

and properties determine the functioning of soils included in the concept of soil quality and health. By conventional soil classification systems, the development and characteristic of this anthropogenic diagnostic horizon provide a basis to classify it as Anthrosols (WRB, 2015; Holliday, 2017).

Activities that result in Anthrosols development are either deliberate (e.g., prescribed burning and field fertilization) or inadvertent, e.g., waste deposition-charred residues, bones, biomass ashes (McKenzie, 2006; Holliday, 2017). For example, fine-grained soil particles resulting from the decalcification of limestone mortar, destruction of clay buildings, and microcharcoals increase soil micropores, which support water and nutrient retention (Verheijen and Bostas, 2010). Additionally, the decomposition of organic waste can increase microbial count, which enhances the release of nutrients, e.g., N and C, in soils (Gupta et al., 2022). Analysis of organic waste can provide reliable inferences on the elemental impact on these soils. Anthrosols from settlement activities exhibit color modifications- often black, dark brown, and dark gray. However, high temperatures can cause a fast decomposition rate of organic matter (OM), which fades the color to light or looks unchanged, e.g., in the arid and semi-arid (Šmejda et al., 2017).

Large land sizes in the proximity of past settlements, e.g., in the tropics, frequently are weathered and inherently low in elements and OM (Asare et al., 2020a). Insufficient nutrient replacements in agricultural systems on arable lands with worse to moderate potential result in soil degradation. Approximately 25% of arable soils in Africa are acidic and deficient in essential plant nutrients, with toxic Al levels (Reich et al., 2001; McCann, 2005; FAO, 2015). Often this leads to the production of nutrient-imbalanced food crops and herbages. Thus, soils from deserted settlements must be used judiciously for arable purposes, due to the reportedly high nutrients, even after abandonment (Šmejda et al., 2018).

The fertility of Anthrosols from past settlement sites is not well-studied, especially in northern Ghana. In Ghana, the northern part represents locations with high temperatures, soil nutrient leaching, and low soil fertility (Bessah et al., 2022). High temperatures contribute to the poor preservation of the physicochemical properties of soils. The northern belt has a vast land area and numerous deserted settlements due to the decline in the indigenous population through urbanization. Therefore, research on the fertility of soils from past settlement sites is vital and becomes less relevant when vast lands are left ideal in an unprecedented world population growth and limited land resources. Management of lands is critical as the human population grows, and food scarcity stays paralleled by increased and concentrated consumption (Bizoza, 2014; Jayne et al., 2014).

Many studies on soil geochemistry from settlements over-

look the analysis of available nutrients, even on cultivated fields (Katrijn, 2014; Šmejda et al., 2018). However, the concentration of total elements in soils is of little value in diagnosing plants' elemental deficiencies (Tisdale et al., 1985) as a high portion is not accessible by plants. Thus, the releasability (available fraction of nutrient from total) and the level of plant-available nutrients are vital to complete the element requirements of plants.

The study evaluates the fertility of Anthrosols from an abandoned former settlement, Old Buipe, northern Ghana, by a set of measurable attributes and assesses their potential for sustainable agriculture using multi-analytical proxies. We ask the following questions: i) To what level can past human activities affect the fertility of Anthrosols? ii) Are the accumulated physical and chemical properties visible after abandoning the site and under harsh environmental conditions? iii) Can the physical properties of Anthrosols represent suitable proxy indicators of past habitation activities?

2 Materials and methods

2.1 Characterization of the study site

The Old Buipe village (8°45'0" N, 1°31'0" W) is in the Central Gonja district of the Savannah region, about 10 km north of the lower course of the Black Volta River and approximately 530 km north of Accra, the capital of Ghana. The 32-ha abandoned site generally is low-lying, slightly undulating, with an average altitude of 133 m above sea level. The study area has an average air temperature of 31°C to 40°C monthly, the lower range representing the relatively short wet season. The site is characterized by tropical semi-arid climatic conditions, with moderately dense herb and savannah woodlands (Canadian International Development Agency, 2011). The study area observes one rainy season, from July to October, with average annual precipitation of 1099 mm (Dickson and Benneh, 1995). Between December and March, the dominant wind is north-easterly, with the south-west covering the remaining months of the year and a relatively long spell of Harmattan from November to March. The dust-laden deposited during the Harmattan period is not under any significant influence (15 mm depth/ 1000 yrs.) from the Niger and Bodélé depression (Awadzi and Breuning-Madsen, 2009; Lyngsie et al., 2011).

The soil in the study area is savannah Ochrosols (*syn.* Chromic Lixisol) developed on upper Proterozoic (upper Voltaian) sedimentary limestone substrate (Brammer, 1962; ISSS/ISRIC/FAO, 1998) and not affected by loess.

2.2 Historical description of the study site

In the 1950s, the inhabitants of Old Buipe relocated to New

Buipe, about 12 km east, due to the construction of the main route (road and bridge) connecting southern and northern Ghana. Visible relics on the site include collapsed buildings made of clay and limestone (Figure S1). The name of the village appears more frequently in the early Islamic chronicles, which date a mosque and market in the 18th century AD (Wilks et al., 1986; Goddah, 2019).

The site was part of the crossroads at the southern extremity of the sub-Saharan trade routes between Niger and the forest areas of tropical forests (Genequand et al., 2016). Archaeological mounds in the site signified a progressive development with several wards and neighborhoods (Genequand and Apoh, 2017). The Old Buipe site has several shifts of settlements. First, from west to east around the 16th century AD, followed by a phase of expansion and densification. From the south to the north at the turn of the 19th century AD, the colonial period town flourished following the abandonment (Genequand et al., 2018).

2.3 Soil sampling

Five field allocations (A–E) within the settlement site were initially sampled. The sampled fields covered A–3.2, B–3.5, C–3.4, D–3.4, and E–5.4 ha. Field A represents an area of low mounds in the northern part, close to the former marketplace (Wetcher, 2016). Fields B and D are in the central complex with field B, in the south-eastern quadrant, where mounds reach their maximum height. Field D is in the north-western quadrant, one of the elongated mounds bordering the huge square courtyard. Field C corresponds to one of the low mounds with an irregular oval shape in the western part of the site. Physical relics recovered in fields A–D include potsherds, house floors, walls, botanical and faunal remains, and partially burnt palm kernel shells. Field E represents the south-western area, with few discoveries of potsherds, with the absence of building relics, considered control in this case (Genequand et al., 2018).

In each field, soil sampling covered the 0–0.3 m depth (arable layers) using a soil probe (Purchhauer type, core-diameter: 30 mm). We collected randomized soil samples to cover a wide variability of soils in all the fields: Fields A–11, B–15, C–10, D–10, and E–20. A single soil sample represents five mixed subsamples. The procedure average the short-range variation for reliable results and inferences. In total, we collected 66 soil samples for further analysis.

2.4 Sedimentological and morphological analyses

The description of the soil color was after Munsell's soil color chart. The study adopted the use of a laser particle size analyzer (Analysette 22 NanoTec) produced by Fritsch Company to determine particle distribution.

Usage: Initial diluted of 10 g soil sample in 1 L of particle-free H₂O, while the size distribution eventually measured as the suspension pumps around. The process ensures a random orientation of most particles relative to the laser beam. The analyzer calculates the particle size by measuring the angle of light scattered by the particles as they pass through the laser beam. Finally, the soil samples in all fields measured between 0.02 and 2000 μm (Ramaswamy and Rao, 2006).

We collected one sample from macroscopically divided layers (4 cm × 4 cm) of the 0–0.3 m depth from each field and dried them in paper boxes. Preparation of the soil sample included resin impregnation in a vacuum, six weeks of curing, and a thin section. All the collected samples were afterwards studied under a binocular and polarizing microscope (PPL, XPL, and OIL) at magnifications of 1–400×. The micromorphological description, however, was done after Stoops (2003).

2.5 Soil chemical analysis

Soil samples were oven-dried for 48 h, ground in a porcelain mortar, and homogenized with a 2-mm sieve. Soil pH (CaCl₂) was measured using a SenTix 41 electrode (Weilhem, Germany) in a 1:5 (w/v) solution (10 g of soil to 50 mL of solution) containing 0.01 mol L⁻¹ CaCl₂ suspension. The pH (H₂O) of the soil samples again was determined from a 1:5 ratio (soil/water) with the Voltcraft PH-100 ATC pH meter (pH 212) produced by I & CS spol s.r.o., Třebíč (Czech Republic). Organic C (OC) and total N concentrations of all the samples were determined using the Skalar Primacs SNC-100 analyzer manufactured by Skalar, Breda (Netherlands), which has been used successfully for the analysis of all categories of soil (Asare et al., 2020a).

We determined the total concentrations of P, K, Ca, Fe, Mn, Cu, Zn, Al, Si, Sr, Rb, As, Ni, Pb, and Zr using the pXRF (portable X-ray fluorescence) analyzer-Delta Professional, manufactured by Olympus Waltham (USA), in the soil Geochem mode (Canti and Huisman, 2015).

The instrument measures near-total to total concentrations of Mg to U, performed for 1 min, with 30 s of a 10-kV beam and 30 s of a 40-kV beam. All measured samples intermittently were triplicated, and the final values represent the arithmetic average with 30 s of a 10-kV beam and 30 s of a 40-kV beam. Of all the identified elements, Pb concentration was below the detection limit of the device in only two cases at field B. We omitted elements below the detection limit or detected only a few times.

Extraction of plant-available P, K, Ca, Mg, S, Mn, Fe Cu, and Zn followed the Mehlich-3 reagents procedures (Mehlich, 1984), and the concentrations were well-determined by inductively coupled plasma mass spectrometry

(ICP-MS; Agilent 7700 × , Agilent Technologies Inc., Santa Clara, CA, USA). 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.

We determined the cation exchange capacity (CEC) of all the soil samples according to Harada and Inoko (1980). Usage: 200 mg of each homogenized soil sample was put into a sintered glass filter fitted with a rubber tube with a pinchcock. Add 25 mL of 0.05 N HCl solution, stir with a glass rod, and allow to stand for 20 min. Open the pinchcock and filter using an aspirator and add 25 mL of 0.05 N HCl solution and refilter. Samples are washed with distilled H₂O until the washing is free of chloride. Close the pinchcock, add 25 mL of 1 N Ba(OAc)₂ solution, adjust to pH 7, and stand overnight. After filtration, add another 25 mL of 1 N Ba(OAc)₂ solution, filter, and wash the sample with distilled H₂O (about 150 mL). Filtrates were combined, washed, and titrated up to inflection point with standard 0.05 N NaOH solution using a Metrohm potentiometer. We performed additional blank titration with the same quantity of 1 N Ba(OAc)₂ solution. The difference between the two titration values equated with the proton release from the sample, which gives the CEC. Electrical conductivity (dS m⁻¹) was measured in the supernatant liquid of soil/water suspension (1:2) with a conductivity bridge (Richards, 1954).

2.6 Elemental analysis of organic materials (partly burnt palm kernel shells)

Partly burnt and broken palm kernel shell samples often distributed in the soils also were analyzed for total element concentration. The nut samples were thoroughly washed with deionized water to remove soils and other particles and oven-dried for 24 h. Samples were milled manually in a mortar due to their hardness and homogenized through a 2-mm sieve. We divided the powdered samples of the palm kernel nuts to obtain four replicates. The total concentrations of P, Ca, Mg, Na, K, Fe, and Zn were determined by *Aqua regia* extraction procedures (3 mL HCl and 1 mL HNO₃) followed by ICP-MS (Agilent 7700 ×).

2.7 Validity of pXRF

To calibrate the pXRF, we used certified Quality Assurance Material (QCM: Matrenal 31 $n = 10$, clay-loam soil, Analytika Ltd., Czech Republic) certified for the concentrations of Mn, Cu, Zn, Cr, Ni, As, Cd, and Pb. We digested QCM by total chemical extraction procedure with *Aqua regia* (3 mL HCl and 1 mL HNO₃), International Organization for Standardization USEPA 3052, Santa Clara, California (USA), followed by Inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700 × , Agilent Technologies Inc., Santa Clara, CA,

USA). The empirical standard used is certified for calibration of total element concentrations: using a wet chemistry system (Bernick et al., 1995; USEPA, 2007; Croffie et al., 2020). We obtained calibration curves between concentrations of each element obtained with pXRF and *Aqua regia* ICP-MS. As a relatively new approach in the study area, we evaluated the reliability of the data obtained by pXRF by randomly selecting five soil samples from each field. We extracted the samples by *Aqua regia*, and the total concentrations of P, K, Ca, Fe, Mn, Cu, Zn, Si, Al, As, and Pb also were determined by ICP-MS.

The calibration of pXRF for the elements obtained from the analysis of QCM revealed a significant correlation, $r = 0.87$ to 0.96 , $p < 0.01$, and recovery $> 90\%$ (Table S1). For the reliability of pXRF in the analysis of the studied samples, we obtained significant positive correlations – $r = 0.60$ to 0.99 , $p < 0.01$ for the control elements with *Aqua regia* ICP-MS (Figs S1–S3). Hence, the pXRF has enough precision for the analysis of soil total elements.

2.8 Statistical analyses

Statistical evaluations of all data were performed with STATISTICA 13.4 software). Using the Shapiro-Wilk W normality test, the data sets were normally distributed, with homogeneity of variance. We fitted a one-way ANOVA model to test the differences in the chemical properties of the soils in all the fields. In the case of significant ANOVA results, we determine the differences in variables between the different fields using Tukey's HSD test. To evaluate the distribution and relationships between the total elements and fields in the site, we used principal component analysis (PCA). Linear relationship among the concentration of total elements obtained by pXRF and *Aqua regia* ICP-MS and CEC and OC verified by Pearson's correlation test.

We estimated the releasability (fraction of elements available for plants from the total) as

$$\text{Releasability}(R) = \frac{P_{av}}{T_{ot}} \quad (1)$$

where, P_{av} = Concentrations of plant-available,
 T_{ot} = Concentration of total elements (obtained by pXRF)

3 Results

3.1 Sedimentological and morphological characteristics

The main soil morphological characteristics are in Table 1. The sedimental records exhibit some variability in soil physical properties in different fields, even though they are the same soil. The variation in soil pore size is consistence with the distribution of grain sizes and microcharcoal in fields A–D compared to E.

The high fraction of clay particles is well-visible in locations with clay mounds, which can contribute to decreased pore size and subsequent nutrient absorption. The percentage accumulation of charcoal varies in fields A–D (5%–15%) and is absent in E, which contributes to the different color hues of the soils. The amounts of potsherds ranging from

< 5%–30% in all the fields and dirty clay coating only in A–D relate to the intensity of human activities.

3.2 Bulk chemical composition

There was a significant effect of fields on pH, organic C

Table 1 Variability of grain size distribution and other morphological properties of the Anthrosols.

Field	Description	Pores	Grain size	Matrix ^a	Organic matter [OM]	Pottery density	Charcoal	Other pedo-features
A	An area with low mounds in the northern part	Intergrain spaces	C/F(50 μ m) = 70:30; C/F(100 μ m) = 1:99, clay loam	7.5YR 5/2, Dark-brown	Amorphous up to 15%	25% of local pottery fragments	Yes, rare up to 5%	Dirty clay coating, local content of dirty clay
B	South-eastern quadrant, mounds reach maximum height with a slight inclination	Intergrain spaces	C/F(50 μ m) = 70:30; C/F(100 μ m) = 5:95, clay loam	7.5YR 4/3, Dark-brown	Amorphous up to 35% locally lump of OM	15% of local pottery fragments	Few, up to 10%	Dirty clay coating, local content of dirty clay
C	Low mounds in the western part	Intergrain spaces	C/F(50 μ m) = 70:30; C/F(100 μ m) = 3:97, clay loam	7.5YR 5/2, Dark-brown	Amorphous up to 15% locally lump of OM	30% of local pottery fragments	Yes, rare up to 5%	Dirty clay coating, local content of dirty clay
D	North-western quadrant elongated mounds	Intergrain spaces	C/F(50 μ m) = 70:30; C/F(100 μ m) = 3:97, clay loam	7.5YR 4/3, Dark-brown	Amorphous up to 25% locally lump of OM	25% of local pottery fragments	Few, up to 15%	Dirty clay coating, local content of dirty clay
E	South-western area with no mounds and building relics but slightly inclined	Channels and vughs up to 10%	C/F(50 μ m) = 85:15; C/F(100 μ m) = 70:30, sandy clay loam	7.5YR 5/4, Brown, Bf locally granostriatic	Amorphous up to 10% locally, rarely lumps of OM	<5% of local pottery fragments	No	Coating, hyper-coating

a, Indicates Munsell soil color chart.

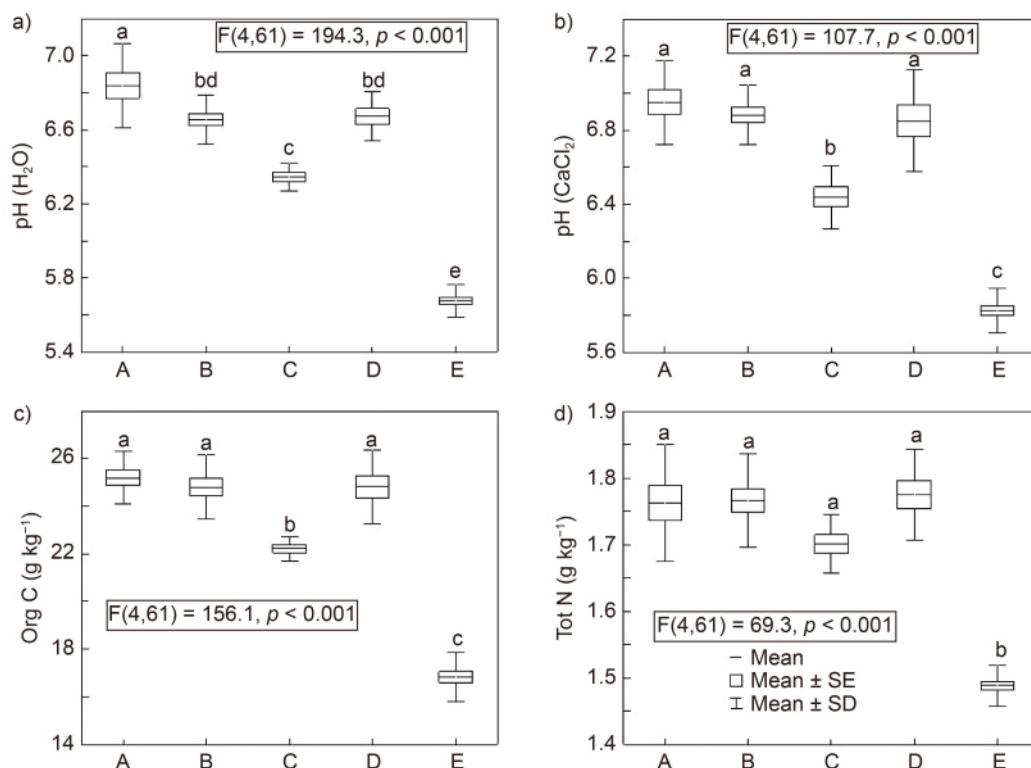


Fig. 1 Effects of past human/habitation activities on the level of a) pH_[H₂O], b) pH_[CaCl₂], and concentrations of c) organic (org) C and d) total (tot) N of the Anthrosols in fields A–E of the abandoned settlement. The F and p values were obtained by one-way ANOVA. Using Tukey's HSD test, the mean values of the fields with different letters indicate a significant difference.

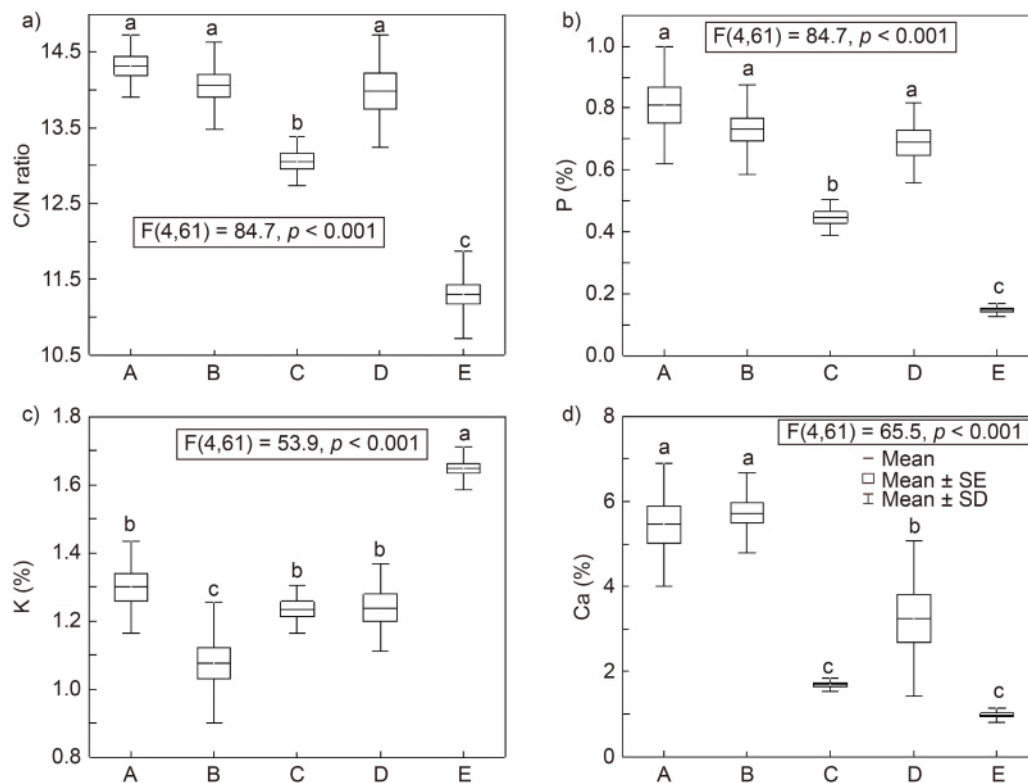


Fig. 2 Effects of past human/habitation activities on a) C/N ratio and concentrations of total b) P, c) K, and d) Ca of the Anthrosols in fields A-E of the abandoned habitation. The F and p values were obtained by one-way ANOVA. Using Tukey's HSD test, the mean values of the fields with different letters indicate a significant difference.

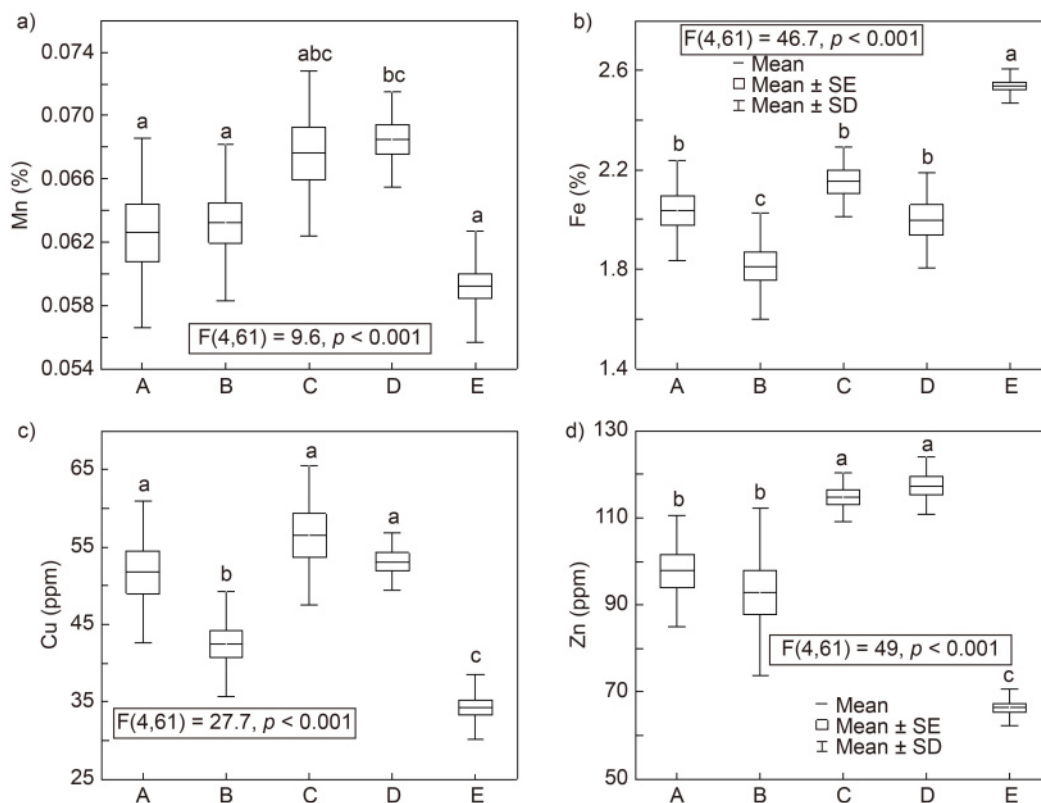


Fig. 3 Effects of past human/habitation activities on the concentrations of total a) Mn, b) Fe, c) Cu, and d) Zn of the Anthrosols in fields A-E of the abandoned habitation. The F and p values were obtained by one-way ANOVA. Using Tukey's HSD test, the mean values of the fields with different letters indicate a significant difference

(OC), N, C/N ratio, and the concentrations of total elements (Figs. 1–4 and Table S2). Relatively similar pH (H_2O and $CaCl_2$), i.e., slightly acidic to relatively neutral reactions, indicating a state of the soil sorption complex and high saturation by cations (Figs. 1a and b). Except for Ca and Mn, there was a significantly higher C/N ratio and concentration of OC, total N, P, Ca, Cu, and Zn in fields A–D compared to E (Figs. 1c and d, 2a, b, and d, and 3c and d). The OC and total N, P, Ca, Cu, and Zn concentrations were approximately 50%–80%, 22%–30%, 25%–65%, 10%–45%, 15%–35%, and 30%–55%, respectively, higher in fields A–D compared to E. In contrast, total K and Fe concentrations were significantly higher in field E than in A–D (Figs. 2c and 3b), representing 30%–50% K and 40%–70% Fe increases.

The concentrations of risk elements (Ni, Pb, and As) pose no toxicity threat to the soil and plant ecosystem – 50, 100, and 20 $mg\ kg^{-1}$, respectively, below the permissible limit in agricultural soils (Table S2; Chiroma et al., 2014). Concentrations of total Rb, Sr, and Zr in all the fields, are considered irrelevant for plant nutrition (Table S2).

Table 2 shows the mean concentration of plant-available nutrients. Available P, K, Ca, Mg, S, Mn, Fe, Cu, and Zn concentrations were significantly larger in fields A–D than in E. The concentration of macro elements ranged from (in

$mg\ kg^{-1}$) 246–686 P, 417–481 K, 5240–9846 Ca, 184.7–250.4 Mg, 33–83.7 S in all the fields. Furthermore, the concentration of microelements available for plants (Mn, Fe, Cu, and Zn) was from ($mg\ kg^{-1}$) 145.9–233, 300–393, 13.5–21.5, and 20.8–31.6, respectively. The available P, K, Ca, Mg, S, Mn, Fe, Cu, and Zn were up to 2.8, 1.2, 1.9, 1.5, 2.6, 1.7, 1.3, and 2 times greater in fields A–D than in E.

The CEC was significantly higher in fields A–D (45.31–33.8 $me/100\ g$) compared to E (8.77 $me/100g$) (Fig. 5a). Additionally, the EC was 0.28–0.36 $dS\ m^{-1}$ in all the Anthrosols, a condition indicating no or less salinity (Fig. 6b).

3.3 Element releasability

The fraction of total P, K, Ca, Mn, Fe, Cu, and Zn available to plants ranged from 0.09–0.12, 0.26–0.38, 0.15–0.29, 0.24–0.35, 0.012–0.02, 0.32–0.41, and 0.24–0.32, respectively (Table 3). The releasability of P, Ca, and Zn was slightly larger in field E than in A–D and vice versa in the case of K and Mn.

3.4 Elemental analysis of organic material

Analysis of the partially burnt palm kernel nut (remains of

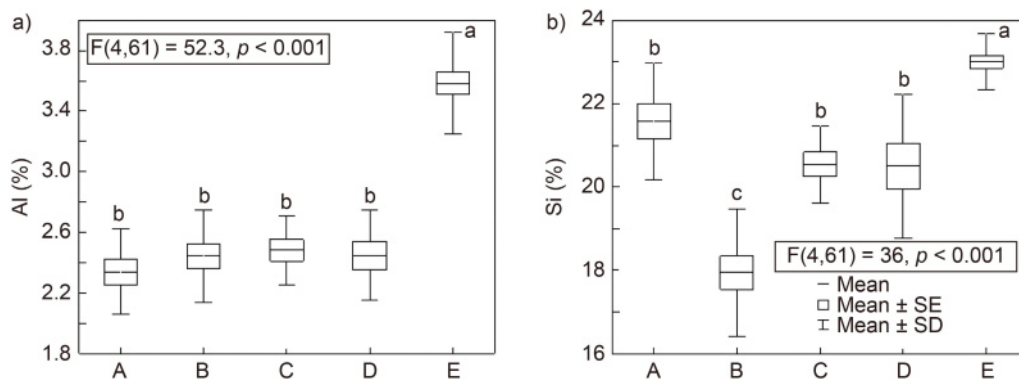


Fig. 4 Effects of past human/habitation activities on the concentrations of total a) Al and b) Si of the Anthrosols in fields A–E of the abandoned habitation. The F and *p* values were obtained by one-way ANOVA. Using Tukey's HSD test, the mean values of the fields with different letters indicate a significant difference.

Table 2 Concentration (mean \pm SD) of plant-available elements in the studied site.

Field	A	B	C	D	E	Mean	<i>p</i> -value
P ($mg\ kg^{-1}$)	684 \pm 6.2a	627 \pm 14.1b	393 \pm 8.4c	616 \pm 19.3b	247 \pm 11.6d	515.4	0.001
K ($mg\ kg^{-1}$)	482 \pm 17a	421 \pm 5.7b	451 \pm 10.2c	462 \pm 10.1d	412 \pm 10.1e	445.6	0.001
Ca ($mg\ kg^{-1}$)	9699 \pm 57a	8517 \pm 46.8b	9226 \pm 20.5c	9850 \pm 42.6d	5263 \pm 145.1e	8511	0.001
Mg ($mg\ kg^{-1}$)	252 \pm 12.6a	217 \pm 7.3b	231 \pm 11.4c	246 \pm 5.4a	171 \pm 9d	223.4	0.001
S ($mg\ kg^{-1}$)	84 \pm 2.4a	70 \pm 3.2b	58 \pm 4.6c	73 \pm 2.8b	33 \pm 3.6d	63.6	0.001
Mn ($mg\ kg^{-1}$)	213 \pm 6.1a	227 \pm 4.7b	195 \pm 8.3c	232 \pm 5.9d	143 \pm 7.1e	202	0.001
Fe ($mg\ kg^{-1}$)	374 \pm 9.6a	367 \pm 3.3a	367 \pm 6a	392 \pm 9.8b	302 \pm 91c	360.4	0.001
Cu ($mg\ kg^{-1}$)	19.9 \pm 2.4ac	16.6 \pm 2b	17.6 \pm 2.2b	21.3 \pm 2.5ac	13.8 \pm 1.9d	17.8	0.001
Zn ($mg\ kg^{-1}$)	26.8 \pm 1.7a	25.1 \pm 0.6a	27.4 \pm 2.5a	31.5 \pm 2.4b	20.7 \pm 1.4c	26.3	0.001

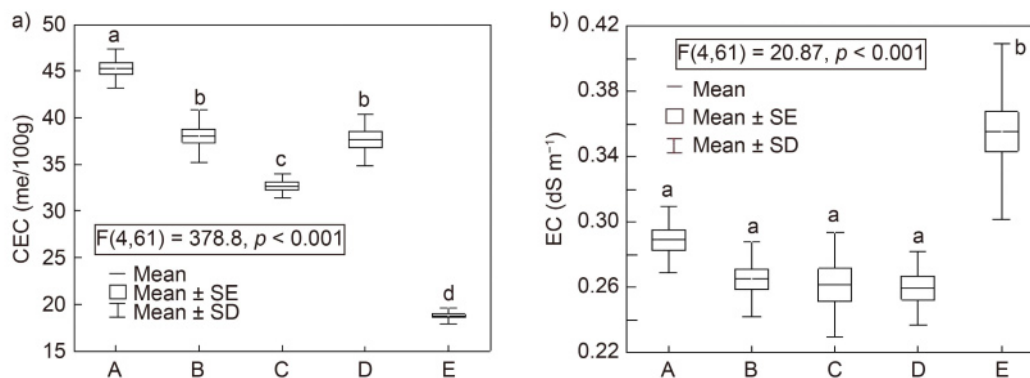


Fig. 5 Effect of past human activities on a) cation exchange capacity (CEC) and b) electric conductivity of Anthrosols from different fields. The F and *p* values were obtained by one-way ANOVA. Using Tukey's HSD test, the mean values of the fields with different letters indicate a significant difference.

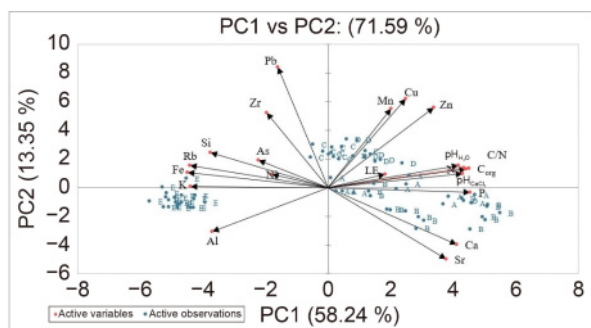


Fig. 6 Ordination diagram showing the first two principal components (PC1 vs PC2) where the red and blue dots represent active variables and observations, respectively.

Table 3 The releasability (bioavailable fraction of the total element) of P, K, Ca, Mn, Fe, Cu, and Zn in the fields A–E.

Field	P	K	Ca	Mn	Fe	Cu	Zn
A	0.09	0.037	0.18	0.34	0.02	0.36	0.27
B	0.09	0.038	0.15	0.35	0.02	0.37	0.26
C	0.09	0.038	0.19	0.29	0.02	0.32	0.24
D	0.09	0.038	0.23	0.35	0.02	0.41	0.26
E	0.12	0.26	0.29	0.24	0.012	0.39	0.32

organic waste) revealed concentrations of (in mg/100 g) P 5.41 ± 0.02 , Ca 21.47 ± 0.01 , Mg 28.29 ± 0.54 , Na 34.83 ± 0.07 , K 20.30 ± 0.023 , Fe 1.14 ± 0.08 , and Zn 2.82 ± 0.30 .

3.5 Correlation and PCA analyses

The pattern of similarity between the observations and the variables and the number of components were considered based on their eigenvalues > 1 , loading factors ≥ 0.53 , and percentage of variability $> 5\%$ (Table 4). In the biplot position of the PCA (Fig. 6), the PC1 explained 58% of the total cumulative variance and 12 of the eigenvalue, which was predominantly dominated by positively and strongly associated variables such as $\text{pH}_{[\text{H}_2\text{O}]}$, $\text{pH}_{[\text{CaCl}_2]}$, $\text{C}_{(\text{org})}$, N_t (total nitrogen), C/N ratio, P, Ca, Zn, and Sr and negatively asso-

Table 4 The principal components (PCs) and their loading factor, eigenvalues, and variabilities (%).

Variables	PC1	PC2	PC3	PC4
$\text{pH}_{[\text{H}_2\text{O}]}$	0.920	0.141	-0.257	0.073
$\text{pH}_{[\text{CaCl}_2]}$	0.912	0.101	-0.221	-0.032
Org C (g kg^{-1})	0.955	0.139	-0.181	0.060
Tot N (g kg^{-1})	0.934	0.136	-0.058	0.044
C/N ratio	0.884	0.157	-0.259	0.067
P (%)	0.963	-0.030	-0.178	0.012
K (%)	-0.931	0.009	-0.327	-0.034
Ca (%)	0.871	-0.398	-0.214	0.101
Mn (%)	0.428	0.560	0.113	-0.150
Fe (%)	-0.950	0.110	-0.135	0.068
Al (%)	-0.781	-0.308	0.142	-0.174
Si (%)	-0.796	0.251	-0.493	0.014
Cu (ppm)	0.527	0.631	-0.044	0.179
Zn (ppm)	0.716	0.569	0.188	-0.051
Rb (ppm)	-0.933	0.158	-0.254	-0.035
Sr (ppm)	0.800	-0.503	-0.170	0.168
Zr (ppm)	-0.416	0.529	-0.519	-0.056
As (ppm)	-0.468	0.194	0.321	0.625
Ni (ppm)	-0.379	0.095	0.136	0.663
Pb (ppm)	-0.341	0.855	0.186	-0.121
LE	0.390	0.095	0.837	-0.176
Eigenvalue	12	3	2	1
Variability (%)	58	13	9	5

Bolded values indicate a strong positive or negative correlation.

ciated with K, Al, Fe, Si, and Rb variables. The second PC2 explained about 13% of the total cumulative variance and 3 of the eigen value, primarily dominated by positively associated variables Mn, Cu, Zr, and Pb. Variability of the distribution of elements is associated with fields.

There was a significant positive correlation between CEC and organic C ($r = 0.92$, $p < 0.001$; Fig. S5a). The level of

CEC indicates a low level of cation (e.g., Ca^{2+} , Zn^{2+} and Cu^{2+}) leaching ($r = 0.59 - 0.78$, $p < 0.001$; Fig. S5 b-d).

4 Discussion

Anthropogenic indicators of the Anthrosols are well visible by the improved physical and chemical characteristics, according to the estimated fertility indices, including pore size distribution, OM, pH, C/N ratio, CEC, and nutrient concentrations in different fields. These modifications are still recognized even after the site abandonment. The different levels of accumulation and retention of nutrients are a function of the types of activity, intensity, and previous land use. Although harsh climatic conditions cause adverse effects on soil ecosystems, the physical and chemical signatures generated by past human activities are strong to remain in the Anthrosols to date.

The accumulation of OM and the availability of nutrients to plants is a topic of interest as the entire area often represents weathered soils with poor nutrients. Hence, optimal enrichment of the Anthrosols due to activities of former settlements can serve as a model for sustainable agricultural production due to conservative practices, e.g., deposition of organic waste, biomass ashes, and field fertilization with excrement.

4.1 Characterization of the fertility of Anthrosols

Although the studied site has the same soil, diverse anthropogenic activities contributed to different modifications according to good predictive indicators of fertile soils.

Pore size: The fertility of the Anthrosols partly relates to the high micropore surface areas of the clay obtained from the standing earthen walls and the sediments resulting from their collapse (Genequand et al., 2016). The influence of micropore size of soils in fields A–D over E contributed to high retention of C, total N, and P and all the studied available elements (Nicosia and Devos, 2014; Asare et al., 2020b). Settlement sites also are noted for clay importation in producing artifacts, evident in the different amounts in the fields. The intergrain pedo-materials in the soils, especially in fields A–D, act as an adhesive to decrease macropores. Microcharcoal increases the homogeneity in the pore distribution, which contributes to water and nutrient retention (Bradl, 2004; Conte et al., 2014). The alteration in charcoal fraction and consequently in the porosity of the soil can affect the physics and hydraulic properties (Conte et al., 2014).

Organic matter: The decomposition of OM influenced the color of the Anthrosols. These locations have relatively high percentages of charcoal, which predominantly contributed to the dark-brown color. Charcoal presence

indicates human-induced fires set for burning or cooking. However, the absence of black soil in fields A–D may partly result from the high decomposition rate of OM from high temperatures, especially the extended duration of harmattan. The OM content contributes to microbial count, which enables the dissolution of the nutrients hence, their bioavailability to plants (Sánchez et al., 2017). Charcoal, as organic waste, contributes to the supply of liable C and other nutrients –K, Mg, Ca, and P (Paramisparam et al., 2021). Organic matter content is consistent with the concentration of C and total N in the study site and increases CEC. Different organic materials reflect varying concentrations of nutrients. For example, the nut of palm, usually used for oil preparation, exhibited a high content of macro/micronutrients. Thus, the content of OM in each field is a function of the kind of human activities. For instance, the highest amount of OM in field B, previously known as a midden area, has high amounts of faunal remains. Field B, identified with a grave pit, can result in the release of Ca and P (Asare et al., 2020c). The extent of human modifications is visible from the variation between morphological properties in fields A–D compared to E, implying that the enhanced physical characteristics of the soils are possible proxy indicators for determining past human habitation and inputs.

Soil reaction: The higher concentration of OC, total N, Ca, and Mn, and plant-available K, Ca, Mg, and Mn, microcharcoal, and OM contributed to the relatively neutral soil reaction in fields A–D compared to E. The slightly acidic soil reaction in field E was due to a higher concentration of available K compared to pH values of 5 (topsoil) and 4.1 (subsoil) of the same soils without past settlement activities (Brammer, 1962). Generally, the reduced acidity is also associated with the deposition of biomass ashes, organism respiration, and decomposition of OM (Falcão et al., 2009). Increased pH and stability of high OM content provide optimum conditions for the persistence of elements, high CEC, and an adequate C:N ratio for mineralization, especially in fields A–D. Reduced soil acidity promotes microbial count (Mhete et al., 2020).

CEC and EC: Soils with high CEC change pH much more slowly under management. Soil OC plays a vital role in providing sites for cation exchange. A higher OC level in soils provides a higher CEC than others with low values (Glaser, 2007). On low-CEC soils (< 5 meg/20000g), e.g., leaching of cations occurs and vice versa (Fig. S5b–d). Charcoal has a greater specific surface area and negative charge density per unit of surface area. Thus, high CEC values result from high charge density per C unit (Liang et al., 2006). A significant positive correlation between CEC and soil OC (Fig. S5a) shows the vital role that OC plays in CEC. Crop production under less influence of salinity (salt in soil solution) will allow N uptake and contributes to high

plant growth and effective reproduction (Hussain et al., 2019; Fig. 6). High levels of salts in soil water taken by plants may flow back into the soil through the root, resulting in dehydration of plants, yield decline, or death of plants.

Element composition: Anthrosols in fields A–D were substantially modified by past human activities, compared to E, according to the highest concentrations and distribution of OC, total (N, P, Cu, Zn, and Sr; Table 4), and plant-available P, K, Ca, Mg, S, Mn, Fe, Cu, and Zn. The enrichment by specific nutrients, e.g., total P, Ca, and Zn, provides evidence of the activity intensity of fields A–D. The distribution of nutrients in the fields partly relates to distinct functional units (Oonk et al., 2009). The pattern of increases of C, total, N, P, Ca, and available elements support the historic land use of fields A, B, and C. For example, field A represented areas containing biomass ash and humus, with significant artifacts, including ceramic pots, noted as an occupational area. Similarly, in the case of field C, high contents of Cu and Zn related to a high fraction of ceramic pots, many of them almost complete (Genequand et al., 2016). Concentrations of OC were 17–26 g kg⁻¹ in all fields compared to 1.2–4.7 g kg⁻¹, considered natural values (Asiamah, 1993). Total N ranged from 1.5–1.8 g kg⁻¹ in fields A–E and 0.3–0.6 g kg⁻¹ as values for background soils (Asiamah, 1993). In contrast to the studied Anthrosols, many arable layers of lixisols are thin with a low amount of OM, C, N, and other elements, especially with age (Finkl, 1999; WRB, 2015).

The mean concentrations of 515.4 mg kg⁻¹ available P in all the fields indicate anthropogenic input compared to approximately 25 mg kg⁻¹, considered value on past sites with no mark of settlement activities (Hejzman et al., 2013b). Usually, available P concentrations from ancient settlements and arable fields with the deposition of biomass ash range from 90 to 12300 mg kg⁻¹ (Hejzman et al., 2011, 2013a; Hejzman and Hejzmanová, 2015). The P in the Anthrosols was higher than the level for crops and vegetables with high P (100–200 mg kg⁻¹) requirements (Šrek et al., 2010). The releasability of P in field E was approximately 1.4 times greater than A–D. The releasability of P (0.09%) in fields A–D compared to 0.12% in E (less human impact) indicates that P signatures in localities with previous human habitations are less mobile and last longer in soils. Hence, this accounts for low P concentrations in most natural soils. Even though P releasability is highest in field E, the portion taken by plants is still comparatively lesser given the lowest total and plant-available concentrations. Also, this is similar in the case of Ca, K, and Zn. Moreover, anthropogenic input of Ca in the past settlement was releasable but probably high in soils with lesser activities observed from the value of releasability from field E. Releasability of Ca was approximately 1.3–2 times greater in field E compared to A–D,

which contributes to its stability in soils from abandoned settlements. Moreover, the high releasability of Ca in field E relates to the slightly acidic condition associated with high solubility.

As an essential micronutrient, the concentration of M-3 Mn was within levels (30–500 mg kg⁻¹) in herbage growing on agricultural soils (Clarkson, 1988) but can increase in very acidic conditions. Meanwhile, there was a relatively high releasability of Mn (0.24 to 0.35) compared to other elements (e.g., P, K, Ca, and Fe). Hence, this can increase the available Mn concentration for other higher plants. Although the concentrations of Cu and Zn are the lowest among the available nutrients, they have a comparatively high releasability to partly compensate for deficiencies in the Anthrosols for the use of arable land. Notwithstanding the recorded availability of Cu as a nutrient (mean value of 17.1 mg kg⁻¹) for crops in this study were within the most recorded (5–20 mg kg⁻¹) without physiological impairment (Marschner, 1995).

Although we confirmed minimal human influence in field E, it recorded the highest total K, Fe, Al, and Rb in field E compared to A–D. Potassium is one of the elements with the highest concentration in biomass ashes (Zajac et al., 2018; Asare et al., 2022). In past settlements, these connect with the fertilization of crofts and arable fields (Hjulstrom and Isaksson, 2009; Vassilev et al., 2013). However, the slight inclination of field E partly supports the eroding of topsoil (Bertol et al., 2003). In field E, the releasability of K was 7 times higher than in A–D. The marginally low K releasability in fields A–D indicates that K was released slowly from biomass ashes and other organic wastes, even with the recorded high total and available concentrations.

The impact of past human activities on the development of the nutrient-rich Anthrosols renders it more suitable for herbage and crop production compared to the low absolute level of nutrients and cation retention by Lixisols unaffected by past settlement activities making recurrent inputs of mineral fertilizers a precondition for cultivation (FAO, 2015).

5 Conclusions

The comparative exploratory study revealed the impact of past settlement activities on the development of Anthrosols with unique physical and chemical characteristics. Although harsh environmental conditions such as high temperatures, rainfall patterns, and harmattan affect the physical and chemical parameters, signatures generated from past human activities are strong enough and can remain in soils for a long time after site abandonment.

The studied Anthrosols represent a modification of physical characteristics (such as improved soil porosity, texture, and

color) due to the inclusion of clay particles, microcharcoal, and organic waste. Human activities also contributed to reduced soil acidity, low salinity, high accumulation, and distribution of available (P, K, Ca, S, Mn, Fe, Cu, and Zn), OM, OC, and total (N, P, K, Ca, Mn, Si, Cu, and Zn) nutrients.

The high OM, OC, and microcharcoals contributed to an optimum C/N ratio and CEC suitable for the retention and mineralization of the elements. The distribution and level of total and plant-available nutrients in different fields indicate the type and intensity of human activity. The distribution of specific nutrients relates to land management of the site and the identification of physical extremities. The level of releasability of P, K, Ca, Mn, Fe, Cu, and Zn in the Anthrosols explain their stability and long-lasting in past human habitations. The improved physical characteristics of soils are also suitable proxy indicators of past human habitations in addition to elemental enrichment. We conclude that past settlement sites represent fertile Anthrosols (according to fertility indices: OM level, OC, pore size, pH, C/N ratio, CEC, EC, nutrient concentration, and releasability) suitable for arable fields and can promote sustainable agricultural management. In locations with extreme climatic conditions, such Anthrosols need cover crops to prevent fast depletion of nutrients. Past settlement activities play a tremendous role in influencing nutrient availability after abandonment.

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Conflict of interest

The authors have no competing interests to declare that are relevant to the content of this article.

The authors declare that they agreed to participate in the present study, and they read and agreed to the publication of the present paper. Data available on request from the authors.

Author contributions

Conceptualization: Michael O. Asare; Methodology: Michael O. Asare, Wazi Apoh; Formal analysis and investigation: Michael O. Asare, Wazi Apoh, Dinkayehu Alamnie Asrade; Writing - original draft preparation: Michael O. Asare, Wazi Apoh, Jerry Owusu Afriyie; Writing—review and editing: Michael O. Asare, Wazi Apoh, Jerry Owusu Afriyie; Funding acquisition: Michael O. Asare, Jiřina Száková; Resources:

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Electronic supplementary material

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