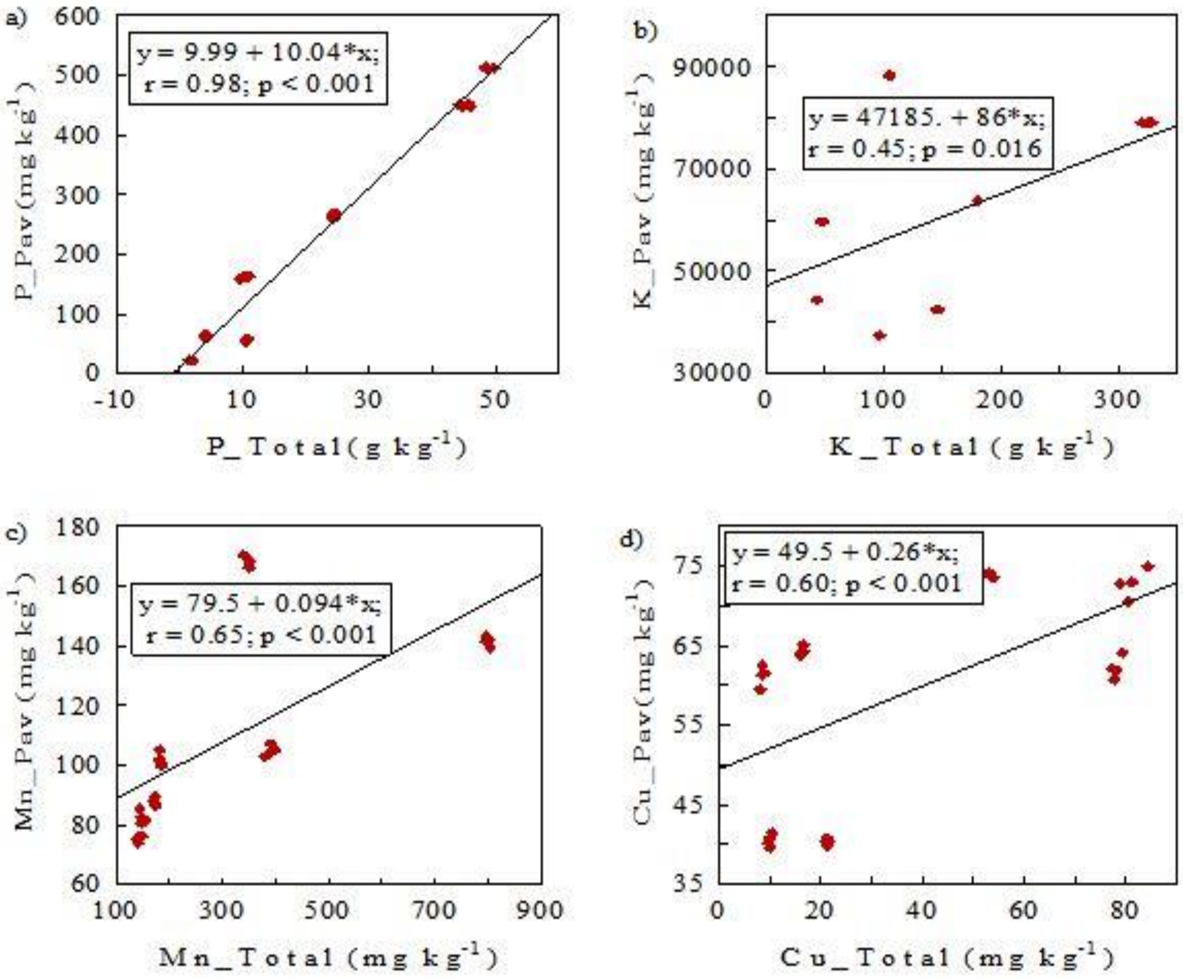


Fig. 5 Relationship between total and plant-available (Pav) a) P, b) Ca, c) K, and d) Mg contents of studied ashes.

The patterns recorded by the total and plant-available elements in this study were different. Generally, the total element contents were higher compared to the plant-available. Except for Ca, Mg, and Na, plant-available P, K, Mn, Cu, Zn, and Fe were a positive linear function of the total contents. Therefore, the available P, K, Mn, Cu, Zn, and Fe increase with their total contents. The message is relevant to farmers in obtaining some knowledge of the content of plant-available elements from the total. However, for other woody species, further research is required.

The relationship between total and plant-available P, Ca, K, Mg, Na, Mn, Fe, Cu, and Zn in the ashes of each species is in Table S2. Except for a significant positive correlation in the total and plant-available Mg ($r = 0.81$, $p = 0.044$) and K ($r = 0.95$, $p = 0.027$) in the ashes of *T. cacao and C. nitida*, respectively, there was either negative or no significant relationship between the other elements in the ashes of *T. cacao, P. americana*, *C. nitida*, *M. indica*, *C. sinensis, P. dulcis,* and *S. siamea*. Additionally, there was a significant positive correlation between the total and plant-available content of P, Ca, Na, Fe, Cu, and Zn in the ash of *M. indica*. Hence, the content of available plant nutrients in the ash of *M. indica* is predictable from the total content. Notably, many elements form complexes at high pH and are not releasable easily. For example, at < pH 7.5, plant-available P can quickly react with Mg, Ca, and other elements to form less soluble compounds [46]. However, this was contrary to the obtained results of the ashes of this study, especially in the case of Ca, K, Mg, Mn, Cu, Zn, Na, and Sr. The releasability and content of plant-available macro, micro, and other trace elements recorded in this study indicate that the ashes of the selected species can be used to improve the nutrient's need for agricultural soils, e.g., arenosols, oxisols, and acrisols with mostly low fertility and high pH [12]. However, the application of these ashes must be applied to soils according to agronomic rates [12].

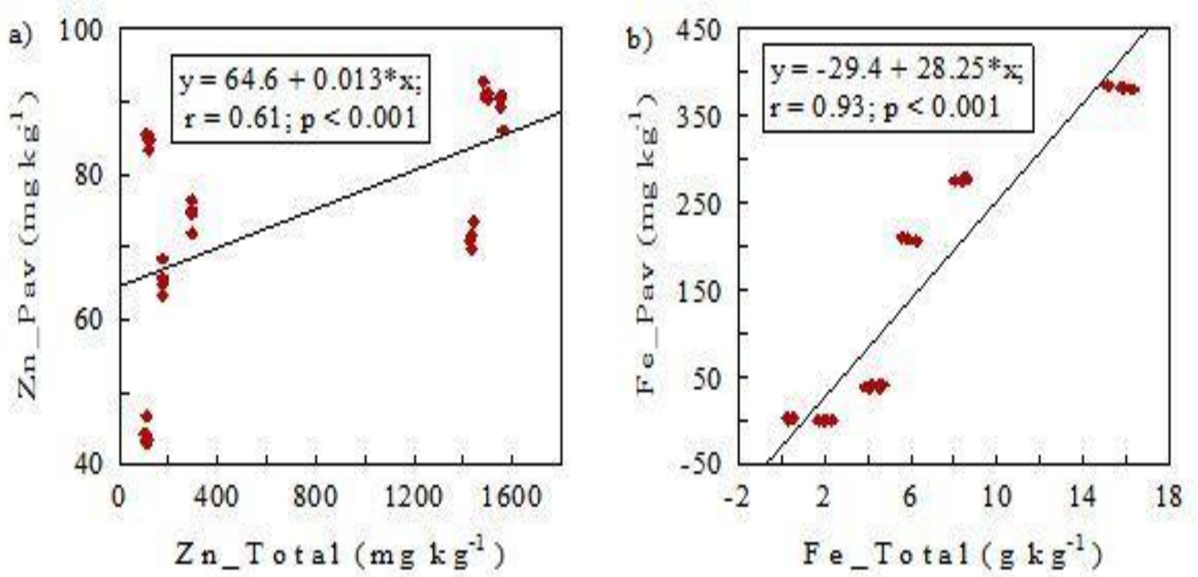


Fig. 6 The relationship between Total and Plant-available (Pav) (a) Mn, (b) Cu, (c) Zn, (d) Na, and (e) Fe contents of studied ashes.

As both extractants in our study were acids, the content of some elements may not be fully recovered due to neutralization, resulting from the reaction of acid and base (ash). For instance, extraction of Mehlich-3 P can decrease with increasing pH potentially due to changing P forms, a partial neutralization of extractant pH, and consumption of extractant fluoride (F^{-}) by non-P-containing Ca minerals [47]. Further research should, therefore, examine different analytical/extraction techniques to maximize the recovery of the content of total and plant-available elements in ashes at pH ≥ 7.

Conclusions

We recorded high pH and high contents of the total (P, Ca, K, Mg, S, Mn, Cu, Zn, Na, Fe, and Sr) and plant-available (P, K, Ca, Mg, Mn, Cu, Zn, Na, Fe, and Sr) elements in the ashes of *T. cacao, P. americana, C. nitida, M. indica*, *C. sinensis*, *P. dulcis,* and *S. siamea*.

The ashes of the studied species are a good source of total and plant-available contents of macro (P, Ca, K, Mg), micro (Mn, Cu, Zn, Na, and Fe), and other elements such as Sr for agricultural soils. Thus, the investigated wood ashes are suitable for soil amendments and as fertilizers, depending on the P, Ca, K, Mg, Mn, Cu, Zn, Na, and Fe needs of agricultural soils.

According to their pH level, the ashes of *C. sinensis, C. nitida, P. americana, M. indica, P. dulcis, S. siamea, and T. cacao* are most suitable to alleviate the different levels of soil acidity in that order. We concluded that the ash of *T. cacao* is considered the most appropriate to amend high soil acidity due to its high ash yield and pH.

All the studied ashes have very high Cu releasability but low P and Fe. Based on the releasability of Ca (*C. sinensis* and *M. indica*) and K (*C. sinensis*, *P. americana*, and *P. dulcis*), ashes of these species are the most suitable fertilizer for agricultural soils. Additionally, the

releasability of Mg (*C. nitida* and *T. cacao*), Mn (*T. cacao, M. indica, P. americana*, and C. *nitida*), Zn (*T. cacao, M. indica, S. siamea*, and C. sinensis), Na (*P. americana* and *M. indica*), and Fe (*P. dulcis* and *S. siamea*) makes the ashes more preferred fertilizers.
The contents of risk elements (Ni, Cr, Co, Pb, Cd, and As) were low and in full compliance with regulatory requirements. The relatively high amounts of plant-available elements and the bioavailable portion of the total content (releasable fractions) well reflect the fertilizer values of the ashes of this study. Multielement analyses of wood ashes can provide reliable inferences in the use of ashes as fertilizers, especially on acidic and low fertility soils for arable purposes.

Credit authorship contribution statement

Study concept and design: [**Michael O. Asare]**; Data acquisition, data analysis, and interpretation of data: **[Michael O. Asare, Jerry Owusu-Afriyie, Michaela Jungová Krbová]**; Obtained funding **[Michal Hejcman, Michaela Jungová Krbová]**; Supervision: **[Michal Hejcman]**.

Declaration of competing interests

The authors have declared no conflict of interest.

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Supplementary material

Can wood ashes of commonly planted tree species in Ghana be applied as fertilizers?

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Table S1. Relationship (Pearson correlation) between total and plant-available Ca, Mg, and Na in selected wood ashes

Parameter	Ca	Mg	Na
Linear equation	y = 15804–156*x	y = 25942–633*x	y = 3511–710*x
corelation coefficient (r)	r = - 0.25	r = - 0.24	r = - 0.21
p-value	0.199	0.21	0.279

Table S2. The relationship (Pearson's correlation) between total and plant-available elements in the ashes of individual species. The bolded r and P values indicate significant positive correlations.

Species	P	Ca	K	Mg	Na	Mn	Fe	Cu	Zn
Theobroma cacao	r = 0.16 p = 0.841	r = - 0.8 p = 0.156	r = - 0.87 p = 0.134	**r = 0.81** **p = 0.044**	r = 0.45 p = 0.550	r = -0.64 p = 0.352	r = -0.44 p = 0.560	r = 0.53 p = 0.467	r = - 0.43 p = 0.610
Persea. Americana	r = 0.80 p = 0.200	r = -0.60 p = 0.396	r = 0.57 p = 0.424	r = 0.4 p = 0.510	r = -0.63 p = 0.369	r = - 0.24 p = 0.754	r = -0.62 p = 0.372	r = 0.17 p = 0.833	r = 0.34 p = 0.660
Cola nitida	r = 0.03 p = 0.966	r = - 0.7 p = 0.249	**r = 0.95** **p = 0.027**	r = - 0.27 p = 0.726	r = - 0.48 p = 0.516	r = - 0.92 p = 0.079	r = - 0.94 p = 0.052	r = 0.85 p = 0.149	r = 0.63 p = 0.360
Mangifera indica	**r = 0.94, p = 0.034**	**r = 0.81** **p = 0.018**	r = - 0.39 p = 0.600	r = 0.17 p = 0.829	**r = 0.71** **p = 0.028**	r = -0.69 p = 0.302	**r = 0.95** **p = 0.041**	**r = 0.84** **p = 0.045**	**r = 0.66,** **p = 0.051**
Citrus sinensis	r = 0.82 p = 0.171	r = 0.16 p = 0.837	r = -0.41 p = 0.593	r = - 0.91 p = 0.083	r = 0.56 p = 0.435	r = 0.88 p = 0.110	r = -0.38 p = 0.615	r = 0.65, p = 0.346	r = -0.92 p = 0.079
Prunus dulcis	r = - 0.50 p = 0.498	r = 0.39 p = 0.603	r = 0.72 p = 0.275	r = - 0.600 p = 0.399	r = 0.81 p = 0. 194	r = 0.65 p = 0.341	r = -0.99 p = 0.001	r = 0.69 p = 0.307	r = 0.80 p = 0.190
Senna siamea	r = 0.22 p = 0.748	r = 0.47 p = 0.524	r = - 0.71 p = 0.292	r = 0.42 p = 0.579	r = - 0.04 p = 0.959	r = -0.89 p = 0.109	r = 0.63 p = 0.361	r = -0.96 p = 0.039	r = - 0.95 p = 0.040

CHAPTER 6

Human burials can affect soil elemental composition for millennia—analysis of necrosols from the Corded Ware Culture graveyard in the Czech Republic

Michael O. Asare[1] & Ladislav Šmejda[1] & Jan Horák[1] & Petr Holodňák[2] & Miroslav Černý[2] & Vilém Pavlů[1] & Michal Hejcman[1]

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From left, Michael O. Asare, next Petr Holodňák, followed by Černý Miroslav, and extreme right Michal Hejcman

Adopted from:

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ORIGINAL PAPER

Human burials can affect soil elemental composition for millennia—analysis of necrosols from the Corded Ware Culture graveyard in the Czech Republic

Michael O. Asare[1] & Ladislav Šmejda[1] & Jan Horák[1] & Petr Holodňák[2] & Miroslav Černý[2] & Vilém Pavlů[1] & Michal Hejcman[1]

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Abstract

How long decomposed buried human bodies affect soil elemental composition is so far not well-known. Using portable X-ray fluorescence spectrometry, we determined the elemental composition of sandy necrosols from a Corded Ware Culture (ca 2800–2500 BCE) graveyard, Chudeřín, Czech Republic. The elemental compositions of soils in the grave infills were studied and compared with arable and subsoil layers. After removal of the arable layer, infills of graves were identified by the black color in contrast with their reddish surroundings. The burials affected the content of elements even after more than 4500 years. Increased C contents compared with arable and subsoil layers were recorded only close to bones. The lowest P content was in grave infill, where soft tissues decomposed, because of P leaching. Therefore, increased P content in the infill of the prehistoric graves mentioned by previous authors is not a reliable indicator of soft tissue decomposition. In the acidic environment, P and Ca released from bones partly fixed in the grave infill ≤ 5 cm to bones. The high contents of P and Ca in bones and soils close to bones were a source of these elements for plants, indicated by a high density of fine roots. The highest contents of trace elements (Mn, Cu, As, and Pb) were in the arable layer because of recent disposition. The most reliable soft tissue decomposition indicator was an increased Zn content in the grave infill. The multi-elemental analyses of prehistoric necrosols were neglected so far and require further detailed research as the chemical signatures are well-preserved for millennia.

Keywords Arenosol · Bones · Carbon · Phosphorus· Portable X-ray fluorescence spectrometry · Zinc

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Introduction

Necrosols are anthropogenic soils commonly found in graveyards and cemeteries. Necrosols are characterized by the presence of human remains and other grave goods together with changed soil stratigraphy, due to the mechanical disturbance of the original soil profile of graves (Bednarek et al. 2004; Amuno and Amuno 2014; Howard 2017). The term necrosol was first introduced by Graf (1986) during his study of vegetation at cemetery in Berlin. So far, necrosols are generally neglected by soil scientists, while published studies emanate only from sub-recent and recent cemeteries or mass graves. These studies were connected with the estimation of time for human body decomposition and re-use of the site for another burial (Sobocká 2004) or with chemical signatures of graves and soil contamination by risk elements (Majgier and Rahmonov 2012; Majgier et al. 2013; Amuno and Amuno 2014). More recently, the analyses of P, Ca, Fe, Cu (Cannell et al. 2018), organic C in necrosols, and lipid variations in decomposed buried human bodies from medieval cemeteries also studied by Burns et al. (2017) and Pickering et al. (2018).

According to our knowledge, prehistoric necrosols have so far not examined for their multi-elemental composition. The only exception is the analysis of P content in the infill of graves to determine whether there was (1) burial of the whole body, (2) burial of only bones, or (3) burial with no human remains in a Kenotaf ritual grave (Holliday and Gartner 2007; Ernée and Majer 2009; Hlavica et al. 2011; Limburský 2015). However, there are no records of whether higher P found in necrosols was the result of the decomposition of the soft tissues, bones, or both. The use of P content in grave infills to determine soft tissue decomposition is an unreliable indicator owing to post-depositional soil-forming processes, e.g., podzolization, gleying, and leaching, which influence its retention and distribution (Pierce et al. 1998). Hence, the content of other elements should be studied to determine those more suitable to indicate human body decomposition, even after thousands of years for archeological prospection.

Moreover, it is necessary to examine the elemental composition not only of the grave infill but also of surrounding soils to know the elemental composition within the soil profile from the arable layers up to layers below the grave. Such knowledge is useful in the determination of movement and leaching of elements in the undisturbed control soil and graves profiles. Thus, making it easy to estimate the level of enrichment factors and depletion of elements in graves. Moreover, the analysis of preserved bones is pertinent to identify whether there was the release of Ca, P, and others into the grave infill.

Notably, Ca and P signatures from bone weathering and decomposition are higher in comparison with that of soft tissues because 99% of Ca and 80% of P in the human body are in bones (McCawley and McKerrell 1971; Mann and Truswell 2002). Although such a sampling strategy is necessary to make reliable conclusions about the extent of accumulation of elements in the soil, detailed multi-elemental studies analyzing the elemental composition of prehistoric necrosols are not well known.

Additionally, the mineralogical and particle size analyses of the soil and sediments are pertinent to provide additional information on whether the accumulation of elements results mainly from human body decomposition as well as retention and leaching. For example, argillaceous minerals contain clay, which can chemically comprise of metal oxides and aluminium silicate–containing minerals and other elements due to its absorptive capabilities (Heckroodt 1991; Tong 2000).

The body of an adult man of 70 kg contains approximately 50 L of H2O (71%), (in grams) 16,000 C, 1800 N, 1100 Ca, 500 P, 140 S, 140 K, 100 Na, 95 Cl, 19 Mg, 4.2 Fe, 2–3 Zn, 0.1–0.6 Cu, 0.68 Rb, 0.32 Sr, and 0.012 Mn (Dent and Knight 1998; Ucisik and Rushbrook 1998; Mann and Truswell 2002; Anne Marie 2019). Elements associated particularly with soft tissues are C, S, N, K, and Zn (Mann and Truswell 2002). The content of C, S, and N can be lost quickly through gas emissions or leached with K from the grave infill after soft tissue decomposition (McCawley and McKerrell 1971; Ucisik and Rushbrook 1998; Spongberg and Becks 2000; Jonker and Olivier 2012). Therefore, we hypothesize that Zn is the element whose content would still be higher in the grave infill after soft tissue decomposition even after thousands of years. The hypothesis stems from previous knowledge that Zn is present in tissues, with high contents in archeological sites, even after thousands of years of abandonment (Šmejda et al. 2017). To test this hypothesis that Zn can be a useful indicator of soft tissue decomposition, as well as the effect of buried human bodies decomposition on the elemental composition of soils, we analyzed necrosols from the Corded Ware Culture (CWC) graveyard, Chudeřín, Czech Republic. Upon rescue excavation on the foreland of an expanding gravel sand mining area, all the graves were discovered.

The establishment of the CWC was related to the largescale migration event of the Yamnaya people from the Pontic-Caspian steppe region into Central Europe (Furholt 2003; Kristiansen et al. 2017; Furholt 2019). The nutrition of the CWC people was based primarily on meat and dairy products as well as fish and seeds from wild plants (Kolář et al. 2012; Sjögren et al. 2016; Piličiauskas et al. 2018). During the era of CWC (ca 2900–2500 BCE), people placed burials into shallow pits cut into the ground and covered by earthen mounds. A single un-cremated individual usually is buried in the pit grave (Kolář et al. 2012; Furholt 2019). Women were buried in the crouched position with the head oriented toward the east and laid on the left side, with males facing west and laid on the right side (Furholt 2019). Pottery vessels in the shape of beakers decorated with cord imprints were the most common burial goods.

In this study, we performed a multi-elemental analysis of prehistoric necrosols using the portable X-Ray fluorescence spectrometry (pXRF). Generally, the use of X-Ray fluorescence spectrometry in the analysis of soils is relatively new, especially in archaeology. However, it has been in use in the last decades for environmental monitoring (e.g., Kalnicky and Singhvi 2001; Ulmanu et al. 2011; Parsons et al. 2012), but it is still experimental to some degree, and the instrument methodologically contested (Speakman and Shackley 2013). That said, it is increasingly becoming established as an efficient and effective means of analyzing the total contents of multiple elements with minimal sample preparation. The use of the pxrf is supported widely by a rapidly increasing volume of published studies on archeological and agricultural soils (Gauss et al. 2013; Grattan et al. 2014; Šmejda et al. 2017), as well as the elemental components of various biological samples, such as bones (Gonzalez-Rodriguez and Fowler 2013; Nganvongpanit et al. 2016). In this exploratory research, we aimed to determine the extent to which buried human bodies affect the elemental content (especially C, P, and Ca) of necrosols and whether the effects are visible even after several thousands of years.

In an attempt to answer unresolved questions on which elements are more suitable to indicate the decomposition of soft tissue and bone in an archeological perspective, we asked the following questions: (1) Is the increased P content in the grave infill a good indicator for soft tissue decomposition? (2) Can the content of Zn in the grave infill be used as a better indicator for soft tissue decomposition in comparison with P?

Materials and methods

Study site

The Corded Ware Culture (ca 2800–2500 BCE, Dobeš and Limburský 2013; Neustupný 2013) graveyard studied was in Chudeřín village (50° 19′ 48″ N, 13° 32′ 40″ E) near Žatec, 80 km west of Prague, Czech Republic (Fig. 1a; Municipal Authority Žatec 2020). The altitude of the study site is 233 m. asl. The average annual temperature and precipitation are 7.8 °C and 559 mm, respectively (Czech Hydrometeorological Institute 2020). The study site is on the Pleistocene sandy-gravel terrace of the Ohře (Eger) River mined for sand and gravels. The area of the graveyards excavated in 2017 was approximately 1 ha (Fig. 1b). The soil of the study site was Arenosol (syn. Arenic regozem). The area previously was used as arable land for crop production before the start of rescue excavations in the foreland of the sand and gravel mining area (Regional museum KA Polánka 2016).

Archeological excavations

We discovered the graveyard after the removal of the arable layer and individual graves identified as black stains in comparison with the reddish sandy-gravel background (Figs. 2 and 3). The study site is characterized by a long-term archeological research project ongoing for 30 years, according to the progress of sand and gravel mining. The archeological research carried out under the supervision of Petr Holodňák from the Regional Museum of K. A. Polánka in Žatec, unearthed 64 features during the excavations in 2017. From this, we determined that 17 features were graves (archeological features marked in Fig. 1b).
We selected 12 graves for further analysis with high reliability according to the presence of human bones or vessels or both found in graves (see Table 1 for the description of individual graves). Except for grave number 43, which, according to the type of pottery identified, indicated a grave from Funnel Beaker Culture (3800–3400 BCE; Table 1, Fig. 2c and d), all analyzed graves identified as graves of CWC.

Sampling design

We applied a specific sampling design to cover the variability of soils and sediments of the arable and subsoil layers within the graveyard and compared them with necrosols in the grave infills (see Table 2 for detailed stratification of the soil layers). We sampled soils and sediments from 0 to 0.5 m (arable layer) up to 5.4-m depths of the graveyard. The sampling of the grave infills was based on the physical characteristics of the soil layers and identified artifacts. We collected five mixed samples, each from the arable layer and the subsoil layer representing exactly 0.5-m depth, exposed after removal of the arable layer. In this case, we used the samples from the subsoil layer as the control, collected from the same depth of discovered graves (Table 2). The control soils, in this case, were compared with the grave infills for their elemental composition. Furthermore, we collected 12 mixed samples from the grave infills > 5 cm from the bones and five from ≤ 5 cm from the bones. Five samples inside the identified pots/vessels (pot infills) in the graves were collected. We also collected five mixed-soil samples, each from the clay layer and grave bedrock (layers below human bones). Five mixed-soil and sediment samples additionally were collected from the layers below grave bedrock (numbers 57–61). We collected all mixed samples as an accepted procedure to eliminate outliers making the generation of the results more reliable. In total, we collected 47 soil and sediment samples for further analysis.

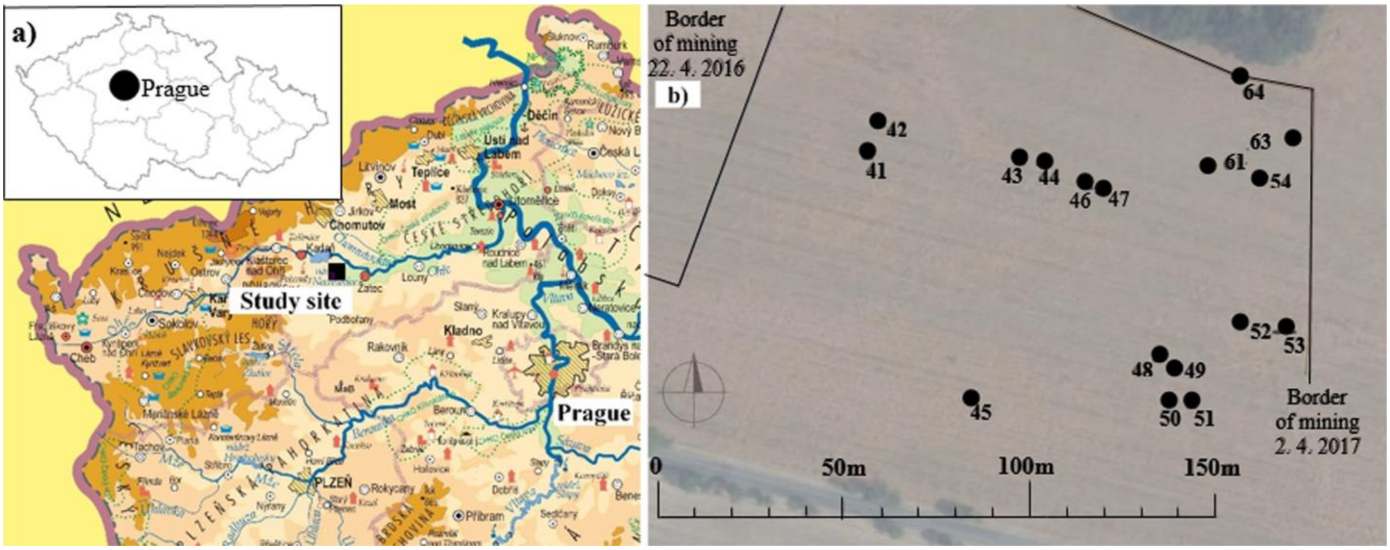

Fig. 1 a Location of the study site Chudeřín within the Czech Republic and b the position of individual graves with their numbers within the study site before removal of the arable layer. The archeological features with numbers 47, 48, 52, 54, and 63 were omitted from the analysis because we were unsure whether they represented graves.

Fig. 2 Graves 41, 43, and 46 before excavation after removal of the arable layer (a, c, and e) and after excavation (b, d, and f). b The single grave with one complete well-preserved skeleton and with one partly preserved skeleton (only legs preserved), d the grave showing two complete vessels with no bones, reflecting the marks of secondary manipulation, and f the grave with the skeleton of one person from which only the femur, tibia, and fibula poorly preserved.

Analytical and statistical methods

All the soil samples were air-dried and subsequently, oven-dried at 40 °C for 24 h. Plant residues, pebbles, and other organic materials in the soil samples were carefully separated. The soil samples after manual grinding in a porcelain mortar, subsequently homogenized by passing through a 2-mm sieve.

The total element contents in the soil samples were determined with pXRF analyzer- Delta Professional, by Olympus InnovX (Waltham, MA, USA), calibrated in soil Geochem mode. In this case, the measurements were performed over 1 min, with 30 s each for 10-kV and 40-kV beams. Each measured sample was in triplicate, and the final value is the arithmetic average. The pXRF detects the total or near-total contents of elements (Magnesium up to Uranium) in the matrix (Kalnicky and Singhvi 2001; Canti and Huisman 2015; Hunt and Speakman 2015; Šmejda et al. 2017). The quality of the pXRF measurements successfully tested by BAS Rudice Ltd. Czech Republic (https://www.bas.cz/) on 55 reference materials (e.g., SRM 2709a, 2710a, 2711a, OREAS 161, 164, 166, RTC 405, 408). We used Quality Assurance Material (QCM: matrenal 31 n = 7, clayey-loam soil, Analytika Ltd., Czech Republic) certified for the contents of several metals (Cr, Mn, Ni, Cu, Zn, As, Cd, and Pb) for calibration of the pXRF for each element. We digested the QCM by the total chemical extraction procedure (International Organization for Standardization. 2012. ISO 12914:2012 Soil quality – Microwave-assisted extraction of the aqua regia soluble fraction for the determination of elements), and their contents obtained by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700×, Agilent Teachnologies Inc., Santa Clara, CA, USA). The calibration curves for each element (Figs. S1 and S2) revealed a significant correlation for all the elements ($r > 0.8$, $p < 0.05$). The recovery (mean value of element ÷ reference value × 100), according to Eurachem (Magnusson and Qrnemark 2014), was > 85% (Table S1).

We determined the total element contents in three bones samples from the graves with pXRF (Gonzalez-Rodriguez and Fowler 2013; Buddhachat et al. 2016; Nganvongpanit et al. 2016). For this purpose, the pXRF was in the mining plus mode. Each bone sample was carefully placed directly in contact with the puncture-resistant window of the pXRF to limit the distance between the detector and samples. The pXRF uses two excitation X-ray beams whose duration can be modified based on the analytical requirements. To achieve better resolution of the spectral peaks, which in turn could result in decreasing detection limits of the elements, the duration of the excitation time was increased to 120 s in the case of the elemental analysis of the bone samples. We measured each bone thrice, and the final values represent the arithmetic mean.

In all, we measured 38 elements, as this was the setting of the measuring device. The contents P, K, Ca, Fe, Mn, Al, Si, Cu, Zn, Sr, Rb, As, and Pb were considered pertinent in our study as they were above the detection limits. The contents of some elements were omitted from further analysis as they were below the limit of detection or detected only in few cases. The content of P in the soil was two cases (in the pot infill) under detection limit—missing values replaced with ½ of the detection limit.

The content of organic C in all the soil samples was measured using a Primacs SNC-100 Carbon/Nitrogen analyser produced by Skalar Analytical, Breda, Netherlands, successfully used for the analyses of archeological soils (Asare et al. 2020). We determined the pH (H2O) of the soil samples at ratio 1:1 (soil/water) using a Voltcraft PH- 100 ATC pH meter (pH 212) produced by I & CS spol s r.o., Třebíč, Czech Republic.

For soil elemental analysis, the pXRF results are influenced by matrix effects such as density, porosity, and grain size (Kalnicky and Singhvi 2001; Newlander et al. 2015).

Therefore, the reliability of data obtained by pXRF was assessed by randomly selecting five homogenized soil samples ($n = 5$). We then extracted the samples by Aqua regia (International Organization for Standardization USEPA 3052), and the total content of the elements determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent technologies incorporation, Waltham, MA, USA) in an accredited laboratory. Except for Rb and Si (not fully soluble in Aqua regia), we compared data for all analyzed elements obtained by both methods. The comparison of the results obtained from the pXRF and Aqua regia ICPOES revealed a stronger linear relationship among the elements ($r > 0.97$ for P, Fe, and Zn at

$p < 0.01$ and $r > 0.8$ for K, Ca, Mn, Cu, As, Sr, and Pb at $p < 0.05$), except for Al ($r = 0.30$, $p = 0.62$) (Figs. S3 – S5). Based on the obtained results, we concluded that pXRF data were of adequate precision for this study and suitable for the tracing of geochemical signatures in archeological localities (Hayes 2013; Frahm et al. 2016; Šmejda et al. 2018).

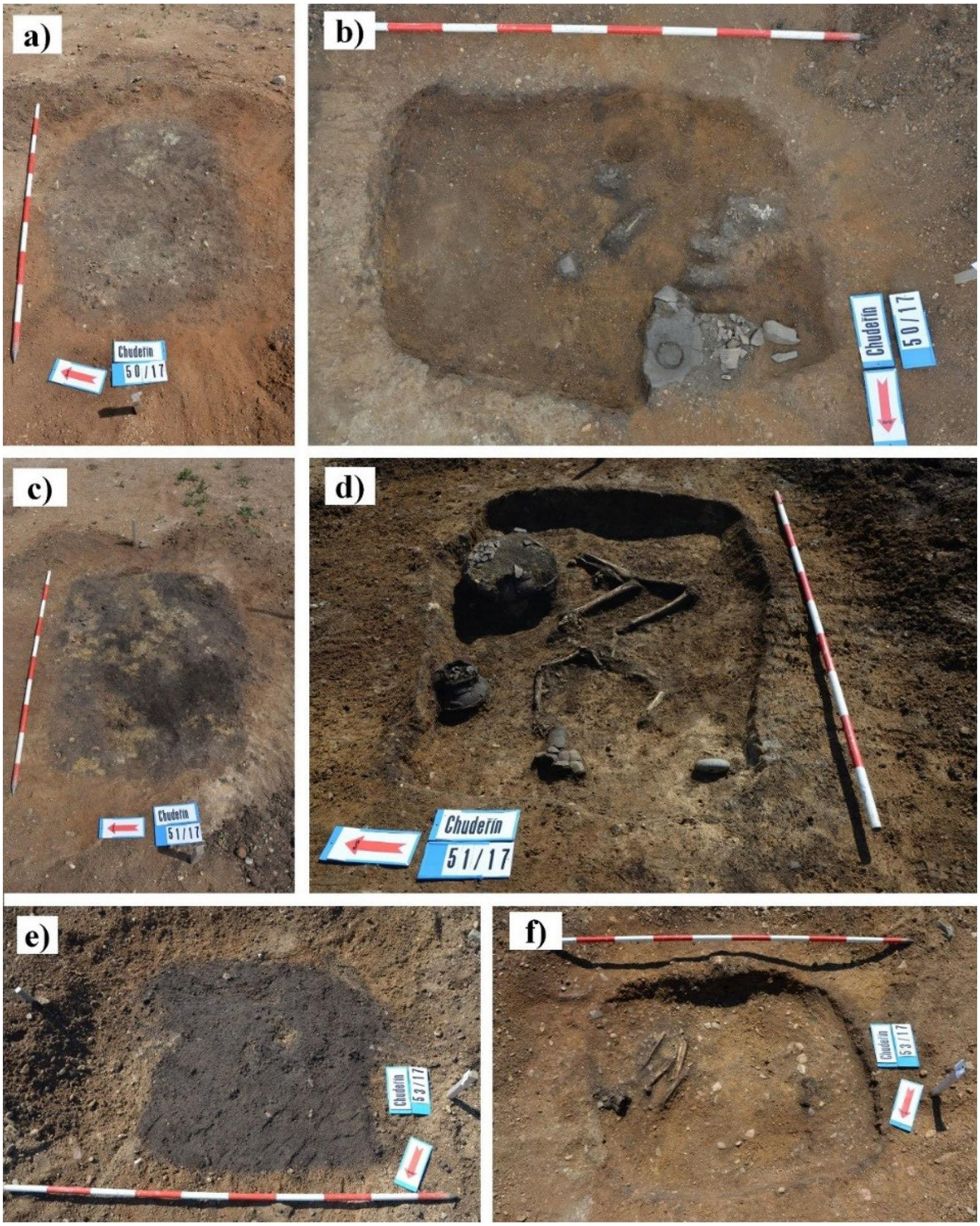

Fig. 3 Graves 50, 51, and 53 before excavation after removal of the arable layer (a, c, and e) and the same graves after excavation with recorded skeleton fragments and vessels. Yellow clay admixture is easily visible in the infill of grave 51 (c). b Grave with micro-remains of bones (part of the skull and a pelvic bone) and one vessel, d the grave with a preserved bone of the body and a fully decomposed skull, and f the grave with not well-preserved bones (tibia and fibula).

Table 1. Description of individual graves. Grave numbers are following Figures 1b, 2, and 3

Grave No.	Description
41	Well-preserved complete skeleton and the bottom of another preserved skeleton
42	Grave with poorly preserved bones and fragments of vessel
43	Grave with no bones with two complete vessels
44	Grave with fragments of vessel but without bones
45	Micro-remains of bones, whetstone and without vessel
46	Grave with femur, tibia, and poorly preserved Fibula
49	Grave with poorly preserved micro-remains of bones
50	Grave with a pelvic bone and part of skull
51	Presence of a complete skeleton without the skull
53	Grave with tibia and fibula
54	Grave with two complete vessels without bones
64	Grave with poorly preserved micro bones

Table 2 Stratification of soil and sediment layers and a brief description

Soil layers	Depths	Pedo-features
Arable layer	0–0.5	Rounded sandy brown sediment
Subsoil layer	0.5	Sub rounded sandy-gravel reddish sediment
Grave infill >5 cm to bones	0.5–0.7	Relatively subrounded sandy black humus-rich sediment
Grave infill ≤ 5 cm to bones	0.5–0.7	Relatively subrounded sandy black humus-rich sediment.
Pot infill	0.7	Complex microstructure, partly subrounded sandy black humus-rich sediment attached to bones
Grave clay	0.5–0.7	Fine-grain white clay sediment with high sphericity
Grave bedrock	0.5–0.9	Coarse subrounded sandy sediment
Layers below grave bedrock (sample no.)		
57	0.9–1.4	Subrounded sandy sediment
58	1.4–2.4	Subrounded gravel sediment
59	2.4–3.4	Subrounded sandy-gravel sediment
60	3.4–4.4	Mostly subrounded grain sandy sediment
61	4.4–5.4	Very coarse and mostly subangular blocky gravel sandy sediment

Grain size distribution and mineralogical analysis

Of all the soil samples, we analyzed 10 g from each layer for the determination of the grain size with 2-, 1-, 0.5-, and 0.25- mm sieves following Motsara and Roy (2008). For the analysis of the mineralogical phase of the soil samples, we used the X-ray diffraction (XRD). Firstly, 0.5 g homogenized soil samples from each layer were pressed into sample holders for XRD analysis. A D8 ADVANCE diffractometer (Cu-Kα radiation, wavelength $\lambda = 1.54178$ Å) manufactured by Bruker AXS, Germany, was used to determine the mineral composition. The operating conditions of the XRD analyzer were as follows: goniometer step size 0.02°, time speed 1 s/step between 2 and 65° 2θ. The pattern smoothing and background subtraction additionally were performed with the Diffrac-Plus EVA software package (Bruker AXS, Germany). And the XRD patterns were simulated with the Diffrac-Plus Topas (Bruker AXS, Germany). The peak heights and reflecting powers, according to Cook et al. (1975), were used to quantify the different mineral phases detected.

Data analysis

Differences in the elemental contents in the soil samples from the different layers initially evaluated using the nonparametric one-way ANOVA on ranks (Kruskal-Wallis test).

We used the non-parametric Kruskal Wallis test as most of the elements were not normally distributed. In the case of a significant result, we used a post hoc rank test. As the bones had very different elemental compositions compared with soils and sediments, we excluded them from the statistical analysis. In the case of the relationship between the pH and elements, we used the Spearman correlations. We performed all statistical analyses using STATISTICA 31.3 (www.statsoft.oi).

Results

The grain sizes of the samples were mostly coarse, which can support the leaching of many elements. The highest fractions of 1–0.5-mm, 1–0.5-mm, and < 0.25-mm grains were in the arable layer up to grave bedrock compared with the layers below grave bedrock. The fraction of skeleton grains (≥ 2 mm) was highest in the layers below grave bedrock compared with all the other layers. Primarily all the soil samples were of six mineral components: K-feldspar ($KAlSi_3O_8$), ilmenite ($FeTiO_3$), goethite (α- FeO (OH)), aluminosilicate (Al_2SiO_5), kaolinite ($Al_2Si_2O_5(OH)_4$), and granite (Table 4). The results show that the mineral characteristics change with grain size in the layers.

All the layers had primary minerals containing silicates and oxides of iron, which are ubiquitous minerals, resistant to weathering, and promote the dissolution of other minerals.

Except for the arable and subsoil layers, feldspar was interstratified only in all layers, with a trace amount of granite below the grave bedrock. The $Al2SiO_5$ content varied between 1 and 19% and decreased with increasing particle size. Of all the analyzed elements, organic C and total P, K, Ca, Fe, Mn, Zn, Cu, Al, Si, Sr, Rb, As, and Pb were pertinent in this study (Figs. 4, 5, 6, 7, and 8 and Table S2).

The content of P, K, Ca, Fe, Mn, Zn, Cu, Al, Si, Sr, Rb, As, and Pb in the preserved bones presented in Fig. 4. There was a significant effect of the soil layers on the pH and content of all analyzed elements (Figs. 5, 6, 7, and 8). There was an acidic reaction (5–5.5) from the arable layer up to the grave bedrock except for moderately acidic (5.8) in the subsoil layer, which can result in the retention of elements. Within the grave infills, the content of organic C was marginally higher only in the infill ≤ 5 cm to bones compared with the arable and subsoil layers. The content of P was significantly higher (1.7 ± 0.6%) in the infill ≤ 5 cm to bones in comparison with the arable (0.16 ± 0.03%), subsoil (0.18 ± 0.02%), and all other layers of the grave infill (0.01 ± 0.002 to 0.15 ± 0.05%), with 6.4 ± 1.4% in the bone. The content of K was similar in all the analysed layers but relatively higher in the arable layer (1.7 ± 0.1%) and both grave infill > 5 cm to bones and pot infill (1.6% for both). The content of K in the bone was lower (0.7 ± 0.1%) compared with values in the soils. Additionally, Ca content was significantly higher (3.8 ± 1.0%) in the infill ≤5 cm to bones compared with all the other layers (0.3 ± 0.01 to 2.6 ± 0.6%), with 19.1 ± 2.5% Ca in the bone. There was significantly lower content (2.7 ± 0.1%) of Fe in the infill ≤ 5 cm to bones compared with the other soil layers.

However, Fe content was relatively similar in the arable and subsoil layers, as well as the grave bedrock. The Fe content was 2.3 ± 0.2% in the bone. Except for pot infill and grave clay, there was no difference in the contents of Mn in all the layers.

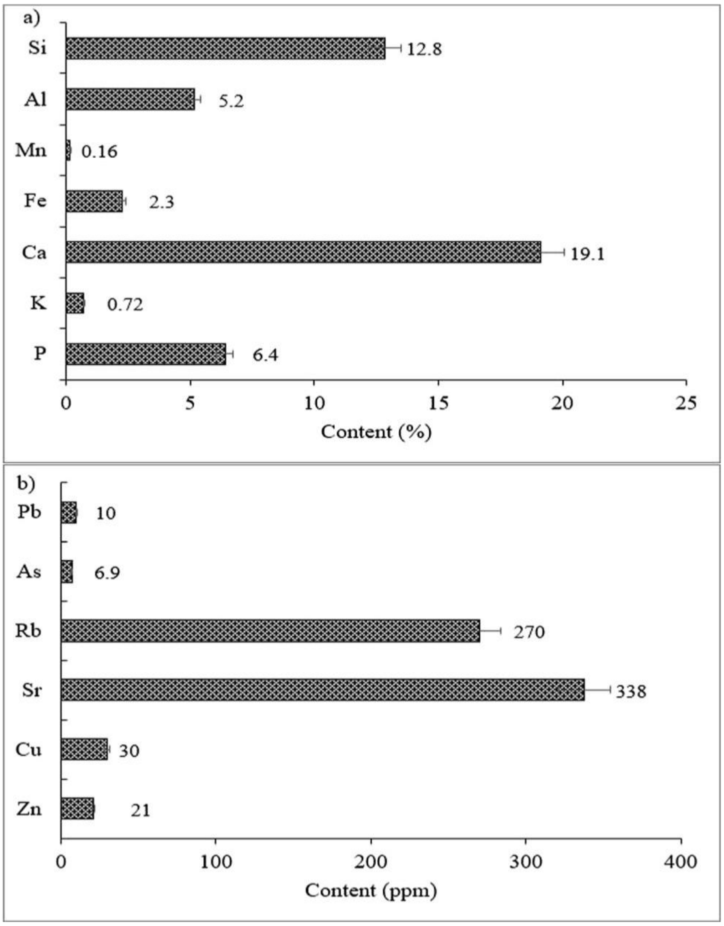

Fig. 4 Mean content of studied elements in a percentage (%) and b ppm in preserved human bones from the Corded Ware Culture grave.

The content of Al was significantly lower in the infill ≤ 5 cm to bones in comparison with other layers of the grave infill and the arable and subsoil layers. The content of Zn was significantly higher (100 ± 3.9 ppm) in the infill ≤5 cm to bones compared with all the other soil layers (62 ± 3.0 to 83 ± 2.5 ppm). The contents of As and Pb were significantly higher in the arable layer compared with values in the subsoil and layers within the grave.

In comparison with the subsoil layer, the contents of P, Ca, and Zn were approximately 9.4, 1.5, and 1.6 times, respectively, higher in the infill ≤ 5 cm to bones.

The content of Fe, Al, Si, Zn, Cu, Sr, Rb, As, and Pb was higher in the soil from all the layers compared with the bones and vice versa in the case of P, Ca, and Mn. There were increases in P, Ca, Fe, Cu, Sr, Rb, As, and Pb contents with increasing depth from 0.9 to 5.4 m. We recorded no pattern of changes in the contents of C, K, Zn, Al, and Si with depth (Table 5). Except for P ($p = 0.01$) and Ca ($p < 0.01$), there was no significant correlation between pH and the content of C and Zn (Fig. 9). There was a negative correlation ($r = -0.15$, $p = 0.34$) between pH and the content of Zn

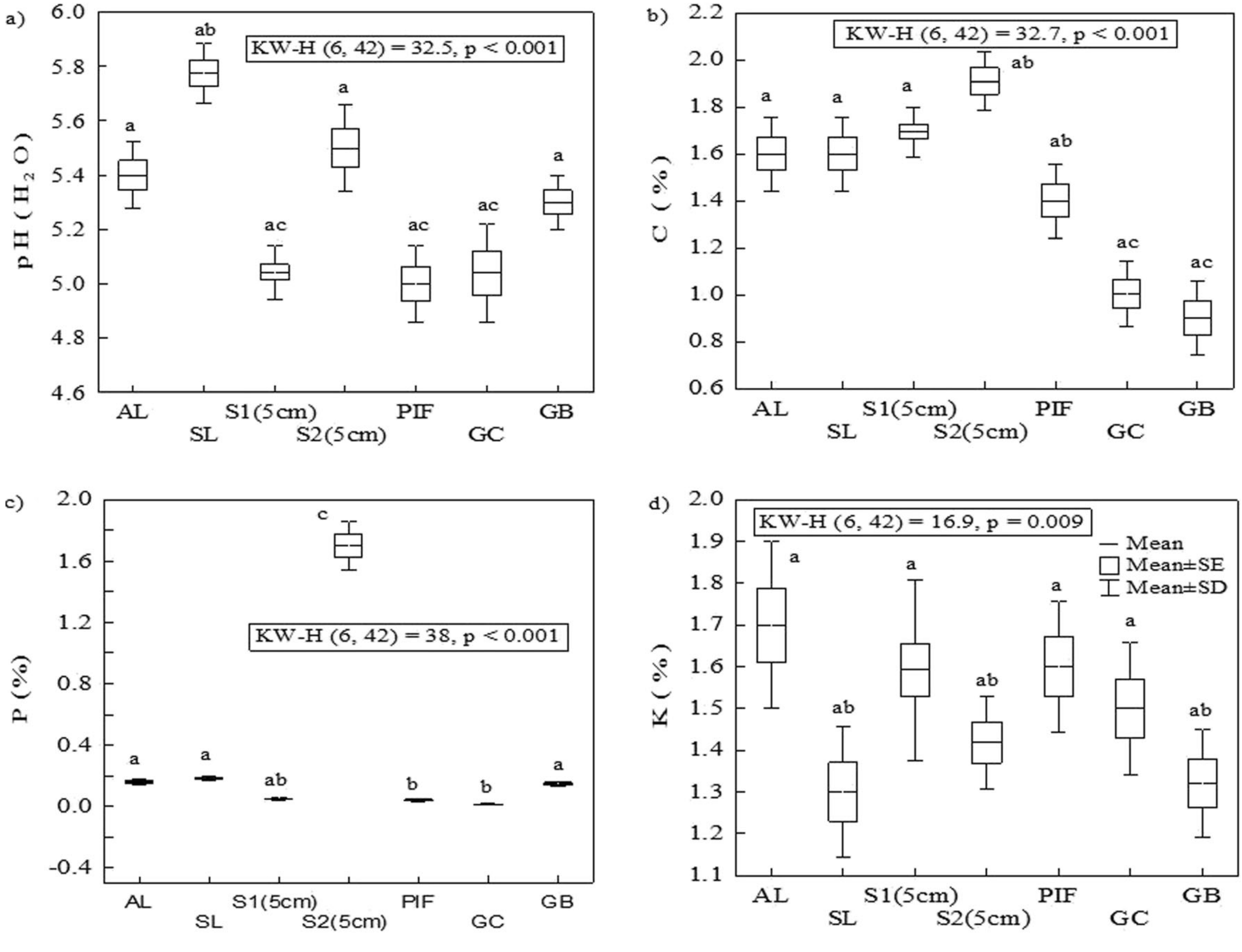

Fig. 5 Effect of different environments on a pH and content of b organic C, c P, and d K in the graveyard. AL, arable layer; SL, subsoil layer; S1(5 cm), grave infill > 5 cm to bones; S2(5 cm), grave infill ≤5 cm to bones; PIF, pot Infill; GC, grave clay; and GB, grave bedrock. Using the Kruskal-Wallis mean rank test, mean values with different letters were significantly different.

Discussion

The main finding of this study was that prehistoric burial activity substantially changed the elemental composition of the soil, well-preserved for thousands of years. Although the human body with a live weight of 70 kg contains 16 kg of C, the increased C content was only in the grave infill ≤5 cm to bones. Thus, the majority of C from the decomposed bodies were leached or lost in the form of gases and are not reliable indicators of soft tissue decomposition over time.

The soft tissues of the human bodies had decomposed in the graves, as indicated by typical black stain (silhouettes) of the grave infill caused by ferrous sulfide produced during anaerobic decomposition (Dent et al. 2004) and by the anatomical position of the remaining preserved bones (Figs. 2 and 3). However, there was low P content in the grave infill > 5 cm from bones. Despite decomposition, there was a depletion of P (P content 0.05%) in comparison with the control soil (0.16%of P), not an accumulation. One possible explanation is the leaching of P. During body decomposition, there is the release of organic acids, and the human body contains 71% of H_20, which contributed to the relatively increased acidity of the grave infills. Furthermore, the mechanical disturbance of the soils in the graves supports the preferential gravitational flow of precipitation water and other fluids.

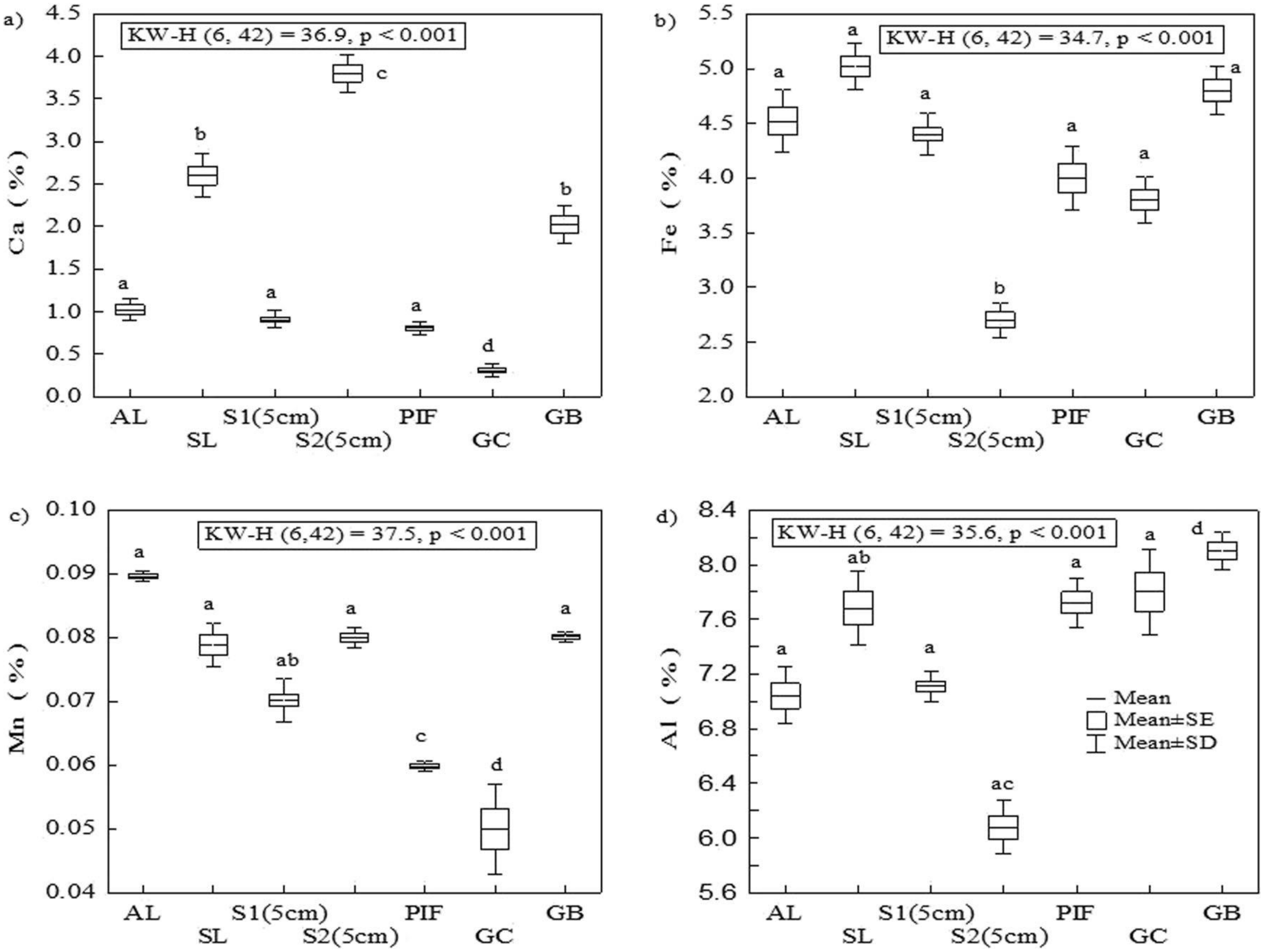

Fig. 6 Effect of different environments on the content of a Ca, b Fe, c Mn, and d Al in the graveyard. AL, arable layer; SL, subsoil layer; S1(5cm), grave infill > 5 cm to bones; S2(5cm), grave infill ≤5 cm to bones; PIF, pot Infill, GC, grave clay, and GB, grave bedrock. Using the Kruskal-Wallis mean rank test, mean values with different letters were significantly different.

The decomposition of a human body can increase the solubility of P hence contributed to its leaching. Sandy soils in the study area are also known for their low P retention capacity, and P-leached from them after several decades (Crowther 2002), evident in the high proportion of coarse sand particles (Table 3). Moreover, a human body with a 70-kg live weight contains 0.5 kg of P, and from this amount, only 0.1 kg P (20% of P) is in soft tissues. In this study, the dead bodies from visual evidence reflect laying in crouched positions. If the grave infill was approximately 1 m^3 of soil, and the bulk density of compressed sandy soil was 1.5 t m^{-3}, there would have been the addition of 0.1 kg P into 1500 kg soil. Should all P released from soft tissues be fixed into the necrosol in the grave infill, the total amount of P in the grave infill would increase only by 0.03%. The control soil had a P content of 0.16%, and this was 2.25 kg P m^{-3}. If all the P released from the soft tissues get fixed in the necrosol, the P content must have been 0.18%, representing 2.35 kg P m^{-3}. The infill of the grave had a P content of only 0.05%, which is only 0.75 kg P m^{-3}, with 1.6 kg of P lost from the grave infill. Because the grave infill was from the same sandy sediment as the control soil, there was no different soil in the grave infill. The clay probably was imported but very poor in P. Therefore, the possible explanation of low P content in the grave infill is that P-leached into deeper soil layers, evident by its gradual increase in the soil with depth from 0.09% at 0.9 m to 0.31% at 5.4 m (Table 5).

The gradual leaching of P and other elements (such as K, Cu, Zn, and Al) is eased by the high coarse grain, especially the layers below the grave bedrock. The influence of leaching again is supported by the gradual accumulation of the mineral component with decreasing grain sizes (Table 4). In the depths with a comparatively high fraction of fine sand, e.g., 3.4–4.4 and 4.4–5.4 m, P and other elements accumulated. Therefore, there was a substantial increase of P content in a grave, most probably connected with the decomposition of P-rich bones, not P-poor soft tissues, as 80% of P in the human body is found in bones. Some authors have discussed body decomposition in the grave because of increased P content in grave infills or burials of only bones, because of no increase in P content in the grave infill (Ernée and Majer 2009; Majgier and Rahmonov 2012; Limburský 2015). We concluded that the bodies could have decomposed in the graves even when the P content in the grave infill was lower than in the control soil.

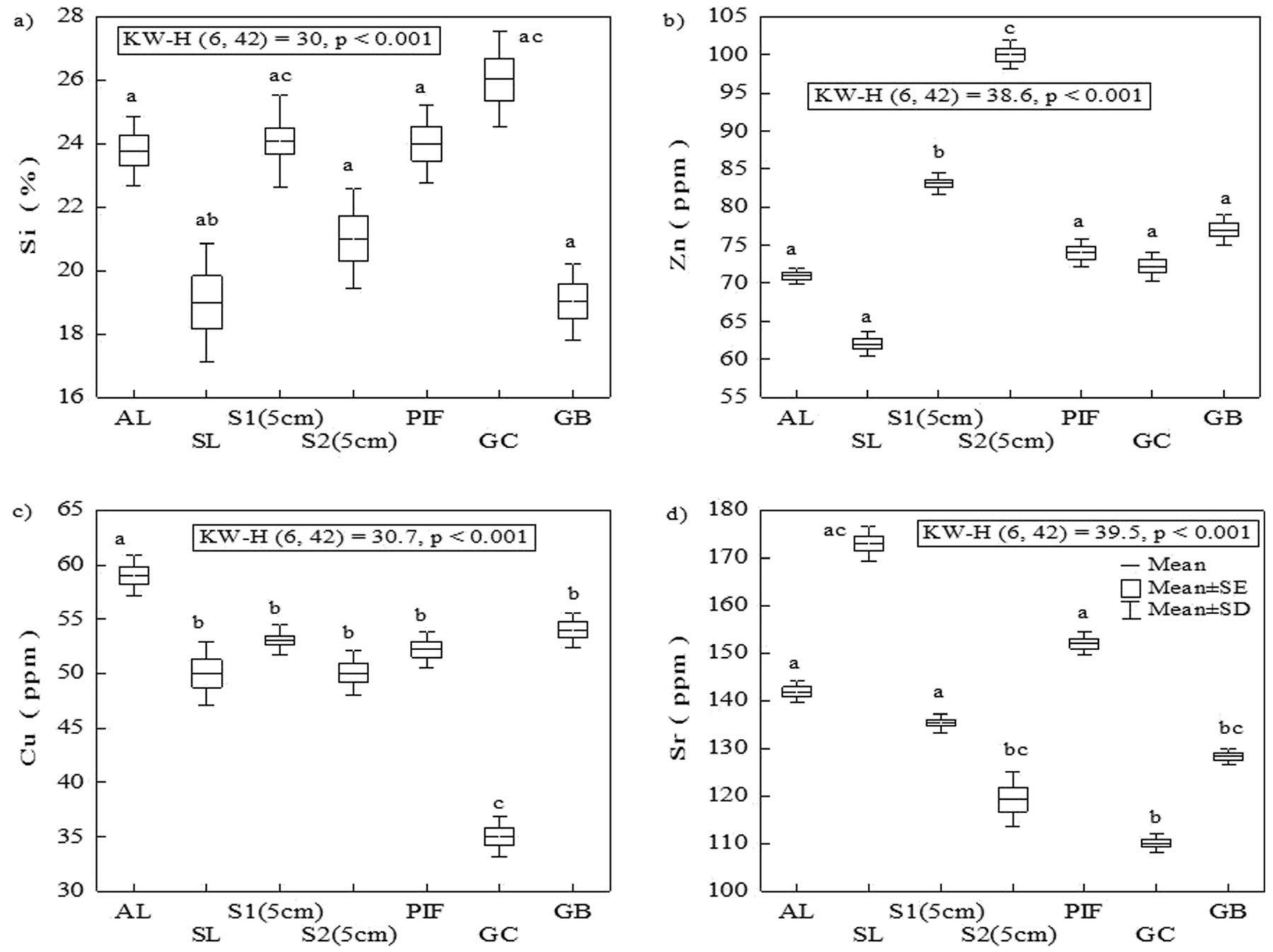

Fig. 7 Effect of different environments on the content of a Si, b Zn, c Cu, and d Sr in the graveyard. AL, arable layer; SL, subsoil layer; S1(5cm), grave infill > 5 cm to bones; S2(5cm), grave infill ≤ 5 cm to bones; PIF, pot infill, GC, grave clay; and GB, grave bedrock. Using the Kruskal-Wallis mean rank test, mean values with different letters were significantly different.

The use of P content in graves as an indicator of soft-tissue decomposition is therefore unreliable, especially in sandy soils with low P retention capacity, as in this study.

Phosphorus content in human bones is 16%, but in the studied bones, we recorded only 6.4% P, and this is equivalent to 0.16 kg P for the human body with 70 kg (Fig. 4a).

Therefore, the majority of P from bones (0.24 kg) was released into the soil, as bone minerals have high solubility, especially in acidic soils (Berna et al. 2004), which contributed to the high P content in the grave infill ≤5 cm from bones. Some amount of P from bones was probably also taken up by microorganisms (Collins et al. 2002) and plants because they produce organic acids and dissolve the inorganic lattice of bone made from hydroxyapatite (Crenshaw 2001; Metcalf et al. 2016). In several cases, we recorded fine roots of plants attached to bones, indicating direct uptake of P from soil close to bones by plants. The retention of P in the soil ≤ 5 cm from bones partly relates to the lesser amount of very coarse sand (≥2 mm).

The average pH (H2O) of soils in the study site was 5.3, which makes the soil acidic and unfavorable for bone preservation, as well as the retention of P (Fig. 9b). Acidic soil can dissolve the hydroxyapatite in bones (Abdel-Maksoud and Abdel-Hady 2011) and soften collagen (Abu Dalou 2017).

Some amount of P in the soil ≤ 5 cm to bone fixed by Al oxides and hydroxides, e.g., goethite (Parfitt 1989), and this explains the accumulation of P in this soil (Table 4). Notably, the lowest pH for all soils was in the grave infill > 5 cm from bones (pH 5), and there were not enough Al and Fe oxides to fix P, and so it was leached.

The decomposition of soft tissues in graves was highly indicated by increased Zn content in grave infills. Zn is a microelement present in the human body; there is approximately 2–3 g of Zn in a 70-kg live weight human body. Also, Zn content may have come from roots and bacteria that feasted on the dead body (Janaway et al. 2009; Tsonev and Lidon 2012). The Zn content in the grave infill increased about 20 ppm in comparison with the control soil, representing 3 g of Zn per m^3 of soil. The majority of Zn from the decomposed body was still present in the grave infill. The content of Zn was higher in the infill >5 cm and ≤ 5 to the bones (only where the human body decomposed) compared with the control. It explains the release of the Zn mainly from the soft tissue supported by no accumulation in the layers below grave bedrock. The presence of aluminosilicate (fine particles) with a relatively large surface area of grains supports the assertion of Zn retention in the grave infill > 5 cm to bones (Perrott 1977; Miyazaki et al. 2003). The Zn content in the soil ≤ 5 cm admittedly could be immobilized by the comparatively high P content there (Kempane et al. 2008).

However, low surface area and low net negative charge of the kaolinite create a low affinity for Zn ions (Barton and Karathanasis 2002). Hence, the comparatively lower Zn content in the clay layer (kaolinite) than the other grave infills.

Furthermore, the increased Zn content in human tissues is an indication of an animal-based diet, and there are differences between vegetarians and non-vegetarians (Cunnane 1990; Farnum et al. 1995; Allmäe et al. 2012). Notably, the high content of zinc in the human body is in the choroid of the eye and the prostate (FAO 2001; Cortesi et al. 2008). In the acidic arenosol, there was no or little influence of the pH on the retention of the content of Zn (Fig. 9d), which supports its ability to be a suitable indicator of soft tissue decomposition in this study. We concluded that the Zn content in the grave infill is a better soft tissue decomposition indicator in graves than P content.

The content of Ca was highest in the grave infill ≤ 5 cm to bones (3.8%) compared with the other analyzed samples. Only 1% of the total amount of Ca in the body is in soft tissues, representing 0.1 kg Ca in the case of a 70-kg body. The remaining 99% Ca (1.09 kg) is in bones. The enrichment of the grave infill ≤ 5 cm to bones by Ca was caused by Ca release from bones (e.g., dissolution due to acidic soil or water and decalcification)

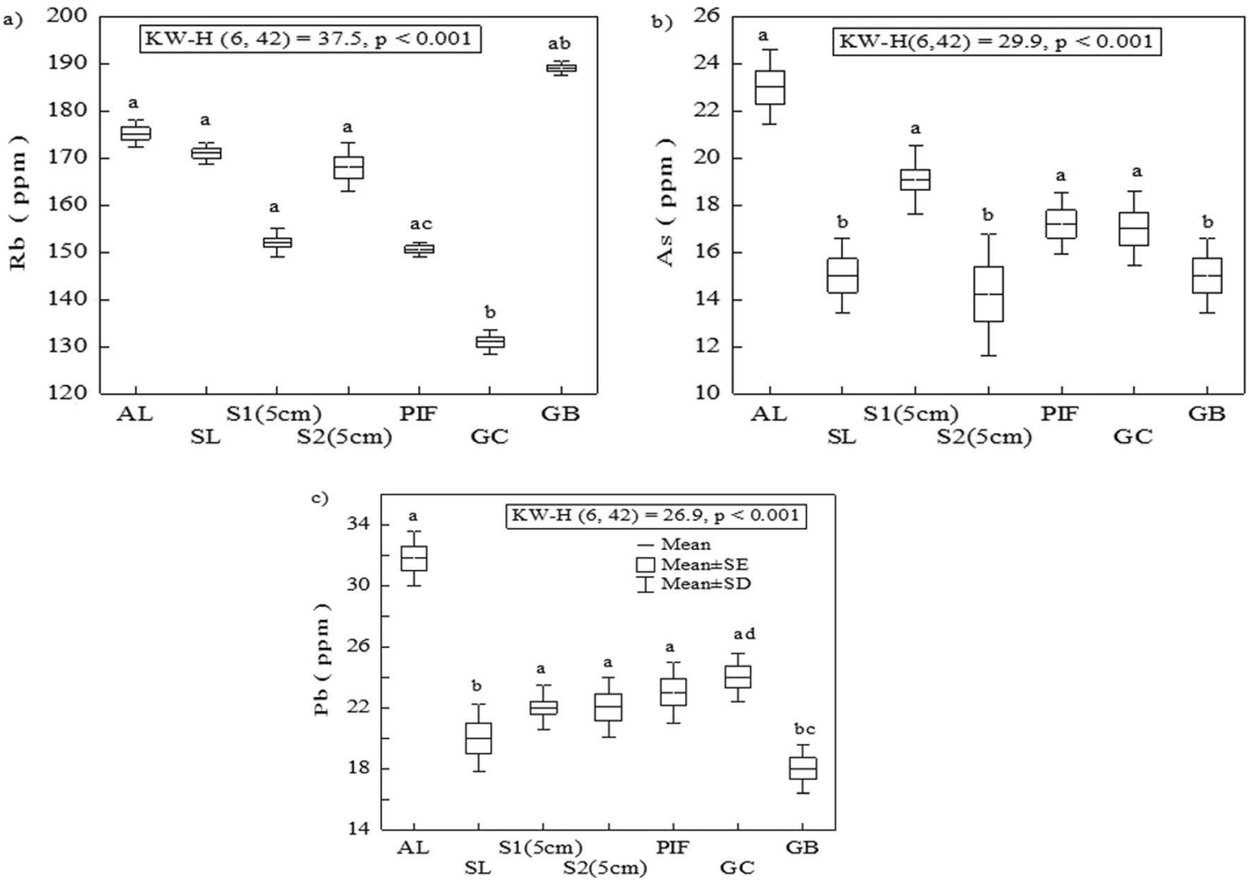

Fig. 8 Effect of different environments on the content of a Rb, b As, and c Pb in the graveyard. AL, arable layer; SL, subsoil layer; S1(5cm), grave infill > 5 cm to bones; S2(5cm), grave infill ≤ 5 cm to bones; PIF pot infill; GC, grave clay, and GB, grave bedrock. Using the Kruskal-Wallis mean rank test, mean values with different letters were significantly different.

The release of Ca from bones was also indicated by the Ca content in bones, which was only 19%, representing 0.6 kg Ca. Human bones contain 35% Ca (Mitchell et al. 1945); therefore, 0.49 kg of Ca lost from the bones through leaching and other processes, and some accumulated in the grave infill ≤ 5 cm to bones. Soil conditions such as low pH (Fig. 9c) and seemingly high content of Al may explain the low Ca in the grave infill >5 cm away from bones, pot infill, and clay in the grave. Because Al has a much higher affinity for negatively charged surfaces than Ca, thus an increased amount of Al in soils tends to displace available Ca, which causes more intensive leaching.

Moreover, the presence of skeletons in the shallow graves helps gather insects and fungi, which can digest bone collagen (Metcalf et al. 2016). Besides, these insects digest Ca and P from bones (Brady et al. 2008), which may have influenced their content in the soils studied.

There were only small differences in K content in different soils and sediments. Although there is 140 g K in the 70-kg live weight human body, K is generally a highly mobile element in the human body and the soil. Therefore, we cannot assume that the K accumulation in the grave infill was because of body decomposition. About 95% of body K is intracellular and located in the soft tissues, fulfilling a role concerning intracellular water (Patrick 1977). We, therefore, suppose that the K quickly leached during the soft tissue's decomposition.

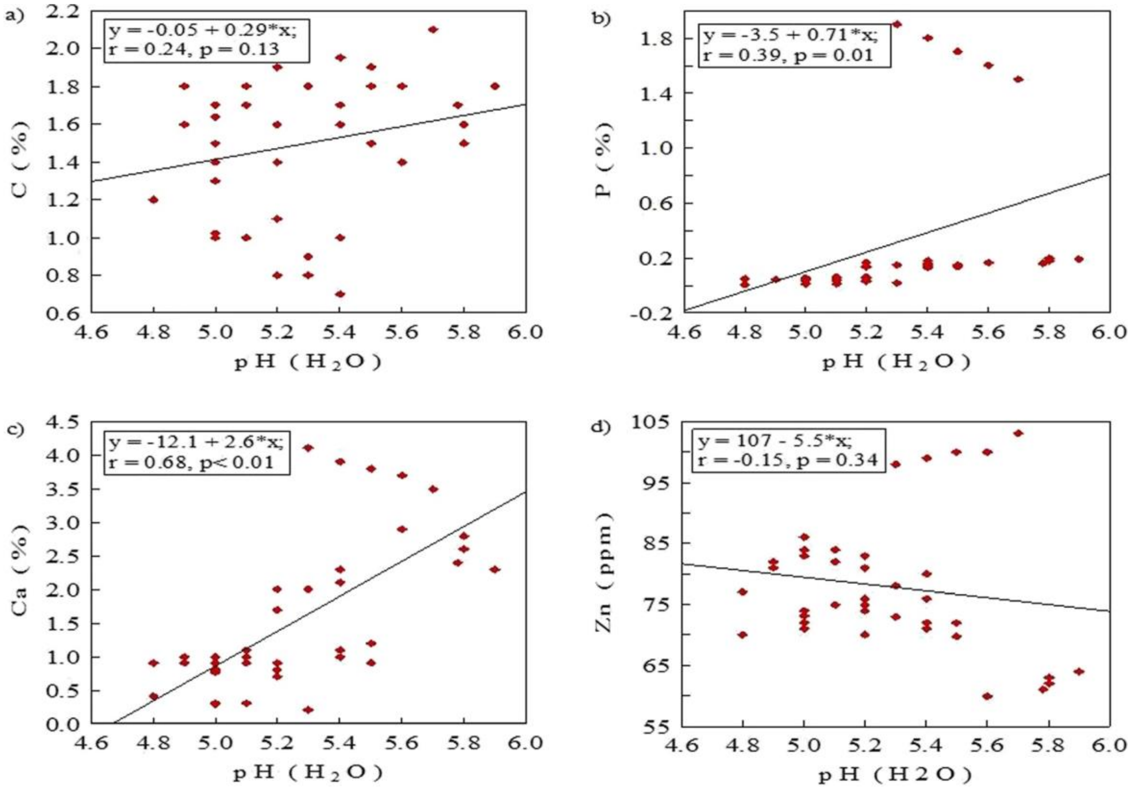

Fig. 9 The relationship between pH and a) C, b) P, c) Ca, and d) Zn

Table 3 Grain size (in %) distribution of soil and sediment samples from the studied graveyard

Soil layers	Soil grain size [%] ≥ 2 mm Very coarse	 1 - 0.5 mm Coarse	 0.5 - 0.25 mm Medium	 < 0.25 mm Fine
Arable layer	24.5	32.9	26.4	16.2
Subsoil layer	1.8	41.8	33.2	23.2
Grave infill > 5 cm to bones	1.5	45.9	39.2	13.4
Grave infill ≤ 5 cm to bones	0.7	56.7	31.7	10.9
Pot infill	2.1	43.1	37.4	17.3
Grave clay	0.04	40.6	35.9	22.9
Grave bedrock	1.3	53.7	34.9	10.1
Mean	4.6	45	34.1	16.3
Layers below grave bedrock (sample number)				
57	42.9	31.6	18.7	5.8
58	36.6	45.3	14.8	3.3
59	52.9	38.1	8.4	0.6
60	45.8	34.9	8.2	10.7
61	50.3	30.2	9.4	10.1
Mean	45.7	36	11.9	6.1
Overall Mean	20.8	42.2	24.9	12

Table 4 Fraction of major mineralogical components in the soil layers

Soil layers	Depths (m)	Mineral phase	≥ 2 mm %	1–0.5 mm	0.5–0.25 mm	<0.25mm
Arable layer	0–0.5	K-feldspar ($KAlSi_3O_8$)	11	11	21	26
		Ilmenite ($FeTiO_3$)	8	4	4	10
		Goethite (α-FeO (OH))	7	7	5	9
Subsoil layer	0.5	K-feldspar ($KAlSi_3O_8$)	14	12	10	17
		Goethite (α-FeO (OH))	12	11	11	14
Grave infill > 5 cm to bones	0.5–0.7	K-feldspar ($KAlSi_3O_8$)	2	4	4	6
		Aluminosilicate (Al_2SiO_5)	1	4	5	19
Grave infill ≤ 5 cm to bones	0.5–0.7	Goethite (α-FeO (OH))	16	17	22	29
		K-feldspar ($KAlSi_3O_8$)	3	5	7	19
Pot infill	0.7	Goethite (α-FeO (OH))	3	6	3	11
		Ilmenite ($FeTiO_3$)	4	4	8	10
		Kaolinite ($Al_2Si_2O_5(OH)_4$)	0.2	2	2	20
Grave clay	0.5–0.7	Kaolinite ($Al_2Si_2O_5(OH)_4$)	0.7	2	7	> 50
Grave bedrock	0.5–0.9	K-Feldspar ($KAlSi_3O_8$)	4	8	9	14
		Kaolinite ($Al_2Si_2O_5(OH)_4$)	0.6	1	4	22
Layers below bedrock (sample no.)						
57	0.9–1.4	K-feldspar, goethite, ilmenite				
58	1.4–2.4	K-feldspar, goethite, ilmenite				
59	2.4–3.4	K-Feldspar, granite, goethite, ilmenite				
60	3.4–4.4	K-feldspar, granite, goethite, ilmenite				
61	4.4–5.4	K-feldspar, kaolinite, goethite, ilmenite				

The content of Cu in the human body with a live weight of 70 kg is approximately 0.1 g (Mann and Truswell 2002). Generally, the content of Cu in bones is 24 ppm but 30 ppm in this study. There was some enrichment of bones by Cu, probably because of post-depositional processes, as there was a higher content of Cu in surrounding soils (50–59 ppm) than in bones. The increased Cu in the bones also relates to the animal-based diet of people from the CWC People with animal-based nutrition generally have a higher content of Cu in tissues compared with vegetarians (Allmäe et al. 2012). There was a slightly increased Cu content in the arable layer in comparison with other soils, and this was probably connected to the use of modern pesticides and fertilizers as the studied site has no records of past metallurgy. On the other hand, the low Cu content in the grave clay relates to its collection from different locations during burials. The contents of Al and Si in all the analyzed soils were probably from the natural origin without any effect from human activities in the study site.

The content of Fe was highest in the arable and subsoil layers compared with grave infills. In cultivated soils (arable and subsoil layers), the average contents of Fe range from 2 to 4% (Cornell and Schwertmann 2003). The lowest Fe content in infill ≤ 5 cm from bones relates to the higher proportion of Ca and P compounds released from bones and the smaller amount of the original soil there. Iron is only 4.2 g in the human body (70 kg), and cannot affect the total content of Fe in the grave infill or layers below the grave. Accumulation of Fe in the layers below grave bedrock indicates natural Fe leaching not directly related to the grave. The content of Mn in the grave infills was in a similar range to both arable and subsoil layers. The movement of Mn with depths in the grave bedrock is similar to Fe, which indicates leaching since the accumulation of sand deposits in the Pleistocene. The amount of Mn in a 70-kg human body (about 0.012 g) is too small (Niziolomski et al. 2016) to have any effect on the content of Mn in grave bedrock.

Although the content of As and Pb in the arable and subsoil layers were comparatively higher than the grave infills, there was continual accumulation along the gradient of the layers below the grave bedrock (Table 5). However, the content of these elements in the bones indicated that the leached elements were not from the decomposition of the buried human bodies. Moreover, this was not consistent with previous authors, as many cemetery soils reported metal contamination (Majgier et al. 2013; Amuno and Amuno 2014) due to accumulation in the human body, especially in settlements with intensive mining and metallurgy. Moreover, the increased content of Pb in the arable layer relates to the use of alkyl-lead additives to gasoline, resulting in large Pb emissions between 1950 and 2000, with a peak accumulation of about 6000 tons (Novák et al. 2008; Asare et al. 2020).

Furthermore, the increased content of As in the arable layer resulted from the sub-recent use of pesticides and fertilizers. These elements do not reflect ancient metallurgical activities as the establishment of the graveyard was before the onset of metallurgy in the region. Strontium and Rb are non-essential trace elements with reported contents in human bones ranging from 200 to 390 ppm (Hodges et al. 1950; Yamagata 1962; Lengfelder et al. 2018). The contents of Sr and Rb in the bones of this study were consistent with the reported values.

Meanwhile, the increasing accumulation of elements in depths below the grave bedrock most probably associated with the deposition of gravel-sandy river terraces during the Pleistocene. The alternation of feldspar into kaolinite is very common in the decomposed granite below the grave bedrock (Table 4). The clay minerals are common in the filling materials of joints (≥ 2 mm) for the retention of elements in these layers (below grave bedrock). Besides human bodies, some chemical signatures of grave infill related to the use of the wooden chamber in the grave, recorded several times in the case of CWC graves in the Czech Republic (Limburský 2015). In the case of the graves of this study, we recorded no remains from wooden chambers, decomposed clothes, and other grave goods. Therefore, all the chemical signatures of the grave infill are mainly from the decomposition of human bodies.

The grave clay related to the construction of the grave chamber or the coffin most probably used to prevent the fall of sand. There has been a long tradition of building barrows above the characteristic shallow graves since the Late Neolithic constructed from the surrounding soils. In our study site, graves respected each other, and there was no overlap between them, explained by the presence of barrows on graves. Therefore, the position of individual graves was probably well known for a long time after their establishment.

Lately, in the last several centuries, barrows were destroyed as they represented obstacles during field plowing.

Table 5 Content of organic C, P, K, Ca, Fe, Mn, Cu, Zn, Al, Si, Sr, Rb, As, and Pb in sediment samples collected below the grave bedrock from different depths of the Pleistocene gravel-sandy river terrace

Sample No.	Depth [m]	pH [H_2O]	C [%]	P [%]	K [%]	Ca [%]	Fe [%]	Mn [%]	Cu [ppm]	Zn [ppm]	Al [%]	Si [%]	Sr [ppm]	Rb [ppm]	As [ppm]	Pb [ppm]
57	0.9 – 1.4	5.4	0.1	0.09	1.6	0.71	2.7	0.21	29	34	8	24	97.2	143	11	16.3
58	1.4 – 2.4	5.5	0.1	0.11	1.9	0.33	1.6	0.04	55	47	8.4	24	118	138	8.7	23.6
59	2.4 – 3.4	-	0.1	0.15	1.9	0.48	2.5	0.04	23	27	7	27	121	169	13	18
60	3.4 – 4.4	4.8	0.1	0.29	2.0	0.42	2.8	0.08	48	38	8.3	23	122	173	14.7	23.6
61	4.4 – 5.4	5.8	0.1	0.32	1.6	1.46	4	0.38	62	41	7.6	23	126	232	27.7	25.6
Mean		5.5	0.1	0.19	1.8	0.5	2.7	0.08	48	37.4	8	24	117	169	13	23.6

Conclusions

The main message of our study is that the buried human body can significantly affect soil chemical properties even after more than 4500 years. The increased content of organic C, elements related mainly to natural leaching and accumulation since the Pleistocene and not directly related to the graves. Even though the human body represents a high amount of C, the increased C content was only close to bones, indicating the mineralization and leaching of body C, and also associated with the high fraction of coarse sand.

Although an increased P content in graves is supposed to be an indicator for soft tissue decomposition, there can be even lower P content in the grave infill than in the surrounding soil, due to leaching, especially in soils with low P retention capacity. The content of P in the infill of prehistoric graves is, therefore, not a reliable indicator for soft tissue decomposition. However, in the acidic environment, P and Ca released from bones can be partly fixed in the grave infill ≤ 5 cm to bones. P and Ca enriched soil close to bones, and bones can be a source of these elements for plants, as indicated by the recorded high density of fine roots.

The most reliable indicator for soft tissue decomposition was an increase in Zn in the grave infill. Thus, Zn is probably a better indicator in this case compared with P.

Authors' Contributions Conceptualization: Michael O. Asare, Michal Hejcman. Methodology: Michael O. Asare, Petr Holodňák, Miroslav Černý, Michal Hejcman. Formal analysis and investigation Michael O. Asare, Petr Holodňák, Miroslav Černý, Vilém Pavlů, Michal Hejcman. Writing—original draft preparation: Michael O. Asare, Michal Hejcman. Writing—review, and editing: Michael O. Asare, Michal Hejcman. Funding acquisition: Jan Horák, Ladislav Šmejda, Michal Hejcman. Supervision: Michal Hejcman.

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Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

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SUPPLEMENTARY MATERIAL

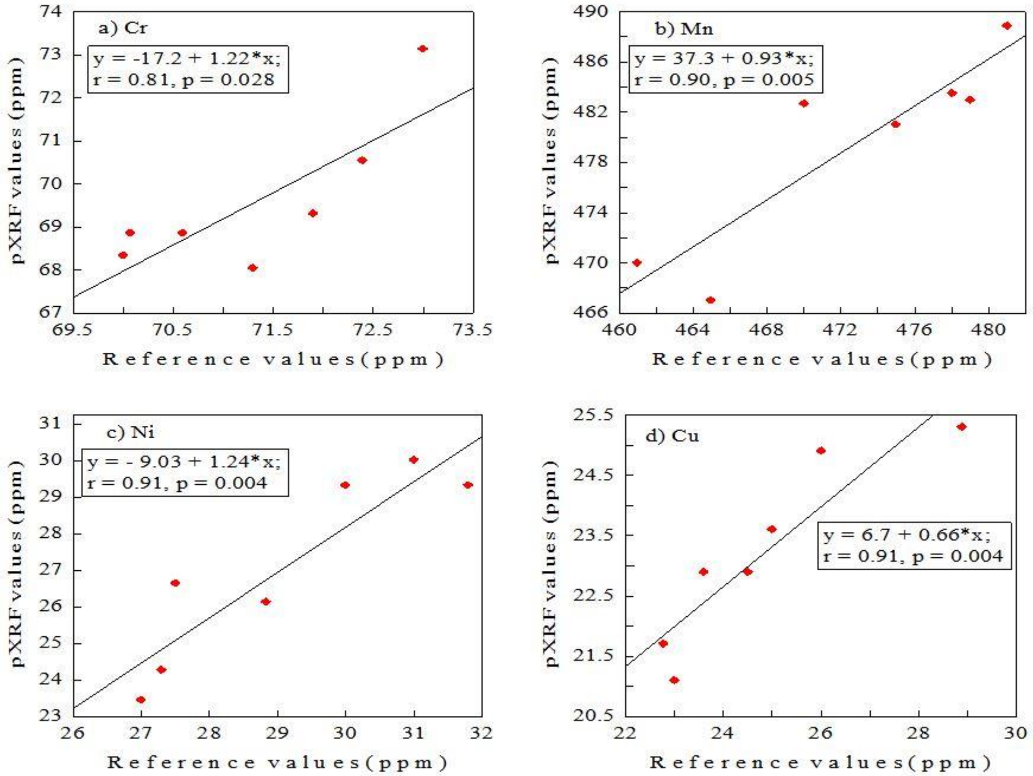

Fig. S1. Examples of calibration curves obtained with the pXRF instrument (continuous lines), which include Pearson correlation coefficients (*r*) for (a) Cr, (b) Mn, (c) Ni, and (d) Cu

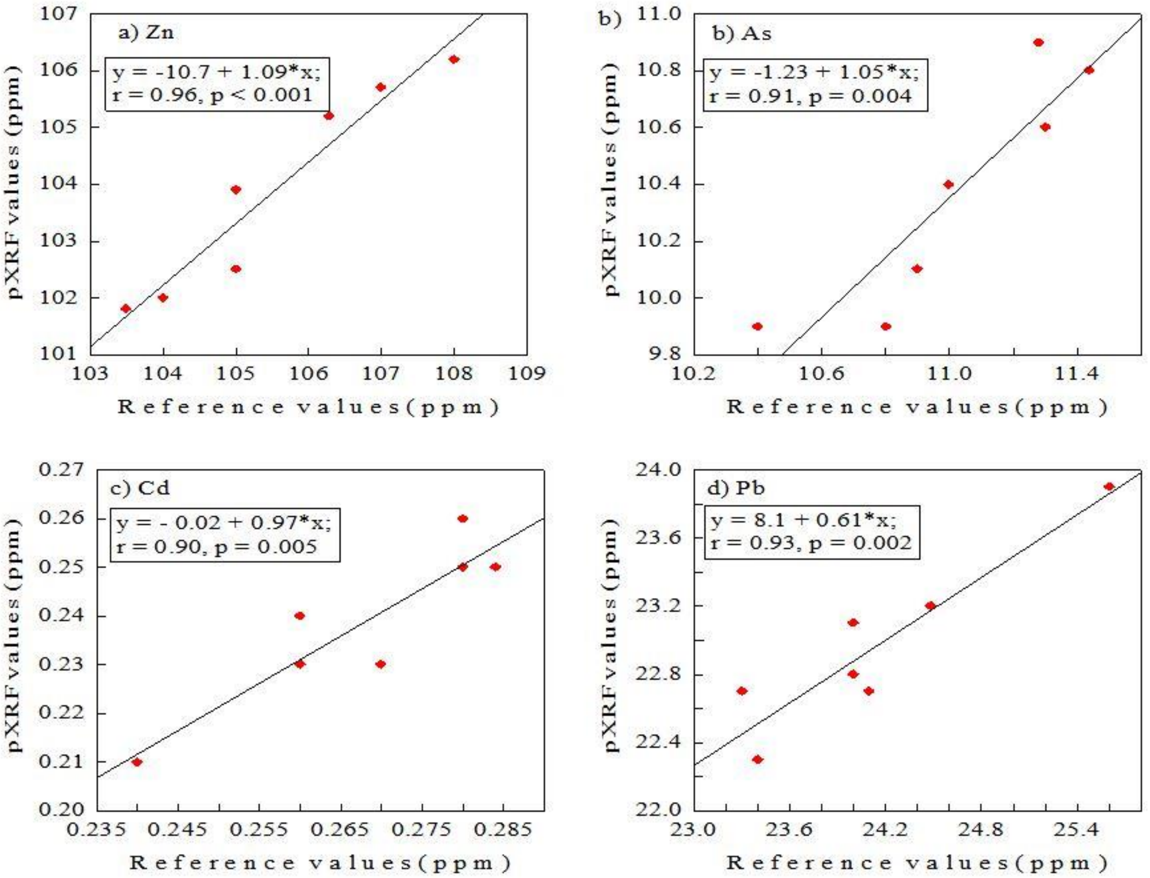

Fig. S2. Examples of calibration curves obtained with the pXRF instrument (continuous lines), which include Pearson correlation coefficients (*r*) for (a) Cr, (b) Mn, (c) Ni, and (d) Cu

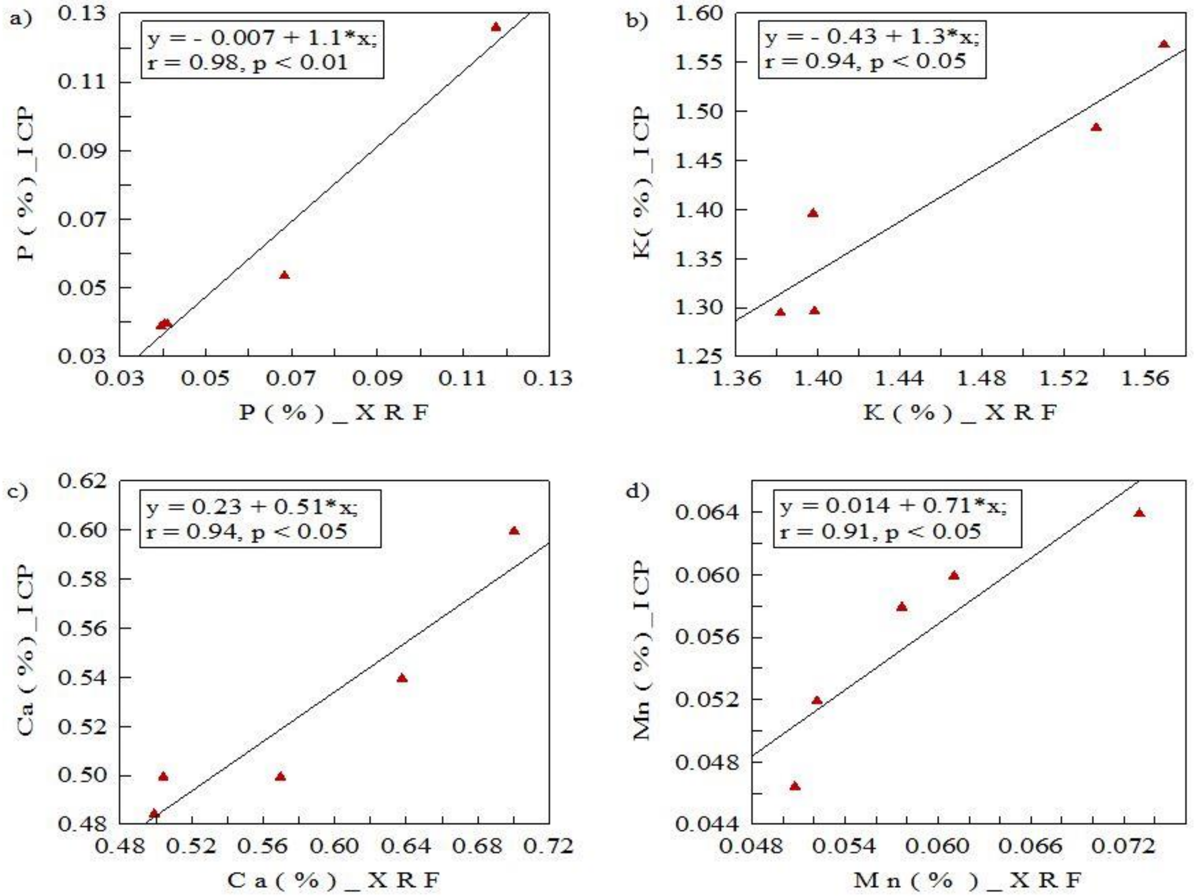

Fig. S3. The relationship between pXRF and Aqua regia ICP data for P (a), K (b), Ca (c), and Mn (d)

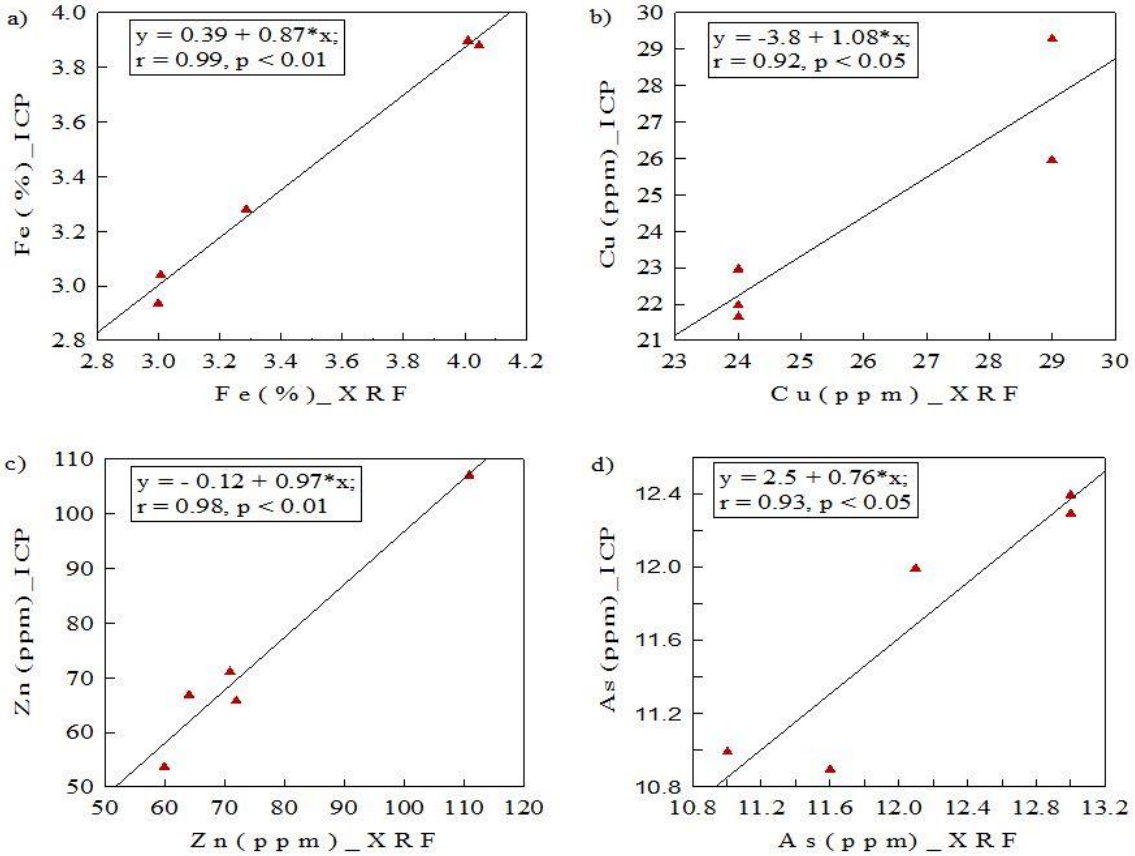

Fig. S4. The relationship between pXRF and Aqua regia ICP data for Fe (a), Cu (b), Zn (c), and As (d)

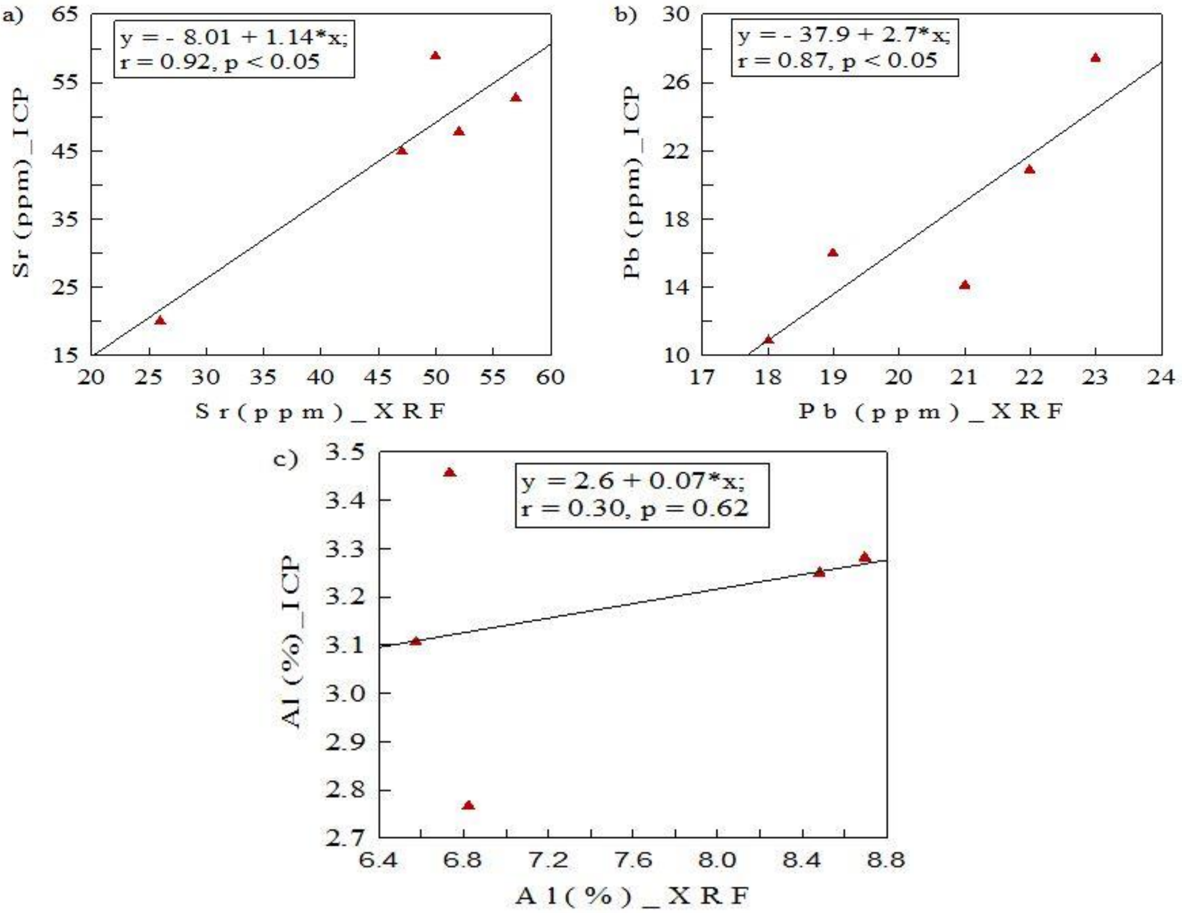

Fig. S5. The relationship between pXRF and Aqua regia ICP data for Sr (a), Pb (b), and Al (c)

Table S1. Percentage recovery (mean values of element ÷ reference values x 100) of the element by pXRF after extraction by aqua regia obtained by inductively coupled plasma mass spectrometry

Element	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
% recovery	97.6	101	92.7	93.5	94.4	94.1	88.9	95.4

Table S1. Content of organic C, P, K, Ca, Fe, Mn, Cu, Zn, Al, Si Sr, Rb, As, and Pb in twelve grave infills taken from distance > 5 cm from bones. Grave numbers are following Figures 1b, 2, and 3

Grave No.	**C** [%]	**P** [%]	**K** [%]	**Ca** [%]	**Fe** [%]	**Mn** [%]	**Cu** [ppm]	**Zn** [ppm]	**Al** [%]	**Si** [%]	**Sr** [ppm]	**Rb** [ppm]	**As** [ppm]	**Pb** [ppm]
41	1.78	0.05	1.6	1.05	4.3	0.07	49	77	6.7	24	137	175	18.7	22.3
42	1.77	0.04	1.6	0.85	4.4	0.06	51	83	6.7	24	136	143	20	23
43	1.46	0.04	1.4	0.78	5.1	0.08	65	88	7.5	23	149	141	17	21.7
44	1.44	0.05	1.4	0.96	4.6	0.06	57	84	8.5	22	148	152	27.7	24
45	1.64	0.04	1.6	0.74	4.2	0.07	52	80	7	26	134	151	16.3	21.3
46	1.04	0.08	1.4	0.87	4.6	0.09	62	64	7.7	22	130	152	18.3	19
49	1.33	0.03	1.8	0.84	4.1	0.06	53	79	6.8	26	135	151	19	22.3
50	1.64	0.01	1.6	0.81	4	0.06	48	76	6.7	24	134	152	18.3	22.7
51	1.81	0.01	1.6	0.91	4.1	0.06	49	83	6.7	25	131	162	17.7	21.3
53	1.42	0.07	1.7	0.86	4.4	0.07	49	88	6.8	25	131	164	17.3	21.3
54	1.64	0.07	1.5	0.85	4.5	0.06	56	88	7.4	23	140	155	21.3	22
64	1.73	0.05	1.6	0.88	4.6	0.07	62	91	6.6	24	133	154	19.3	20.3
Median	**1.64**	**0.05**	**1.6**	**0.9**	**4.4**	**0.07**	**53**	**83**	**7.1**	**24**	**135**	**152**	**19**	**22**

CHAPTER 7

General Conclusions

In these comparative researches, the influences of ancient human activities are reflected by the accumulation of different elements in the archaeological soils even after the abandonment of such sites for decades, hundreds, and thousands of years. These imprints to a certain degree are directly detected according to the color changes and other physical properties of the soils. According to this study, the chemical signatures are varied, and the variations are mainly connected to specific human activities ranging for example, from the deposition of organic wastes, excrement, biomass ashes, construction/destruction of houses as well as agricultural and burial practices.

The color of the studied archaeological dark earth (European dark earth and African dark earth) characterizes dark soils, which indicate high soil organic matter content. The effect of fire in causing the dark color corroborates with the presence of homogeneously high amounts of charcoal in the sites with developed archaeological dark earth (ADE). Due to incomplete combustion, organic materials (such as burnt palm kernel shells in the case of African dark earth) become charcoal (pyrogenic) with a dark black color. Additionally, the decomposition of organic wastes by microbes contributes to the dark color of ADE, increases soil aggregation and aggregate stability (FAO, 2005). The reaction between the characteristic high content of Fe and S (iron sulfide) in the ADEs also partly contributes to the dark color of the soils, however, this needs further studies.

These human impacts eventually are distinguished by an anthropic diagnostic horizon with several artifacts (such as pottery fragments, kitchen wastes, agricultural residues, excrements, and bones) and are grouped in soil classification systems as Anthrosols (FAO, 2015). Besides, the inclusion of silt and clay particles by diverse human activities (e.g., decalcification of stone-tempered mortar and sand-tempered lime plaster, construction/destruction of clay and daub buildings), black carbon (highly porous) improves a wide range of physical properties of the soil, including micro and total porosity and high H_2O retention capacity.

Considering the soil reactions of the studied ADEs, the relatively neutral status is a requisite for the release and retention of many elements, e.g., P. The soils pH in all cases were influenced by higher organic matter contents reflected by the accumulations of organic C, total N, and plant-available Mehlich-3 (M-3) content of P, K, Ca, S, Fe, Cu, and Zn compared to their respective control without past settlement activities. Additionally, the decomposition of the organic matter by microorganisms contributes to the retention of the pH status of these soils for a long period. The ADEs have reduced acidity (pH [H_2O]) in comparison to neighboring control, which is also associated with processes that change soil acidity, including deposition of biomass ashes, organisms‘ respiration, and decomposition of organic matter. Biomass ashes have high pH which can range from 7.5 to 13 and are suitable to alleviate soil acidity. The increased pH and stability of high organic matter content provide optimum conditions for the persistence of elements, high cation exchange capacity (CEC), adequate C: N ratio for mineralization. Organic matter increases the CEC (ability to attract and retain nutrients) and contributes to N, P, and other nutrients. The pH values of 6.5 and above in the European dark earth (EDE) and African dark earth (AfDE) of these studies are consistent with studies on *terra preta* (Amazonian dark earth), with a substantial accumulation of elements. Conversely, the long-term application of mineral fertilizers and other agrochemicals can result in acidic soils. Even though the Dřevíč hillfort also observed some conventional application of mineral fertilizers similar to the fertilizer experiment site for at least 50 years, its effect can not mask the strong imprint (soil reaction- pH) of medieval settlement activities.

The marked differences in elements between the studied ADEs and respective adjacent control without past human activities are associated with the higher accumulation of total N, P, K, Ca, S, Mn, Cu, Zn, Fe, Sr, and Rb in the former. Additionally, there are enrichments by plant-available M-3 contents of P, K, Ca, Mg, S, Mn, Cu, and Zn in the ADEs.

Generally, phosphorus signatures in the ADEs were stronger than the effect of short-term intensive mineral fertilizer application. Phosphorous signature in soils is more stable than in the case of many other elements. P has a releasability of less than 1 % and this is very typical in soils with the application of wood ashes and indicates the presence of past human occupation. Although the Dřevíč hillfort was settled from the Neolithic through to the High middle age, the P signatures from the EDE and AfDE with relatively shorter duration of the settlement were relatively similar. This provides a clue regarding the type and intensity of human activities. Thus, less than 100 years of intensive settlement activities resulted in the development of AfDE with a substantial accumulation of P. This is corroborated with the presence of animals bones, ashy deposits, and burnt palm kernel shells.

The accumulation of Ca moreover was higher in the ADE sites and this signature results mainly from bones which contain approximately 5-45 % of Ca depending on the type of animal. Notably, Ca in bones is released gradually, especially in less acidic environments. Additionally, the deposition of wood ashes contributes a significant amount of Ca. Calcium signature is among the highest macro element in wood ashes. Clay minerals (e.g., kaolinite) resulting from house constructions/destructions and manufacturing of potteries also contain Ca, which contributed to the higher contents in the studied ADEs. In all the studied sites, the content of Ca was significantly higher than their respective control, supporting its assertion as an anthropic marker in archaeological localities.

When soil alkalinity increases and the pH rises, necessary minerals such as P, Fe, B, Mn, Cu, Zn, and K become chemically tied to the soil and are not readily available for plant use. This partly contributes to the higher total element content than the plant available in archaeological localities. For instance, P signatures may tie-up with Fe/Al oxides and other minerals e.g., Geotithes (α-FeO (OH)), and persist in archaeological localities rendering it a suitable human existence indicator. However, the anthropogenic sources of P coincide with those of K, Mn, Fe, Cu, Rb, and Sr, and show strong positive correlations among these elements. Therefore, the content of K, Mn, Fe, Cu, Rb, and Sr can be considered as anthropogenic indicators of past human activities in archaeological localities. However, this is connected to the level of elemental accumulation in specific archaeological sites.

It was well established that the accumulation of anthropogenically-induced elements in archaeological soils from different geographical locations related to relatively similar activities. However, the extent of accumulation of elements relates to specific human activities, the extent of human activities (longevity), and the local environmental features of the study site. For example, in a comparative analysis of ADEs from the tropics and temperate regions, the content of Mn was substantially higher in the former than the latter although the EDE site was settled for a far longer duration. Notably, locations with higher contents of Mn in the AfDE were consistent with areas that recorded higher amounts of organic wastes such as bones, burnt palm kernel shells, broken ceramics, potsherds, broken wooden smoke pipes, and ashy deposits. These areas were identified as midden pits. Also, the locations with ashy deposits were noted with high contents of total and plant-available macro, micro, and other elements vital for biomass growth, which supports the study by Hejcman et al. (2010). The high accumulation of multi-elements in biomass ashes, particularly wood ashes relates to the elemental composition of the soils as well as the kind of anthropogenic activities in the location of the tree species. Although the use of wood ashes can sometimes be problematic due to the accumulation of risk elements, e.g., Pb, Ni, As, and Cd, these can be below the permissible limit for agricultural soils and in such cases very suitable as fertilizers. According to this study, wood ashes have relatively low releasability (proportion of available element from the total) of elements, e.g., P, hence, its retention in archaeological localities for millennia.

Although the human body represents an accumulation of high content of elements, most of these elements such as C can not be used as an indicator for soft tissue decomposition. These elements are easily lost through the gaseous emission during decomposition similar to that of N and S. Other contributing factors such as leaching resulting from large pore space of soil particles (e.g., coarse sand) lead to the loss of these elements as well as K over time and thus from an archaeological perspective not suitable to indicate the decomposition of buried human bodies. The persistence of elements e.g., P in the acidic medium is connected with the fact that a huge accumulation of P is found in bones and may take a long period for total decay. Hence, the gradual release in soils with proximity to bones. In light of this, necrosols can retain elements for a substantial period, especially in less acidic environments as the putrefaction of the buried human body is also connected with the release of acidic fluids. The decomposition of soft tissues in graves was highly indicated by increased Zn content in grave infills. The increased Zn content in the body tissues is an indication of animal-based diets common with the Yamnaya people. The majority of Zn from the decomposed body was still present in the grave infill. Zinc is a microelement present in the human body and may come also from roots and bacteria that are feasted on the dead body. The content of Zn was higher in the infill >5 cm and ≤ 5 to the bones (only where the human body decomposed). It explains the release of Zn mainly from the soft tissue. The presence of aluminosilicate (fine particles) with a relatively large surface area of grains supported the assertion of Zn retention in the grave infill > 5 cm to bones. The content of Zn in the soil ≤ 5 cm could be immobilized by the comparatively high P content there. However, low surface area and low net negative charge of the kaolinite (clay particles) created a low affinity for Zn ions leading to a comparatively lower Zn content in the clay (kaolinite) layer in comparison to the other grave infills. In the acidic arenosol, there was no or little influence of the pH on the retention of Zn content, which supports its ability to be a suitable indicator of soft tissue decomposition.

Even though the use of portable X-ray fluorescence spectrometry (pXRF) is relatively new in the multi-elemental analysis of archaeological soils, comparative quantitative elemental analysis with conventional approaches such as *Aqua regia* followed by inductively coupled plasma mass spectrometry (ICP-MS) resulted in the strong correlation of the tested elements. Hence, this indicates that pXRF data have adequate precision in the determination of the total content of elements in archaeological soils and other biological samples, e.g., bones. However, strict adherence to protocols, e.g., homogeneity of samples, complete dryness of the matrix, and in the case of bone samples, close contact with the puncture-resistant window of the pXRF is encouraged. Pertinent in using the device is the cost-effectiveness and the ability for in-situ and ex-situ measurements.

The chemical signatures of archaeological soils are preservable even in different geographical and environmental conditions and the analysis of these signatures not only answers the archival records of human activities but of contemporary relevance in agricultural production, e.g., in sustainable agricultural management. In summary, the following specific conclusions were made after the mapping of the different types of archaeological soils and the analysis of the chemical composition of wood ashes from different tree species;

1. The intensive application of mineral fertilizers (N, P, and K fertilizers) can hardly mask the content of N, P, K, and other trace elements in European dark earth soil. This key message is of great importance as many farmers apply the same amount of mineral fertilizers to arable fields on past settlement sites. The signatures generated as a result of past human activities are thus, strong and can be maintained in the soils for several thousands of years even after the abandonment of sites.
2. Archaeological dark earth soils (European and African dark earth) are characterized by a substantial accumulation of total N, P, K, Ca, Mn, Fe, Cu, Zn, Sr, and Rb as well as available P, K, Ca, Mg, S, Cu, and Zn. According to these studies, the extent of elemental accumulation in the soils is connected to the type and intensity of past human activities as well as the longevity of the settlement. The intensity of past human activities is reflected by an even higher enrichment factor of elements compared to those reported for *terra preta* by several authors. Elemental records of the soils from past settlement sites provide a basis for such fields to be suitable for arable land use, even with minimal or without mineral fertilizers.
3. The use of traditionally analyzed elements, e.g., P and Ca as indicators of past human activities during post-depositional soil-forming processes, e.g., podzolization, gleying, and leaching, may render them unreliable indicators as these processes influence especially the retention and distribution of P. Hence,

4. the use of trace elements (such as Mn, Cu, Zn, and Sr) represent the best alternative elements to indicate past human activities in archaeo-anthrosols even from different geographical and environmental conditions.
5. Past human activities are connected not only with the usually interpreted elements such as P, Ca, Zn, and Cu (so-called traditionally analyzed elements in archaeological studies) but also with Mg, K, Fe, Pb, Ni, Rb, and Sr. Although less studied by many authors, higher contents of Rb and Sr were consistent in all the studied fields than their respective control. Therefore, Rb and Sr have become more promising indicators of past settlement activities.
6. The fertilizer values of soils from past settlement sites are preserved for a long time, according to the relatively small amounts of elements released from soils especially with biomass ash deposition. Biomass ashes obtained from tree species have high contents of macro (P, K, Ca, Mg, and S), micro (Mn, Na, Fe, Cu, and Zn), and other (Sr) elements vital in soils for proper plant growth and high crop yields. The retention of the elements in the ashes results from the relatively low releasability, hence persist in archaeological soils. Although biomass ashes can be applied to contemporary arable fields, the application must be done according to agronomic rates. Additionally, detailed elemental analysis is recommended.
7. The chemical signatures of necrosols can be well-preserved for thousands of years. The retention of the element in the buried human bodies is connected with the soil physical (e.g., porosity) and chemical (such as pH) of the original soil. In soil with high total porosity such as arenosols, the high proportion of coarse sand support the gradual leaching of many elements. Additionally, increased soil acidity is a requisite for high release of elements, e.g., P. However, in grave infills, the Zn and P contents are the most suitable indicators of soft tissues and bone decompositions, respectively, within space and time. As a higher amount of P is found in the bone, in acidic soils P in the body tissue is depleted rendering it an unreliable indicator in this case. Zinc content, however, is maximized in the body tissues, especially closer to the bones is retained for several thousands of years to indicate the decomposition of body tissues. Thus, the long-time argument on which elements best indicate bones and body tissues decomposition is resolved.
8. The chemical signatures of the cultural layers of previous settlement sites are well-represented by a thorough analysis of the undisturbed upper soil layers (arable layers). In most cases, the lower profiles present relatively similar physical and chemical properties as the upper soil profiles.
9. The analytical methods used in archaeological studies should be relatively inexpensive. From the critical analysis of the total and plant-available contents of the same elements, we concluded that the total content is more suitable in the study of soils involving the estimation of enrichment factors in archaeological localities. This stern from the fact that the analysis of the plant-available elements must undergo vigorous laboratory protocols which can not be easily obtained in the field. Moreover, the patterns recorded using plant-available contents of elements are affected by some soil chemical properties (e.g., soil reactions and total element contents). It is, therefore, difficult to draw straightforward inferences without a detailed analysis of soil properties, which may be hard to perform by geoarchaeologists in the field.
10. The study has proven beyond doubt the suitable applicability of the pXRf in the elemental analysis of abandoned sites and archaeological soils, even on current arable fields. Per obtained results of the overall study, in the multi-elemental analysis of soils, the pXRF has adequate precision and has the advantage of in-situ and ex-situ measurements over wet acidic methods (laboratory analysis, eg., *Aqua regia*) of total content measurements.

CHAPTER 8

Future perspectives

1. Geochemical and geophysical mapping of archaeological localities in the sub-Sahara. The mapping of sub-Sahara African endangered archaeological sites to identify and document endangered archaeological heritage sites using a combination of remote sensing, magnetism, elemental analysis, and selective archaeological surveys. Identification of past, present, and potential future threats to these sites and approaches to enhance site protection measures. Such studies are rare in Africa and in-depth studies will provide a platform to understand the contribution of archaeological localities to contemporary settings.
2. Practical production of biomass and their comparative yield differences between anthrosols from past human activities, fields with the application of mineral fertilizer, and control without both past human activities and mineral fertilizers.
3. Impact of Archaeological dark earth on the mitigation of greenhouse effect and sequestration of carbon.
4. Microbial activities in archaeological dark earth- fecal analysis as biomarkers, organic matter analysis.
5. Palaeoento-faunal remains analyses to trace ancient human activities.
6. Tracing past human activities through the analysis of rare earth elements (REEs) in archaeological localities. The development of a methodological approach based on multi-elemental analyses focusing on REE (e.g., La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) marker concentrations with archaeological stratigraphical interpretation and to characterize different natural and occupational episodes.

CHAPTER 9

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CHAPTER 10

Curriculum Vitae

Michael Asare Opare

Laboratory and field experiments

CURRICULUM VITAE

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Education

1994–1997 SDA High School, Agona, Ghana, specialization: General Science [Physics, Chemistry, and Biology]
2000–2003 Wiawso Anglican College of Education, Ghana, Specialization [Science and English Language]
2010–2014 University of Education, Winneba, Ghana, specialization: [Integrated Science – Physics, Chemistry, Biology, and Agricultural Science]
2015–2017 Czech University of Life Sciences Prague, Czech Republic, specialization: [Landscape Engineering – Environmental Modelling]
2017– Czech University of Life Sciences Prague, Czech Republic – postgraduate studies [Ph.D.], specialization [Soil science, General Ecology]

Research interest

Soil chemistry, Geochemistry, Stratigraphy analysis, Soil contamination, Organic waste analysis, Waste management, Environmental Archaeology, Biodiversity management, and Protected area management

Employment

Laboratory analyst of soil and sediment samples

Diploma Thesis consultations

2020 Anna Peslova - (Bachelor thesis)- Is it possible to distinguish wood ash from horse feces according to the elemental composition
2020 Noheem Abiola Tijani – (Master thesis) – Soil contamination by risk elements in Awotan dumpsite.
2020 Ramgopal Biswas – (Master thesis) – Estimation of the intensity of settlement activities in the Early Medieval Hillfort Kralovice according to the accumulation of anthropogenic elements in the soil.
2021 Moses Ayodeji Olalekan – (Master thesis) – Can wood ashes of selected European woody species be used as fertilizers?

Professional experience

2018 July – Tel Burna Excavation Project [Israel] - Chemical analysis of soils.
2018 August – Protected Areas Management [Ghana] – management effectiveness of Wildlife and tracing of former settlement sites within protected areas.
2018 September – Internship [University of Education, Winneba, Ghana]
2019 March-May – Mlada Boleslav, Kolin [Czech Republic] field practice on soil analysis
2018 Practical application of analytical tools [Institute of Geology, Czech Republic]
2019 June – Practical attachment in the analysis of soils in the Volta Region of Ghana [Under University of Ghana]

Computer skills

Statistical tools: Statistica, IBM SPSS statistics, R studio
Microsoft Office: Word, Access, PowerPoint, Excel
Operating systems: Windows, Ubuntu Linux

Participation in projects

CIGA 20185007 Evaluation of Management Effectiveness of Protected Areas in Ghana (2018-2019), co-investigator.

Conferences/seminars

2017 January - 31st Conference on Hydrology, Washington State Convention Center, US
2017, 2018, 2019 Kostelic Inspiravoni, Czech Republic
2018 Euroleague for Life Sciences conference, Wageningen, The Netherlands
2020 January - 16th Conferences of Environmental Archaeology, CZU, Prague
2021 Global Biodiversity Conservation Conference, Prague, Czech Republic

Academic awards

2021 Excellent results in Ph.D. studies
2021 Rector's Award for publication in the 1st decile

Journal contributions and Review activities

2020-12-14 to present Editorial board member- Global Journal of Art and Social Science Education

- Reviews in Environmental Science and Bio-Technology
- Proposal review for National Research, Development, and Innovation Office (NRDI), Hungary NKFIH- 'DAAMBA? Domestic Anthropic Activity Markers of Bronze age settlements: A multiproxy methodological approach to understand household-related activities'

Publication activities

1. Papers in scientific journals with impact factor

Asare, M. O., Apoh, W., Afriyie, J. O., Horák, J., Šmejda, L., Hejcman, M., (2020). Traces of German and British settlement in soils of the Volta Region of Ghana. Geoderma Regional 21, e00270. https://doi.org/10.1016/j.geodrs.2020.e00270.

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Janovský, M., Karlík, P., Horák, J., Šmejda, L., **Asare, M. O.,** Beneš, J., Hejcman, M., (2020). Historical land use in an abandoned mountain village in the Czech Republic is reflected by the Mg, P, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Zr, and Sr content in contemporary soils. Catena. https://doi.org/10.1016/j.catena.2019.104347.

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Afriyie, J. O., **Asare, M. O.** (2020). Use of local ecological knowledge to detect declines in mammal abundance in Kogyae Strict Nature Reserve, Ghana. Environmental Management.

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Anning, C., **Asare, M. O.,** Junxiang W., Yao, G., Xianjun, L., (2021). Effects of physicochemical properties of Au cyanidation tailings on cyanide microbial degradation. Journal of Environmental Science and Health Part A Toxic/Hazardous Substances & Environmental Engineering. 56, 1-21. https://doi.org/10.1080/10934529.2021.1885259

Asare, M. O., Afriyie, J. O., (2021). Ancient mining and metallurgy as the origin of Cu, Ag, Pb, Hg, and Zn contamination in soils– A review. Air, Water, and Soil Pollution 232 (6) https://doi:10.1007/s11270-021-051664.

Afriyie, J. O., **Asare, M. O.,** Osei-Mensah, J., Hejcmanová, P., (2021). Evaluation of long-term law enforcement monitoring in a West African Protected area. Oryx 55, 1-7. https://doi:10.1017/S0030605320000228

Asare M. O., Afriyie, J. O., Hejcman, M., Jungová, M., K., Can wood ashes of commonly planted tree species in Ghana be applied as fertilizers? Waste and Biomass Volarization. https://doi.org/10.1007/s12649-021-01588-7

Afriyie, J. O., **Asare, M. O.,** Hejcmanová, P., (2021). Exploring the knowledge and perception of local communities on illegal hunting: long-term trends in a West African protected area. Forest 12(11), 1454. https://doi:10.3390/f12111454

2. Submitted papers

Asare M. O., Afriyie, J. O., Hejcman, M., Origin, distribution, and characteristics of

Archaeological Dark Earth soils- A review. Soil.

Asare, M. O., Apoh, W., Afriyie, J. O., Hejcman, Human altered soils: Impact of past settlement activities on the physicochemical attributes of Anthrosols in Northern Ghana by physicochemical analyses of soil. European Journal of Soil Science.

Anning, C., **Asare, M. O.,** Li, H-J., Zhao, J., Wang, L., Nyabire, A., Yao, G., Xianjun, L., Detoxification of cyanide-containing gold mine tailings by indigenous Aeromonas media strain C4. International Journal of Environmental Research and Public Health.

Afriyie, J. O., **Asare, M. O.,** Hejcmanova, P. Perception of law enforcement rangers about factors affecting their attitude to work in West African protected areas. Oryx

Jungova, M., **Asare M. O.,** Jurasova, V., Hejcman, M., (2021). Distribution of micro (Fe, Zn, Cu, and Mn) and risk (Al, As, Cr, Ni, Pb, and Cd) elements in the organs of *R. Alpinus L.*

3. *Papers in other scientific journals*

Asare, M. O., Afriyie, J. O., Hejcman, M. (2019). What constitutes Archaeo-anthrosols? Review on the effects of ancient anthropogenic activities on the chemical signatures of archaeological soils. African Journal of Soil Science.

4. *Papers in proceedings from scientific conferences*

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