

RESEARCH ARTICLE

Could oxalate-extractable phosphorus replace phosphorus fractionation schemes in soil phosphorus prospecting?—A case study in the prehistoric Milseburg hillfort (Germany)

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Abstract

A geoarchaeological soil phosphorus (P) prospection is used to identify a gate within the prehistoric rampart of the Milseburg hillfort (Hesse, Germany). This study compares the application of a P fractionation scheme and P extraction with ammonium-oxalate. We hypothesized that oxalate-extractable P (P-ox) and the related degree of P saturation (DPS) could replace the more expensive and time-consuming fractionation schemes for geoarchaeological investigations. Comparing the results, the P fractionation helped to verify the existence of another section of the prehistoric ramparts and to identify the location of a gate within it. It also helped to discover the archaeologically relevant soil depths in the investigated area. This information could not be retrieved from the P-ox data alone. Soil P-ox contents and DPS values are relatively unspecific with regard to prehistoric land use. However, DPS at least indicates settled versus unsettled areas. Still, the results of the P fractionation more clearly delineate Iron Age land use areas including settlement, non-settlement, rampart, and rampart gap (probable gate). Thus, in geoarchaeological contexts, this method seems to be preferable to a singular P-ox extraction. However, for better results, P-ox determination could be integrated into a P fractionation scheme.

KEYWORDS

Milseburg, oxalate-extractable phosphorus, phosphorus fractionation, phosphorus saturation, soil phosphorus prospection

1 | INTRODUCTION

Soil phosphorus (P) prospecting is based on the assumption that past land use may have accumulated P in soils (e.g., by urine/feces, food waste, ashes; Arrhenius, 1955; Weihrauch, Brandt, & Opp, 2016a; Weihrauch, Makowski, Söder & Opp, 2016b). This surplus can be detected by geochemical soil analyses. There are several analytical procedures available for geoarchaeological soil P prospecting. Holliday and Gartner (2007) provide an extensive but incomplete compilation of these procedures. Regarding this list, one of the major

issues arising when planning a soil P prospection is which method to choose. The decision is even more difficult. Traditionally, soil P prospection techniques are, as a rule, based on one analytical P determination method per soil sample (e.g., Bakkevig, 1980; Kondratiuk & Banaszuk, 1993; Provan, 1971). Initially, P fractionations found only limited appeal with archaeologists (Eidt, 1977; Holliday & Gartner, 2007; Woods, 1977). However, recent applications have proven useful (Weihrauch et al., 2016a, 2016b).

P fractionation extracts several subsets (fractions) of soil P from one soil sample (Hedley, Stewart, & Chauhan, 1982; Tiessen & Moir, 2006),

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while a regular P prospection only determines one P fraction from each sample. As a result, P fractionation generates more data and information. For instance, Weihrauch et al. (2016a) used P fractionation to determine to what extent modern P fertilizer application had distorted soil P contents and how they could still be used for geoarchaeological conclusions. However, P fractionations take more time and money, because soil samples are not just analyzed once but several times. Furthermore, different fractions may represent different processes and spatio-temporal dynamics within the soils (Weihrauch, 2018). Thus, P data can be hard to interpret, especially for archaeologists (Holliday & Gartner, 2007). Moreover, not all P fractions are archaeologically relevant. For these reasons, an alternative analytical procedure may be warranted.

Archaeologically relevant P was introduced into the soils secondarily. Scientists can nowadays determine this anthropogenically introduced P only because the soils retained it by chemical bonding. Different processes of P bonding to the soil exist (Weihrauch & Opp, 2018), but sorption might be the most important process for the retention of archaeologically relevant P. Thus, targeted detection of sorbed P would be favorable for geoarchaeological investigations.

Schwertmann (1964) proposed an extraction with ammonium-oxalate to determine easily soluble pedogenetic iron (Fe) oxides within soil samples. This method may also be used for the determination of P (Binner, Dultz, & Schenk, 2015; Prietzel, Klysubun, & Werner, 2016) because pedogenetic oxides of Fe and aluminum (Al) are regarded as the major P sorption agents within soils (Barber, 1995; Weihrauch & Opp, 2018). Thus, oxalate-extractable P (P-ox) would indicate the amount of P stored within a soil by sorption processes (Eichler-Löbermann, Köhne, & Köppen, 2007; Leinweber, Meissner, Eckhardt,

& Seeger, 1999). Moreover, by detecting P-ox, a soil's P sorption capacity (PSC, the total amount of sorbable P) and its degree of P saturation (DPS, percentage of P already sorbed) can be calculated (Beauchemin & Simard, 1999; Eichler-Löbermann et al., 2007). One would expect soils to be closer to P saturation that have been enriched with P anthropogenically. Thus, DPS might help to clearly tell apart anthropogenically altered areas/soil horizons from unaltered sections, which is often a question of interpretation in soil P fractionations. To test these hypotheses, we carried out a soil P fractionation along with the extraction of P-ox in the area of the Iron Age Milseburg hillfort (Hesse, Germany; Figure 1).

2 | STUDY SITE

The Milseburg (N 50° 32' 41", E 9° 53' 53") is a solitary mountain reaching ca. 835 m above sea level located in the East of Hesse (Germany). The climate is relatively harsh, with an annual mean temperature of 6.5°C and an annual precipitation sum of 950–1,000 mm (Weihrauch, 2018). The Milseburg mountain was intensively settled during the late Urnfield period (1200–800 BC). It was again continuously populated from the late Hallstatt period to the late Latène period (6th–1st century BC; Thiedmann & Söder, 2007). Due to the exceptional finds, this hillfort is archaeologically interpreted as a prehistoric “central place” (*Zentralort*; Thiedmann & Söder, 2007), a nexus of important political, economic, and religious functions within a larger area. More detailed information on the settlement history and its findings can be retrieved from Söder and Zeiler (2012), (2006) and Salzmann, Söder, and Zeiler (2013).

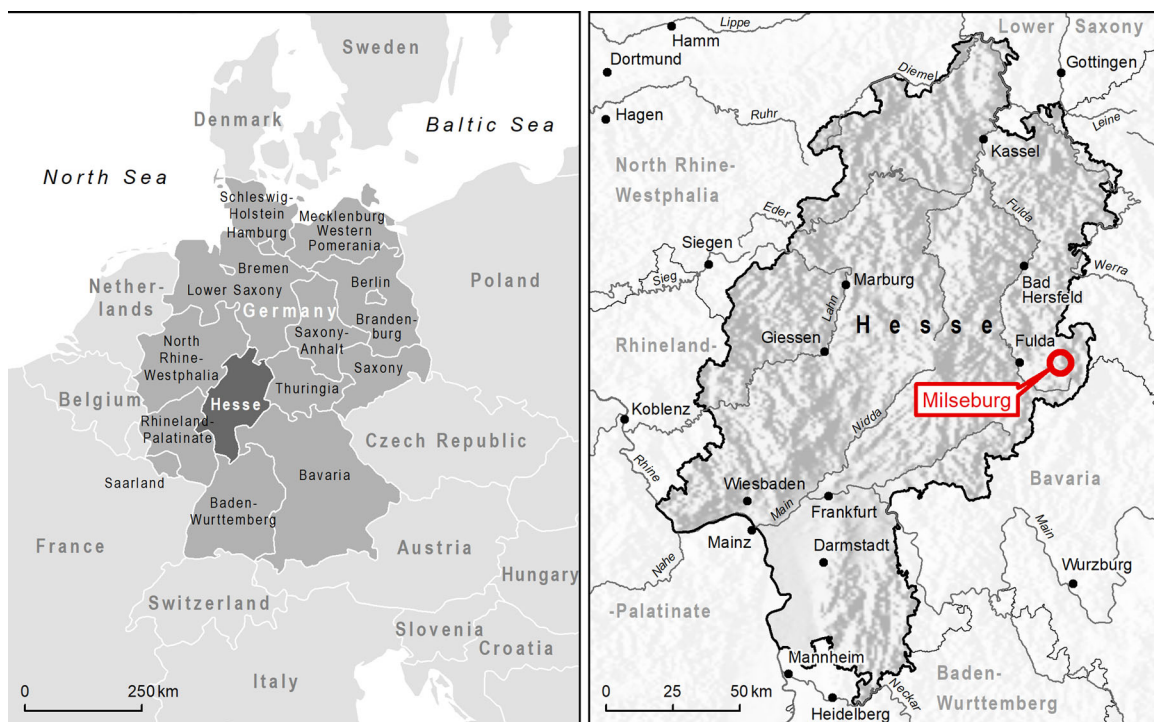


FIGURE 1 Situation of Hesse in Germany and Europe (left panel), and location of the Milseburg in the eastern part of Hesse (right panel; © GeoBasis-DE/BKG 2018; changed) [Color figure can be viewed at wileyonlinelibrary.com]

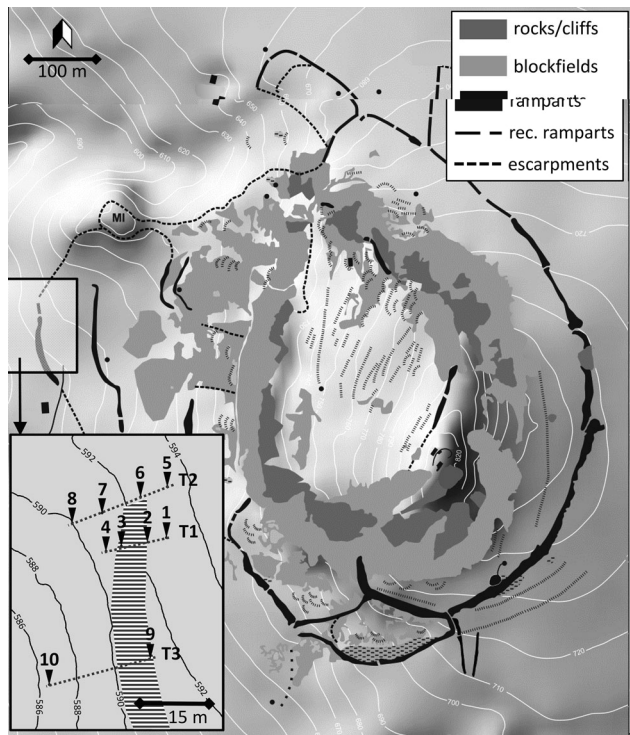


FIGURE 2 Large frame: the Milseburg hillfort and its prehistoric rampart structures (rec. = reconstructed by interpretation; MI = Liedenküppel; Source: M. Zeiler, in Salzmann et al., 2013; edited and translated). The light grey rectangle indicates the position of the area shown in the small frame. Small frame: positions of the investigated soil transects (T1–3 with dashed lines) and soil cores (hatched sector = prehistoric rampart mentioned in the text)

During the Iron Age, extensive ramparts and fortification structures were erected in and around the Milseburg (Figure 2). While these are well preserved in many places, only one gate has so far been verified within the outer circular rampart (Salzmann et al., 2013). It is unlikely that this gate, located on the east, was the only gate to the 45 ha large prehistoric settlement.

In archaeology, gates are focal points of settlement research. On the one hand, the type of construction can indicate a certain time period. On the other hand, gates concentrate the number of people entering and leaving the settlement within a limited space. Thus, certain spatial planning is needed for the gate that could, for example, be reflected in the orientation of nearby buildings. Finally, the position of a gate sheds light on the connection of a settlement with its surrounding landscape. To date, no such information exists regarding the western flank of the Milseburg hillfort.

Based on newly compiled LiDAR scans, a further prehistoric rampart section was discovered in the Western foot of the Milseburg in 2013 (Salzmann et al., 2013). This section is almost completely leveled and so is difficult to identify in the field. This rampart section may include a partially preserved gate. Alternatively, this “gate-like” impression may have resulted from medieval activities: A few hundred meters from this site, a tower called “Liedenküppel” (Figure 2) was constructed during the 11th century AD out of local phonolite stones, very likely by deconstructing the Iron Age rampart.

If this gap within the rampart could empirically be supported as a prehistoric gate, this area would be a promising spot for further archaeological excavations and for focused research on settlement history and the evolution of the cultural landscape. Thus, we carried out a soil P prospection for this purpose.

3 | METHODS

We established three transects of soil cores with a 2-cm diameter Pürckhauer type auger. Transect 1 (cores 1–4) and 3 (cores 9 and 10) crossed the presumed rampart section. Transect 2 (cores 5–8) crossed the gap within the rampart (Figure 2). Of each transect, at least one soil core was located within the settlement, outside of it, or on the rampart (respectively, on its overturned debris). Of transect 2, cores 6 and 7 are located within the rampart’s gap (Table 1). Core 10 was positioned a few meters outside the rampart as a reference to depict the natural vertical P distribution in soil with as little anthropogenic P input as possible. Core 10 is the only forest soil. The other cores are located in a grassland area.

All the soils were classified in the field according to the German classification system (Ad-Hoc-AG Boden, 2005). The cores were sampled in vertical steps of 15 cm to a depth up to one meter. The 53 soil samples were air-dried, ground, and sieved (2 mm) before laboratory analyses. To delineate the general soil conditions within the study area, reference samples of the major soil horizons were analyzed for pH with 0.01 M CaCl_2 (m:V = 1:2.5; DIN ISO 10390:2005–12) and organic matter content (loss on ignition; DIN 19684–3:2000–08). The texture was determined using the Integral Suspension Pressure Method (Durner, Iden, & Unold, 2017) after sample preparation according to DIN ISO 11277:2002–08. Carbonate content was assessed after reaction with 2.86 M hydrochloric acid (HCl), and compaction was estimated with a field knife via the soil’s resistance to pressure (Ad-Hoc-AG Boden, 2005). Soil color was determined using a Munsell soil color chart. The results are given in Table 2.

3.1 | P fractionation

One gram of each sample was treated with 25 ml of 0.1 M HCl and let stand for 24 h in closed vessels (=P-dHCl). Afterwards, the extracts were filtered (2 μm pore size; blue ribbon filter paper). This

TABLE 1 Assignment of the investigated soil cores to archaeological contexts and prehistoric land use

Archaeological context	Soil cores
Settlement	1, 5
Rampart (and debris)	2, 3, 9
Gap within rampart	6, 7
Outside of settlement	4, 8, 10

Note: In the present paper, the accumulation of data according to the archaeological context is based on this classification.

TABLE 2 Pedogenetic characteristics of the major soil horizons in the study area (according to Figure 3)

Attribution	Soil horizon ^a	Genesis	pH (CaCl ₂)	Organic matter ^b	Sand ^b	Silt ^b	Clay ^b	CaCO ₃	Color (Munsell)	Compaction ^c
Within former settlement	M ^o Ah	Coll. slope sed.	5.5	6.62	37.0	36.2	26.8	0	7.5 YR 3/3 (dark brown)	Very slight
	II M ^o Bv	Coll. slope sed.	5.7	5.86	40.2	40.6	19.2	0	7.5 YR 3/2 (dark brown)	Medium
	III jM	Anthr. applied	5.9	3.81	37.3	28.0	34.7	0	5 YR 4/4 (reddish-brown)	High
Gap within rampart	M ^o Ah	Coll. slope sed.	5.5	6.62	37.0	36.2	26.8	0	7.5 YR 3/3 (dark brown)	Very slight
	II M ^o Bv	Coll. slope sed.	6.8	9.00	45.8	41.8	12.4	0	7.5 YR 3/2 (dark brown)	Medium
	III jM	Anthr. applied	7.2	4.18	38.3	28.7	33.0	0	2.5 YR 4/4 (reddish-brown)	High
Outside former settlement	M ^o Ah	Coll. slope sed.	4.7	12.82	32.8	26.6	40.6	0	7.5 YR 2.5/2 (very dark brown)	Very slight
	II M ^o Bv	Coll. slope sed.	5.3	3.58	40.4	31.4	28.2	0	7.5 YR 3/3 (dark brown)	Very slight
	III iCv	Weathering sand	5.9	1.15	66.96	n.d.	n.d.	0	2.5 YR 4/4 (reddish-brown)	High

Abbreviations: anthr. applied, anthropogenically applied soil material; coll. slope sed. colluvial slope sediment; n.d., not determined.

^aGerman classification according to Ad-Hoc-AG Boden (2005).

^bData in mass-%.

^cAccording to Ad-Hoc-AG Boden (2005): very slight = <1.3 g/cm³; medium = 1.55 to <1.8 g/cm³; high = 1.8 to <2.05 g/cm³.

procedure extracts easily soluble phosphates (i.e., labile directly bioavailable phosphates and moderately labile mediately bioavailable phosphates; Weihrauch, 2018). Diluted HCl primarily mobilizes inorganic phosphates (mostly sorbed forms) and few, if any, organic phosphates (Tiessen & Moir, 2006). This easily soluble phosphate fraction is not archaeologically relevant because it hints at recent soil conditions (e.g., hydromorphic). It can also be used to examine how strongly archaeological phosphate contents have been distorted by modern phosphate inputs (e.g., fertilizer; Weihrauch et al., 2016a).

One gram per sample was then processed with 25 ml of 12.1 M HCl for 2 h at ca. 95°C (= P-chCl). Afterwards, the extracts were filtered (2 µm pore size; blue ribbon filter paper) and filled up with distilled water to 50 ml. This procedure extracts easily soluble, but also slightly soluble, stable phosphates (Lauer, Pätzold, Protze, Willbold & Amelung, 2013; Galván-Tejada, Peña-Ramírez, Mora-Palomino, & Siebe, 2014). According to the conception of soil phosphate prospecting, phosphate solubility declines the longer phosphate is in a soil (Bakkevig, 1980). Thus, slightly soluble phosphates are more appropriate for deducing archaeological interpretations (Holliday & Gartner, 2007), while easily soluble phosphates represent recent conditions. In terms of conceptual phosphate pools, an extraction with 12.1 M HCl would mobilize organic phosphates as well as sorbed, occluded and mineral inorganic phosphates (Galván-Tejada et al., 2014; Lauer et al., 2013; Takahashi, 2013; Torrent, Schwertmann, & Barrón, 1992). Recalcitrant phosphate within occlusions or minerals like apatite would not, or at least insufficiently, be extracted by this procedure (Galván-Tejada et al., 2014; Syers, Johnston, & Curtin, 2008).

Therefore, a third extraction was carried out using 20 ml of *aqua regia* (AR; 12.1 M HCl and 14.4 M HNO₃ in a ratio of 1:3) per 1 g of soil sample (=P-AR). After 24 h of reaction time, extracts were heated at ca. 95°C for 2 h, then filtered (2 µm pore size; blue ribbon filter paper) and filled up to 50 ml with distilled water. This procedure extracts easily and slightly soluble phosphates along with recalcitrant organic and inorganic P forms (e.g., strongly occluded P, highly crystalline P minerals; Lauer et al., 2013). However, the procedure does not determine total P (Hornburg & Lüer, 1999). However, including this extraction into the P fractionation may help identify severe hydromorphic conditions that would strongly distort archaeological interpretations (Weihrauch, 2018). AR-extractable P furthermore reflects local geogenic loading by primary P forms (e.g., apatite), which might not be relevant archaeologically. Finally, the AR extraction also indicates the formation of recalcitrant P minerals under certain soil conditions (e.g., alkaline pH and high carbonate content). Nevertheless, the latter was no problem in this study because soils tested negatively for carbonate (Table 2).

The HCl extracts' phosphate contents were determined colorimetrically (Murphy & Riley, 1962; Tiessen & Moir, 2006) at 700 nm on a spectrophotometer (Genesys 10S; Thermo Fisher Scientific, Bremen, Germany). Samples were measured three times and averaged. For comparability, data were arithmetically converted into mg P/kg of soil. P-AR was measured by ICP-MS (X Series 2; Thermo Fisher Scientific, Bremen, Germany).

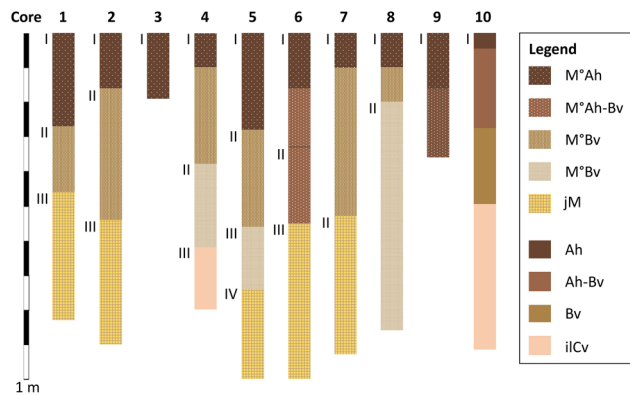


FIGURE 3 Stratigraphy of the investigated soil cores (hatched sectors = allochthonous material; fully filled sectors = autochthonous material; horizons according to Ad-Hoc-AG Boden, 2005; Roman numerals indicate substratum layers) [Color figure can be viewed at wileyonlinelibrary.com]

3.2 | Extraction with ammonium-oxalate

One gram per sample was additionally extracted with 50 ml of a solution of ammonium-oxalate $[(\text{NH}_4)_2\text{C}_2\text{O}_4]$ + oxalic acid $(\text{C}_2\text{H}_2\text{O}_4)$ according to DIN (2003). Thus, 16.11 g of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ were mixed with 10.92 g of $\text{C}_2\text{H}_2\text{O}_4$ in 1 L of distilled water (pH 3.1). Samples were rotated for 2 h in the dark at ambient temperature and afterwards filtered ($2\ \mu\text{m}$ pore size; blue ribbon filter paper). The resulting P-ox was measured by ICP-MS, along with aluminum (Al-ox) and iron (Fe-ox). Data were converted into mg/kg and, for calculation of PSC and DPS, also in mmol/kg.

3.3 | Statistical analysis

Archaeologically relevant P contents were calculated by subtracting easily soluble P-dHCl. Thus, P-sl (slightly soluble) is P-cHCl-P-dHCl. P-rc (recalcitrant) is P-AR-P-dHCl. Slightly soluble oxalate-extractable P (P-sl.ox) was calculated by P-ox-P-dHCl. PSC (in mmol/kg) was calculated as $\text{Al-ox} + \text{Fe-ox}$ (Daly, Jeffrey, & Tunney, 2001; Dayton & Basta, 2005). DPS (in %) was calculated as $\text{P-ox}/\text{PSC} \times 100$ (Eichler-Löbermann et al., 2007; Leinweber et al., 1999).

Basic statistical analyses were carried out in Microsoft Excel (Microsoft, Redmond). Means of grouped data ($n > 2$), their standard errors and significance of differences between means (Tukey's HSD test) were determined in SPSS 24 (IBM Corporation, Armonk). Significances were tested for the $p \leq .05$ level. Results are given in Figures 4 and 5 as mean values with standard error bars and letters indicating the significances between means.

4 | RESULTS

4.1 | Soil conditions

The Milseburg mountain consists of Miocene phonolite that has been carved out of the surrounding bedrocks of mainly Mesozoic origin

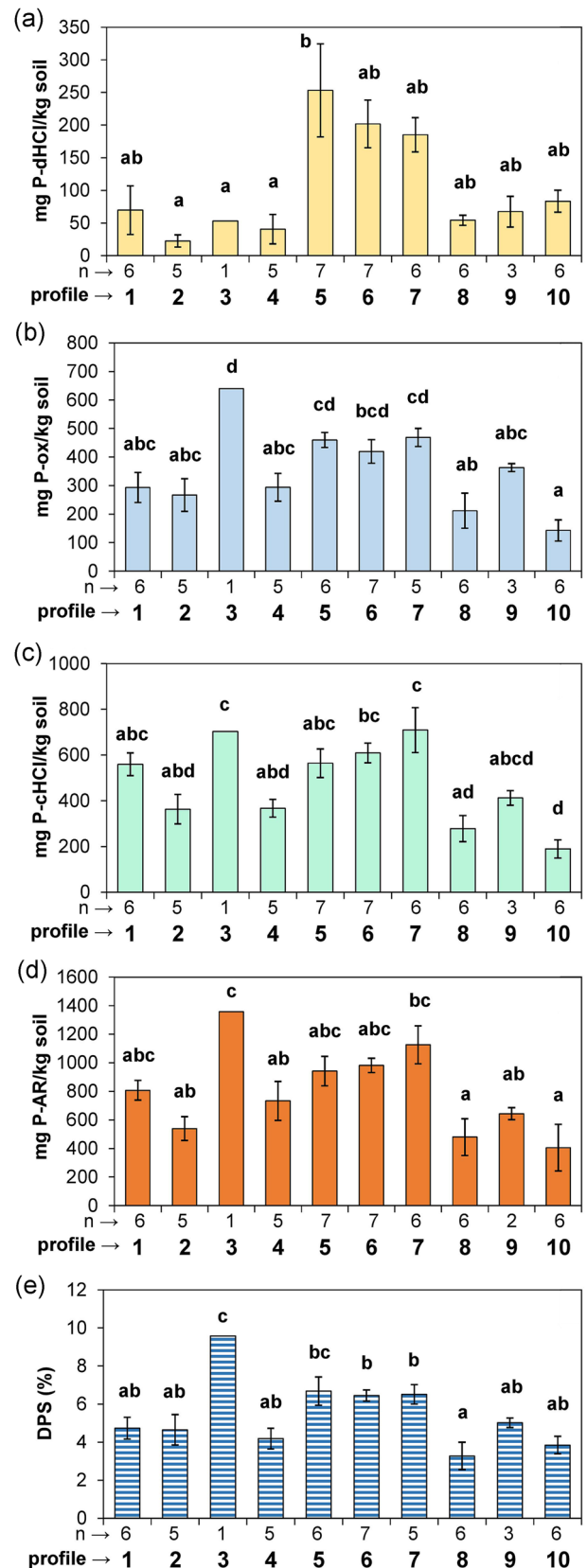


FIGURE 4 Mean contents of each P fraction (a-d) and mean degree of P saturation (DPS; e). According to soil cores, generated from n soil samples. Bars represent standard errors of means. Different letters indicate significant differences between means ($p \leq .05$). P, phosphorus [Color figure can be viewed at wileyonlinelibrary.com]

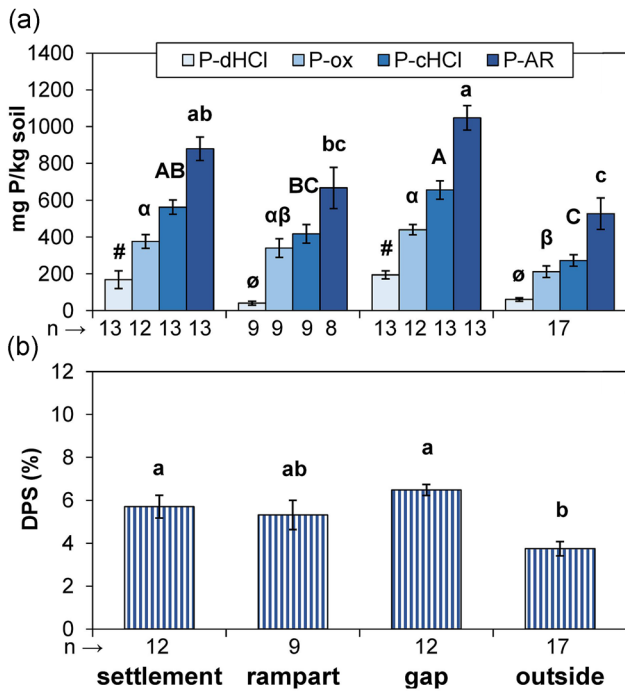


FIGURE 5 Mean contents of each P fraction (a) and mean degree of P saturation (DPS; b). According to archaeological structures, generated from n soil samples. Bars represent standard errors of means. Means of each P fraction were tested for significance of differences: Within the same style of writing, different letters or symbols indicate significant differences ($p \leq .05$). P, phosphorus [Color figure can be viewed at wileyonlinelibrary.com]

(Buntsandstein formation; Weihrauch, 2018). In the study area, the subsurface was originally made up of Pleistocene loamy, phonolite-containing debris (HLfB, 1994), but this changed with prehistoric anthropogenic action resulting in five local types of soil profiles (Figure 3).

- 1) On top of the rampart (cores 3 and 9), organic matter accumulation on massive phonolite debris led to the formation of shallow Leptic Cambisols (Ranker-Braunerden). The soil material forms a *terminus postquem* in relation to the prehistoric settlement. However, core 2, originally planned as lying on the rampart, resembles the soils of the settlement area.
- 2) Within the former settlement, combinations of Anthrosols and Cambisols (Kolluvisol-Braunerden) are found. Cores (1, 2, and 5) are significantly longer than those on the rampart (Figure 3). They are formed of two to three layers of colluvial slope sediments, underlain by strongly compacted, relatively humic loam that has probably been anthropogenically applied (jM horizon). Studies on the eastern foot of the Milseburg showed that, before constructing buildings, the prehistoric settlers dug off the original soil layers approximately 40–60 cm deep into the weathering sands and established terraces topped by artificially applied soil material (Weihrauch, 2018; Weihrauch, Makowski, Söder, & Opp, 2016b).
- 3) The stratigraphy and pedogenesis of the soils within the rampart's gap (cores 6 and 7) are comparable to those of the former settlement. However, the colluvial slope sediments are

strongly enriched with organic matter (Table 2). Moreover, these soils have the highest pH in our study.

- 4) Soils immediately outside of the prehistoric settlement (cores 4 and 8) were also interpreted as combinations of Anthrosols and Cambisols (Kolluvisol-Braunerden). They consist of at least two layers of loosely-packed colluvial slope sediments topping autochthonous weathering sand (ilCv horizon; Table 2). The artificially applied jM horizon (described in cores 1, 2, and 5) is not found outside this section of the prehistoric rampart.
- 5) In core 10, an autochthonous Cambisol formed of Mesozoic sandstone is identified. There are no obvious signs of colluvial deposition or direct anthropogenic interference as identified inside the rampart.

4.2 | P fractionation

Measured P contents differ greatly within the P fractions treated here (Table 3). P-dHCl has a broad range between very low and quite high values. Furthermore, the mean and median are relatively low and different from each other (ca. 50 mg P-dHCl/kg). P-cHCl and P-AR also show broad ranges, but between very low and rather moderate values. However, their means and medians are in the middle of these ranges and do not differ much from each other (ca. 21 mg P-cHCl/kg and 1 mg P-AR/kg). The same applies to P-sl (ca. 9 mg/kg) and P-rc (ca. 24 mg/kg).

4.2.1 | Lateral P distribution

Even though dispersed across a small area, the ten investigated soil cores have significantly different mean P contents (Figure 4). The slightly soluble P fractions display comparable trends (Figure 4c,d). However, the average P-dHCl contents differ (Figure 4a).

Among the slightly soluble P fractions (Figure 4c, d), the highest mean P content was determined for core 3—but based on only one soil sample. The next highest P contents were, on average, found in cores 6 and 7, which mark the gap within the rampart. Mean values within the settlement are somewhat lower and heterogeneous when comparing the average values of cores 1 and 5. Lower mean P contents are found in cores 4 and 8 from outside the former settlement (Figure 2). The lowest mean P content is furthest from the rampart within a forest stand in core 10.

When examining data according to archaeological structures (Figure 5a), the highest average contents of P-cHCl and P-AR were found within the rampart's gap. The mean P contents within the settled area are slightly lower. Significantly lower P contents were calculated for soils on the rampart. It is important to keep in mind that these samples were collected from the top of the rampart. Finally, the smallest mean P contents are recorded outside of the settled area.

4.2.2 | Vertical P distribution

Because colluvial deposition has strongly shaped the study area (Figure 3), the vertical P distribution within the soil cores might give an

TABLE 3 Statistical overview of measured and calculated P contents and of DPS. P fractions and parameters are explained in Section 3 (n = number of samples; min = minimum; max = maximum value)

	Extracted P fractions				Calculated P fractions			DPS (%)
	P-dHCl	P-cHCl	P-AR	P-ox	P-sl ^a	P-rc ^b	P-sl.ox ^c	
n	52	52	51	50	52	51	50	50
Min	1.87	122.37	143.55	67.40	54.97	76.15	0.00	1.87
Max	540.12	1,069.01	1,564.20	639.80	809.72	1,304.90	586.44	10.32
Mean	117.56	472.59	771.68	329.05	355.03	653.59	220.71	5.16
Median	67.40	493.32	770.55	355.95	346.35	629.72	238.27	5.52

Note: P contents in mg/kg of soil.

Abbreviations: DPS, degree of P saturation; HCl, hydrochloric acid; P, phosphorus; P-ox, oxalate-extractable P; P-rc, recalcitrant P; P-sl.ox, slightly soluble oxalate-extractable P.

^aP-sl = P-cHCl-P-dHCl.

^bP-rc = P-AR-P-dHCl.

^cP-sl.ox = P-ox-P-dHCl.

impression of archaeologically relevant soil depths (e.g., former surface horizons). Thus, we examined data according to archaeological structures and soil depth (Figure 6 and Table 4). We calculated archaeologically relevant (i.e., slightly soluble and recalcitrant) P contents to cut out recent P inputs or pedogenetic alteration of P solubility.

The highest mean P contents generally appear at the soil surface, decreasing with increasing depth (Figure 6 and Table 4). For the least easily soluble P fractions, a peak forms at 15–30 cm deep in the formerly settled area, within the rampart's gap and outside of the settlement (Figure 6a,c,d). Another peak is evident 45–60 cm deep within the settled area (Figure 6a). Below this peak, the average P contents decrease with increasing depth. No such peak occurs within the rampart's gap (Figure 6c). Nevertheless, mean P values remain relatively high in 30–100 cm of depth (Table 4). Outside of the former settlement, no peak appears below 30 cm of depth, but mean P contents are relatively low and decrease with increasing depth (Figure 6d and Table 4). This is especially true for core 10 under forest (Figure 6e), where the average P contents are low, from 15 to 100 cm deep. As mentioned above, the lowest archaeologically relevant mean P contents were measured in this core (Table 4). Still, P-rc values are at least moderately peaking in 30–60 cm of depth.

On the rampart and its debris (Figure 6b), P contents are higher than outside the former settlement but lower than within it. The P graphs from on top of the rampart appear to consist of two layers. Mean P contents are relatively high in 0–60 cm of depth and then are abruptly low in 60–100 cm of depth (Table 4).

4.3 | Extraction with ammonium-oxalate

According to P solubility, the P-ox fraction is located between P-dHCl and P-cHCl, with a tendency towards the slightly soluble P fraction (Table 3). A relatively broad range was found among the P-ox contents. The mean and median approximate one another and lie near the midpoint of the range. The same applies to P-sl.ox.

4.3.1 | Oxalate-extractable P

Concerning the lateral P distribution within the study area, the average P-ox contents show a comparable trend as P-cHCl and P-AR (Figure 4b–d; see Section 4.2.1). Average P-ox levels also decline in the following order: rampart's gap > settlement > rampart and debris > outside of the settlement.

Overall, vertical soil P trends are broadly similar. P contents generally decrease with depth across all the extraction methods. Only P-sl values within the settlement area increase in 31–60 cm of depth (Table 4). Despite the similarities in P-ox trends with P-cHCl and P-AR, there are no peaks in the P-ox graphs (Figure 6a–d). Besides this, the general vertical trend of the P-ox graphs is comparable to those of P-sl and P-rc (see Section 4.2.2). However, the latter are more pronounced and thus easier to interpret. Also, one must bear in mind that P-ox still contains easily soluble P-dHCl forms. After they are subtracted, the remaining slightly soluble P-sl.ox still shows no peaks (Figure 6a). However, soil sections with P enrichment of different intensity may be distinguished from each other. Three sections can be identified within the former settlement (0–30, 30–75, and 75–100 cm of depth; Figure 6a), on the rampart and under forest cover (0–15, 15–60, and 60–90 cm; Figure 6b, e). There are four soil sections within the rampart's gap (0–30, 30–60, 60–90, and 90–100 cm; Figure 6c) and outside of the former settlement (0–15, 15–30, 30–45, and 45–90 cm, Figure 6d).

4.3.2 | Degree of P saturation

The DPS calculated from P-ox, Al-ox, and Fe-ox was hypothesized to indicate soil horizons anthropogenically enriched with P and thus closer to P saturation (i.e., higher DPS). In general, the DPS values found in this study are relatively low (Table 3). Accumulating data according to soil cores, the mean DPS (Figure 4e) display a comparable trend as P-ox. Thus, cores 5, 6, and 7 within transect 2 are closer to P saturation. A significantly lower average DPS was found for core 8, which also belongs to transect 2 but which is

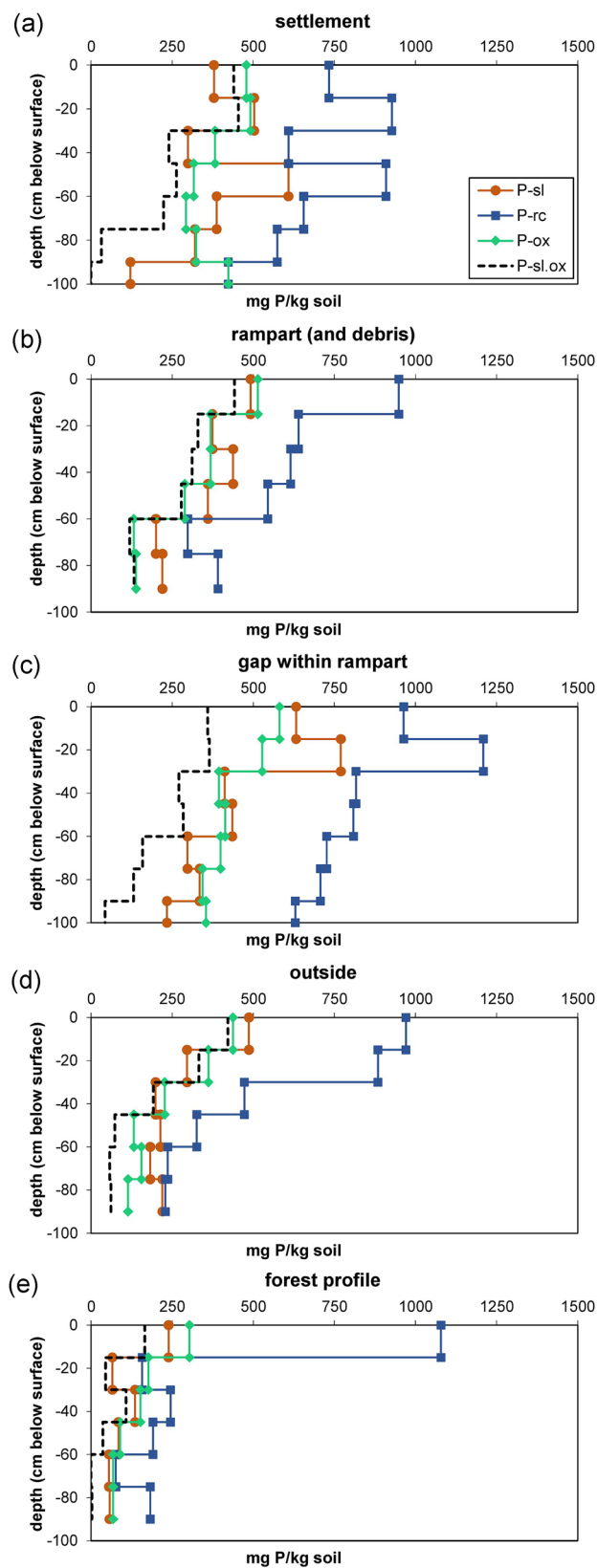


FIGURE 6 Mean values of each soil P fraction by depth within each archaeological context (a-e). Each data point was calculated from one soil sample per depth of the according cores (compare Table 1). P fractions were calculated as follows: slightly soluble P (P-sl) = P-chCl-P-dHCl; recalcitrant P (P-rc) = P-AR-P-dHCl; oxalate-extractable P (P-ox); slightly soluble oxalate-extractable P (P-sl.ox) = P-ox-P-dHCl. P, phosphorus [Color figure can be viewed at wileyonlinelibrary.com]

located outside of the former settlement. The other cores (1, 2, 4, 9, and 10) have somewhat higher and, among each other, comparable mean DPS values, regardless of their position in relation with archaeological structures. The highest average DPS is in core 3 on top of the rampart.

Relating data to archaeological structures, the highest DPS are recorded within the rampart's gap (Figure 5b). Slightly but insignificantly lower values were calculated for the settled area. However, a significantly lower DPS was found for the soils outside the former settlement. DPS on the rampart and its debris lie in between these two extremes and thus do not differ significantly from either one.

Finally, we consider the vertical development of DPS within the soil cores (Figure 7a). The resulting mean DPS graphs mostly differ greatly from those of P-ox and P-sl.ox (Figure 6a-e). Three types of mean DPS graphs can be distinguished, according to a different course of the graphs with increasing soil depth (Figure 7a). First, the graphs for the locations outside of the settlement and for the core under forest cover show a tendency for the mean DPS to decrease with increasing soil depth and to be <4.0% below 30 cm of depth. On the other hand, there are the cores within the settlement and within the rampart's gap where the average DPS goes down slightly until 60 cm deep, and then the DPS increases again. This is most pronounced for the gap locations and reaches mean DPS values of 7.1% in 60–100 cm. Within the settlement, mean DPS values are only slightly lower and reach an average DPS of 6.9% below 60 cm of soil depth. Finally, locations on top of the rampart show a kind of intermediate course in their mean DPS graphs. Until 60 cm of depth, the DPS remains relatively high and comparable to the settlement/gap locations. Below 60 cm of depth, mean DPS decreases to 3.2% and could thus be compared with the locations outside of the settlement.

5 | DISCUSSION

5.1 | Soil stratigraphy and archaeological structures

Auger sampling depths differed within the study area (Figure 3). On the rampart, short soil profiles were cored because stones blocked the auger at the base of the feature. The soil cores within and outside of the settlement were significantly deeper than on the rampart. This corroborates the existence of a linear stone construction which was so far only deduced from LiDAR scans. Soils from the gap within that rampart were also significantly deeper than on the rampart itself. Thus, this gap might have resulted from the complete deconstruction of the rampart in the Middle Ages and the times after, when nearby stone buildings were erected (e.g., Liedenküppel, see Section 2). However, the question arises why it should have been deconstructed only that far, in lateral terms. Alternatively, the missing stone structures within the rampart's gap could indicate an intentional prehistoric gap (i.e., a gate). This is also indicated by soil stratigraphy as the cores within the settlement and within the rampart's gap are comparably composed of different layers of colluvial slope sediments. Below these, anthropogenically applied soil material seems to be present, as was discovered before in different locations of the

TABLE 4 Mean P contents according to archaeological contexts in soil sections of 30 cm. (Letters of significance always relate to one P fraction only.)

	Depth (cm below surface)		
	0–30	31–60	61–100
Settlement			
P-ox	486.97 (40.02) a/A	349.48 (80.41) a/AB	331.41 (49.63) a/AB
P-sl.ox	449.21 (30.74) a/A	251.65 (48.42) ab/AB	102.06 (59.45) b/A
P-sl	441.13 (84.65) a/AB	486.80 (101.59) a/A	319.71 (76.83) a/A
P-rc	830.37 (120.5) a/A	759.35 (103.1) a/A	576.52 (137.7) a/AB
Rampart			
P-ox	441.35 (67.18) a/AB	342.30 (27.38) ab/AB	135.10 (3.50) b/BC
P-sl.ox	385.65 (67.41) a/A	299.86 (27.66) ab/A	125.71 (6.34) b/A
P-sl	432.94 (75.22) a/AB	411.88 (46.88) a/A	209.93 (10.06) a/A
P-rc	794.05 (171.7) a/A	596.37 (51.55) a/AB	344.53 (46.57) a/AB
Gap			
P-ox	554.40 (19.2) a/A	406.70 (23.49) b/A	367.92 (22.22) b/A
P-sl.ox	361.80 (53.64) a/A	280.02 (39.13) ab/AB	124.54 (51.65) b/A
P-sl	700.90 (50.68) a/B	423.41 (17.88) b/A	299.55 (38.34) b/A
P-rc	1,086.56 (131.04) a/A	813.01 (90.81) ab/A	699.43 (68.04) b/A
Outside			
P-ox	399.53 (25.83) a/AB	179.38 (38.66) b/AB	141.40 (37.15) b/BC
P-sl.ox	376.59 (33.7) a/A	132.40 (52.05) b/AB	58.35 (22.81) b/A
P-sl	426.02 (52.65) a/AB	210.88 (31.79) b/AB	194.97 (40.21) b/A
P-rc	927.47 (112.5) a/A	399.35 (84.55) b/AB	233.75 (52.59) b/AB
Forest			
P-ox	240.10 (63.0) a /B	120.75 (31.15) a/B	67.65 (0.25) a/C
P-sl.ox	104.84 (60.66) a/B	72.07 (35.83) a/B	1.32 (1.32) a/A
P-sl	152.11 (86.59) a/B	109.99 (25.74) a/B	56.04 (1.07) a/A
P-rc	617.96 (460.49) a/A	217.80 (26.96) a/B	129.19 (53.04) a/B

Note: Mean P contents in mg/kg of soil. Values in parentheses are standard errors of means. Different letters indicate a significant difference between means ($p \leq .05$). Small letters: comparison of means of one P fraction by column. Capital letters: comparison of means of one P fraction by line.

Abbreviations: P, phosphorus; P-ox, oxalate-extractable P; P-rc, recalcitrant P; P-sl, slightly soluble P; P-sl.ox, slightly soluble oxalate-extractable P.

prehistoric Milseburg hillfort (Söder & Zeiler, 2012; Weihrauch et al., 2016b). However, in the present study, this artificial horizon was not discovered outside of the former settlement. The rampart seems to demarcate two different areas of past land uses. However, colluvial deposits are hard to interpret from auger cores alone. As detailed below, soil P analyses support the suggestions above.

5.2 | P data and prehistoric anthropogenic activity

5.2.1 | Lateral P distribution and land use

Different spatial trends of mean values were discovered for P-dHCl and the slightly soluble P fractions (Figure 4b–d). P-dHCl is composed of easily soluble and bioavailable P forms rather representing recent soil conditions (e.g., waterlogging conditions, mineralization). Thus, it is not directly archaeologically relevant. P-cHCl and P-AR are considered here for archaeological interpretations.

The substrates occurring in the study area are naturally low in P. Milseburg-Phonolite has ca. 200–300 mg total P/kg of dry matter (median values; Ehrenberg & Hicketier, 1994). Mesozoic sandstones on average contain about 170 mg total P/kg dry matter (Blume, 2004; Linhardt & Zarbok, 2005). The measured P-cHCl and P-AR contents within the study area are on average much higher (Table 3), and they differ too much to be explained by natural variation. The

average P contents within the former settlement and the rampart's gap are significantly higher than outside of the settlement (Figures 4 and 5). Thus, the differences of the cores' mean P contents seem to result from anthropogenic activities during the time the rampart was used, which is so far dated to the Iron Age. The difference in mean P results indicates a different intensity of P inputs that correlate with land use.

Within the settled area, the mean P contents are somewhat lower but comparable with the rampart's gap (Figures 4 and 5). This suggests simultaneous P enrichment in both areas. Although the settled area might have received different kinds of P inputs (e.g., feces, ashes, organic waste), the rampart's gap might theoretically have been favored by the effect of a higher frequency of P inputs, even if only of a few kinds (e.g., animal feces). Thus, the strongest P input obviously occurred within the rampart's gap, where the highest P contents were measured (Figures 4 and 5). This also implies that this gap already existed while the settlement was active. People and animals entering and leaving the settlement would have been spatially concentrated and possibly slowed down while waiting for the gate to be opened. This could have led to spatially concentrated P inputs that would have accumulated over time. This accumulation could not have happened if the gap originated only in the Middle Ages or P accumulation would likely be much lower.

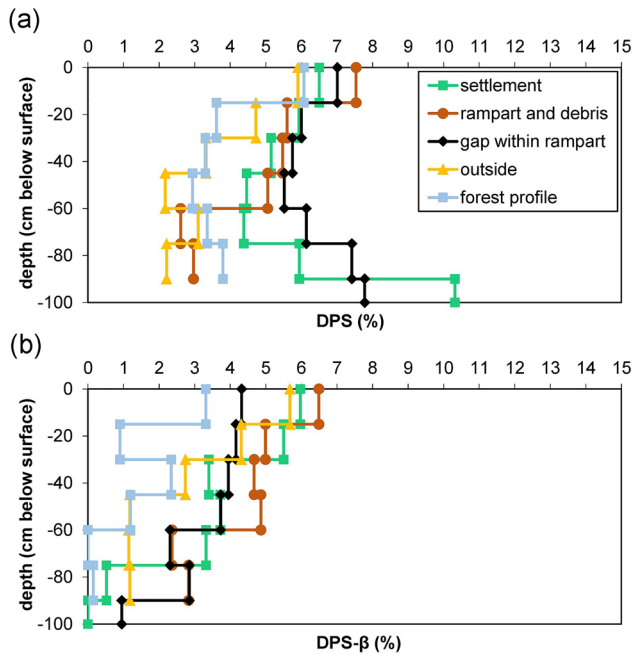


FIGURE 7 Mean degree of P saturation (DPS) within each archaeological context according to soil depth. Generated from no more than one soil sample of the according cores (compare Table 1) and soil depths: (a) regular DPS, based on P-ox; (b) DPS- β , based on P-sl.ox. P-ox, oxalate-extractable P; P-sl.ox, slightly soluble oxalate-extractable P [Color figure can be viewed at wileyonlinelibrary.com]

The relatively high mean P contents on the rampart (Figure 5) might be a product of our sampling. Cores 3 and 9 consists of colluvial slope sediments on top of the rampart. This material might have been enriched with P within the settlement in prehistory. It might afterward have been displaced down the slope and might have come to rest on top of the rampart where it was further enriched with humic material by vegetation. Thus, this material would partly form a *terminus postquam* to prehistoric use. However, core 2, by its thickness, indicates that it might not have been located on the rampart but shortly behind it and within the settlement. This would explain that our mean P on the rampart is comparable with the settled area. Outside of the settlement, P contents are significantly lower. This would be due to fewer anthropogenic P inputs under different land use. Maybe the area adjacent to the rampart was used for agriculture, as was proposed by Weihrauch et al. (2016b) for a comparable location at the southeastern margin of the Milseburg hillfort.

5.2.2 | Vertical P distribution and speculations on chronostratigraphy

Within the investigated soils are different vertical patterns of archaeologically relevant P accumulation (Figure 6). Due to litterfall, edaphic activity, and bioexudation, P contents are naturally highest close to the soil surface (Weihrauch, 2018). However, P-sl and P-rc means peak in 15–30 cm in some locations of the study area. This could indicate a plow layer due to modern agricultural land use with

anthropogenic mineral P fertilizer inputs post 1850 (Weihrauch et al., 2016a). The area is under grassland today, suggesting it was once cleared for agriculture. This can be further supported by the fact that core 10 under forest has no peak at 15–30 cm.

Within the settled area, another peak shows at 45–60 cm (Figure 6a). It could result from prehistoric anthropogenic activity with P inputs on a soil surface compacted by trampling. Thus, it would be important to see whether both settlement cores display this peak (Figure 8a, b). Interestingly, their vertical P graphs differ greatly, probably due to local differences in activity within the settlement (e.g., housing, garden, pathway). In core 1 (Figure 8a), the prehistoric surface might have been at 45–75 cm or 60–75 cm, based on the high P-rc contents. This layer was identified as anthropogenically applied material. Below it, P contents drop drastically to the natural P levels.

In core 5 (Figure 8b), two very pronounced peaks appear below the proposed plow layer. The first one (45–60 cm) corresponds to core 1; however, the second one at 75–90 cm is not present. The 45–60 cm peak may have resulted from P enrichment that developed during the first settling phase (Urnfield Period). Alternatively, this peak might date to the Iron Age. In that case, the surface horizon would be located deeper than in core 1. This could be due to a different intensity of erosion and colluvial deposition with no rampart to block it. The area at the foot of the Milseburg was extensively terraced before settlement (Weihrauch, 2018; Weihrauch et al., 2016b). Therefore, intensive erosion is not very plausible. Still, thick colluvial layers were identified in our soil cores. However, this chronostratigraphic question cannot be solved with only auger profiles.

Within the rampart's gap, no P peak was found below 30 cm (Figure 6c). With no rampart to restrict erosion, P-rich settlement soils could have been lost within the gap. Nevertheless, P contents remain relatively high until 100 cm, suggesting that P might have infiltrated deeper into the soils than within the settlement. However, the soils within the gap are strongly compacted and would hinder vertical P translocation. Rather, the high P contents in the anthropogenically applied soil horizons suggest that this soil material has been enriched with P before in its original location, possibly already in the Urnfield period settlement phase. This hypothesis must be verified by further investigations.

When treating the gap cores separately, in core 6 (Figure 8c), P-rc is strongly enriched in the former plow layer and below it, where colluvial slope sediments were identified (15–60 cm). Another yet slighter peak shows in 75–100 cm within the material that is interpreted as anthropogenically applied. This layer might represent a prehistoric surface horizon according to its high P-rc content. Speculatively, we would date it to the Iron Age even if it would be located deeper than the Iron Age surface horizon within the settlement cores. Nevertheless, more intensive erosion is to be expected within the rampart's gap. Therefore, the former surface horizon could be topped by a thicker colluvial cover.

In core 7 (Figure 8d), P-rc is enriched within colluvial slope sediments below the relic plow layer (30–60 cm). A slight P-rc peak

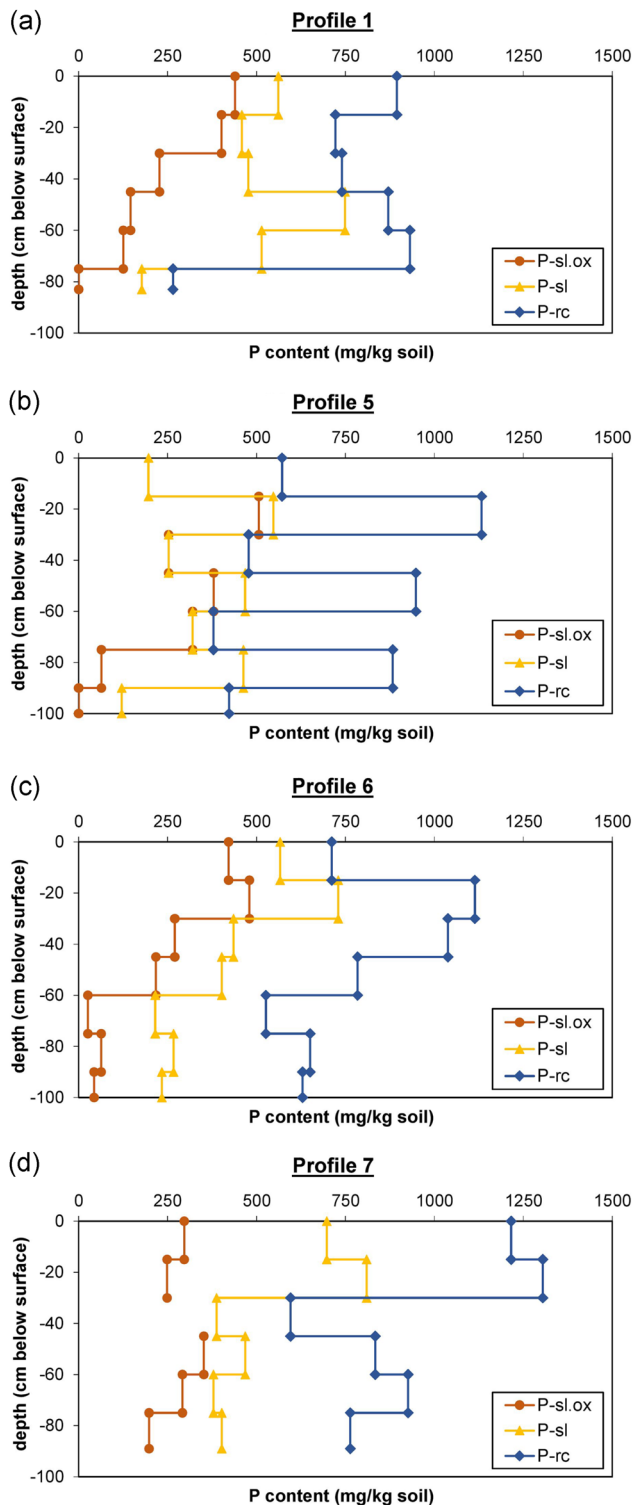


FIGURE 8 Vertical distribution of archaeologically relevant P fractions within the settlement cores (a, b) and within the gap cores (c, d). Slightly soluble oxalate-extractable P (P-sl.ox) = P-ox - P-dHCl; slightly soluble P (P-sl) = P-chCl - P-dHCl; recalcitrant P (P-rc) = P-AR - P-dHCl [Color figure can be viewed at wileyonlinelibrary.com]

shows at 60–75 cm within anthropogenically applied material (jM horizon; Figure 3), marking the Iron Age surface. The rest of the jM horizon is also markedly enriched with P. That the horizon also has a high content of organic matter (Table 2) corroborates that the soil material is not autochthonous but was probably anthropogenically applied.

Finally, outside the prehistoric settlement, while P contents are slightly to moderately heightened until 60 cm there are no clear peaks apparent below 30 cm (Figure 6d,e and Table 4), perhaps a vestige of modern agriculture. As a conclusion, anthropogenic P enrichment attributed to the prehistoric surface horizon could have been located between 45 and 60 cm below the recent surface and has been covered by colluvial slope sediments. The deepest soil sections contain autochthonous weathering sand of Mesozoic sandstone, showing little or no secondary P enrichment (182 mg P-rc/kg soil). This gives an impression of the intensity of anthropogenic P enrichment within the deepest sections of cores 6 and 7 (630 mg P-rc/kg soil).

5.3 | On the applicability of the oxalate-extraction for geoarchaeological research

5.3.1 | Oxalate-extractable P

P-ox should be archaeologically relevant because it is supposed to extract P that accumulates in soil by sorption processes (e.g., Schwertmann, 1964). Our P-ox data display trends according to different land use, thus supporting its geoarchaeological application. In this study, P-ox was on average 144 mg/kg lower than P-chCl and 443 mg/kg lower than P-AR (Table 3 and Figure 4b). In addition, differences between the P-ox values are smaller, resulting in difficulty identifying data peaks compared with those of the other P fractions. As a result, mean P-ox contents are not often statistically significant when estimated according to soil features or land use characteristics (Figure 5a). Hence, the results of the lateral P distribution are clearer for P-chCl and P-AR than for P-ox.

Regarding the vertical P distribution, P-ox and P-sl.ox data helped to identify soil sections with P enrichment (Figure 6). This would be favorable for geoarchaeological P prospection with, for example, the identification of buried surfaces. However, while the P-sl and the P-rc graphs have a similar trend, there are deviations between the P-ox or P-sl.ox and the P-sl and P-rc graphs (e.g. Figure 6a). Thus, the P-ox and P-sl.ox data seem somewhat unspecific with regard to prehistoric land use. Most strikingly, even though P-chCl and P-AR do, the average P-ox and P-sl.ox contents do not show any vertical peaks (Figure 6a–d), also not in the (not averaged) P data from the individual soil cores (Figure 8).

The occurrence of P peaks is an important feature for the interpretation of P data in geoarchaeological prospections because vertical peaks mostly relate to archaeologically relevant P enrichment that occurred in a certain soil horizon (e.g., a buried surface).

Because P-ox data contain so little variability, they do not produce statistically significant peaks. As a result, their vertical trends are hard—or even impossible—to interpret with regard to past land use. Thus, even though it mirrors different land use on the soilscape scale to some degree (i.e., in lateral terms), P-ox is a rather unsuitable parameter for geoarchaeological investigations of soil profiles (i.e., in vertical terms).

We should also reflect upon the chemical association and formation of P extracted by the ammonium-oxalate procedure, as developed by Schwertmann (1964). This method is often interpreted as extracting all the P sorbed within a soil (i.e., P held by sorptive bonding; Binner et al., 2015; Eichler-Löbermann et al., 2007; Galván-Tejada et al., 2014). However, detecting all the sorbed soil P is not possible by geochemical analysis to date because sorbed P is comprised of a spectrum of P forms of very different solubility. For example, P-ox includes easily soluble, unspecifically sorbed P next to slightly soluble, specifically sorbed P forms (Weihrauch & Opp, 2018). Quantitative geochemical procedures rely on the use of acids/bases (e.g., HCl, NaOH) of a certain acidity/alkalinity and thus extract P forms of a corresponding solubility range (Weihrauch, 2018). Thus, the ammonium-oxalate method probably does not extract all the sorbed P, resulting in the exclusion of slightly soluble sorbed P that could be archaeologically relevant (Jiang, Bol, Willbold, Vereecken, & Klumpp, 2015). Moreover, the procedure could also extract other P forms, such as easily soluble P minerals, which are archaeologically not relevant. Therefore, P-ox might not be a sufficient indicator for geoarchaeological research. In terms of P solubility, P-ox data are not very indicative compared with other, more recalcitrant P fractions (e.g. P-cHCl; Figures 5a and 6). The P-ox results in this study gave out low values that significantly differ from P-AR, showing that sorbed P alone might not be an appropriate fraction to focus on in geoarchaeology. The relatively large differences between P-cHCl and P-AR also support this (Table 3). Recalcitrant mineral P forms (Weihrauch & Opp, 2018)—directly introduced into the soils (e.g., bones, dust; Devos, 2018) or secondarily precipitating due to high P inputs (e.g., feces)—may have also played an important role in prehistoric land use. Those would not be extracted by a procedure exclusively focused on sorbed P. Furthermore, slightly soluble organic P forms that could go undetected with P-ox, can be relevant for geoarchaeological research. It is improbable for the oxalate-procedure to extract these fractions because the acid solution used is chemically too mild. Therefore, if P-ox is used, it should be combined with a recalcitrant P fraction in a fractionation scheme.

In this localized study of the Milseburg hillfort, we demonstrate the potential of the separate extraction of P-ox according to Schwertmann (1964) as an inadequate approach for geoarchaeological research questions. The amount of P extracted with any chemical procedure varies according to the specific soil (e.g., pH, electrical conductivity, organic matter and carbonate content, sorption characteristics; Weihrauch & Opp, 2018). Although the ammonium-oxalate method might produce meaningful data

for some soil types, we maintain that it is not generally applicable for geoarchaeological research. In the case study on the Milseburg hillfort, the P fractionation gave out archaeologically significant results, but P-ox data are not indicative. In our case study, P-ox was probably not successful in gaining archaeologically relevant information because the local soils have high organic matter contents (Table 2). Thus, to a large extent, P sorption might be dominated by organic substances and not so much by Fe and Al oxides.

5.3.2 | Degree of P saturation

The DPS values' lateral trend is comparable to that of P-ox (Figure 4b,e). Thus, differences in land use are made visible. However, because DPS values are generally low with this method, differences between means in accumulated data are mostly not significant (Figure 5b).

Vertical DPS graphs (Figure 7a) strongly differ from the corresponding P-ox/P-sl.ox graphs (Figure 6). Three types of DPS graphs resulted: (a) The first type represents the forest profile and locations outside of the former settlement where little anthropogenic P input occurred and where the lower soil sections more or less display natural DPS; (b) the second type stands for locations with larger P enrichment, especially in the deepest soil sections where the maximum DPS was found in this study (settlement and gap within rampart locations); (c) the third type corresponds to soils formed of P-enriched material in the upper sections and non-enriched layers in greater depths (rampart and debris locations). (Judging from the DPS graphs, core 2 seems to represent a rampart rather than a settlement location and was thus classified accordingly in this study).

We calculated DPS to clearly identify soil horizons anthropogenically enriched with P by a significantly higher DPS value. This calculation of DPS is based on the assumption that sorption to Fe and Al oxides is most important for P retention in archaeologically relevant soils. As discussed in Section 5.3.1, this assumption could not be supported by our data. Instead, other slightly soluble P fractions (e.g., mineral, organic) also seem to be important in soils anthropogenically enriched with P during prehistory.

Furthermore, the theory of DPS must be considered. DPS is calculated from PSC. That there are different formulas for calculating PSC (Daly et al., 2001; Eichler-Löbermann et al., 2007) indicates that more research is needed to accurately quantify P sorption in soils. Often, PSC is designed as the sum of P sorbed to Fe and Al oxides. However, there are other sorbing agents in soils that are not taken into account (e.g., Mn oxides in acid soils, Ca and Mg carbonates in alkaline soils; Kabir, Johansen, & Bell, 2015; Missong, Bol, Willbold, Siemens, & Klumpp, 2016). Thus, PSC does not necessarily depict a soil's complete capacity to sorb P. As a consequence, DPS would represent only partially how much P a soil already sorbed.

In addition, as mentioned in Section 5.3.1, it seems implausible that the ammonium-oxalate method extracts sorbed P in general, but rather a (relatively easily soluble) proportion of it. Weakly sorbed P can be easily exchanged in soils and thus reacts dynamically to recent

soil and weather conditions (e.g., during soil sampling). Therefore, the DPS derived from P-ox, Al-ox, and Fe-ox could largely represent P sorption that is not archaeologically relevant but might hint at relatively recent conditions. To illustrate, an alternative DPS called “DPS- β ” was calculated on the basis of P-sl.ox instead of P-ox to display the archaeologically relevant proportion of P sorption measured with the oxalate-extraction. The resulting DPS- β graphs clearly differ from the regular DPS (Figure 7a,b). Thus, the regular DPS does not seem appropriate for geoarchaeological research. In our study, however, the modified formula facilitated differentiation between anthropogenically altered and unaltered soil sections (higher vs. lower DPS- β , respectively).

6 | CONCLUSION

By combining a soil P fractionation scheme with the determination of P-ox, we detected significant anthropogenic P enrichment within the studied soils of the Milseburg hillfort. The intensity of P enrichment declined in the sequence gap within rampart > settlement locations > rampart > locations outside of the settlement. Thus, P enrichment probably resulted from prehistoric activity during the Iron Age settling time. P enrichment within the rampart's gap was nearly as intensive and could be located in the same depth as within the settlement. Thus, the gap must already have existed during the settling time. Therefore, it seems plausible that it marks a former gate where further excavations would be worthwhile. To facilitate those, the archaeologically relevant soil depths were identified.

We compare two methods for geoarchaeological soil P prospections, a P fractionation scheme and P extraction with ammonium-oxalate, according to Schwertmann (1964). To some degree, P-ox can depict anthropogenic P enrichment in terms of the lateral P distribution. However, meaningful vertical P enrichment for slightly soluble and recalcitrant P from the P fractionation is not revealed in the P-ox data. This limited study demonstrates that, regardless of the additional time and costs, a simple P fractionation scheme is superior to single-extraction-procedures for P prospections in geoarchaeological research. Therefore, we deduce that the oxalate-extraction according to Schwertmann (1964) should not replace a P fractionation in geoarchaeological research. Most of the interpretations regarding prehistoric land use of the Milseburg hillfort would not have been possible with just P-ox results. P-ox could be included in a fractionation scheme in the place of a slightly soluble P fraction when combined with an easily soluble and a recalcitrant P fraction. One advantage of such a combination would be that it allows for the calculation of the DPS. Our results indicate that the common DPS is inconclusive, so we propose an alternative DPS formula (“DPS- β ”), which is based on the slightly soluble, archaeologically relevant proportion of P-ox and not on total P-ox. The DPS- β produced indicative results supported by data and could, therefore, have broader geoarchaeological applicability. A targeted combination of proper soil P extractions in a P fractionation scheme could thus

produce valuable results for further geoarchaeological research. However, a P prospection should be combined with other methods and—most of all—with some scale of archaeological excavation to better understand P accumulation and P dynamics within a particular soil environment in relation to human activity.

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CONFLICT OF INTERESTS

The authors declare that there are no conflicts of interests.

DATA ACCESSIBILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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