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P-ed-XRF-geochemical signatures of a 7300 year old Linear Band Pottery house ditch fill at Vráble-Ve'lké Lehemby, Slovakia - House inhabitation and post-depositional processes

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ABSTRACT

Over the past decades multi-element analyses have become increasingly important for archaeological and geoarchaeological research. In particular the recent expansion in availability of portable ed-XRF (p-ed-XRF) devices has allowed for the fast acquisition of large data sets. In the presented paper, we evaluate the quantitative measurement capability of a p-ed-XRF device through comparison with wd-XRF. Sampling, drying, and homogenization (sieving < 2 and pulverizing) ensured comparable measurement conditions. The application of He-flotation in the measurement chamber and measurement times of a sufficient duration at low voltage/high amperage conditions increased measurement sensitivity for lighter elements (here at least 90 s at 6 kV, 100 μA), resulting in measurements of a satisfactory quality.

In a case study, we measured the elemental contents of the archaeo-sediment-sequence fill of a trench of a ca. 7300 year old Linear Pottery house at the site of Vráble-Ve'lke Lehemby, in southeastern -Slovakia. Based on a model applied at the nearby Bronze Age settlement mound of Fidvár, the P content of the archaeo-sediment was considered as a proxy of palaeo-demography. However, the measured P contents were much too small to reflect the metabolism of a reasonable number of inhabitants. Therefore, in addition to the possibilities of shorter than expected duration of house occupation and incomplete garbage deposition within the ditches, the post-depositional settlement history is considered in detail. Furthermore, bio-cycling by plants during different subsequent phases of Holocene landscape development (forested, agricultural field use) has not been considered extensively in interpretations of the archaeological record so far, but might have had a considerable influence on the shallow buried archaeological record. A reconsideration of the interpretation of the geochemical record from a nearby Bronze Age site (Fidvár) is thus suggested.

1. Introduction

Multi-element analysis has gained in importance during the past decades in archaeological and geoarchaeological research as it enables the fast acquisition of large data sets that promote investigation of such diverse questions as provenance of materials (e.g. Helfert and Böhme, 2010; Shugar and Mass, 2012), tracking of ancient economic activities and settlement patterns (e.g. Abrahams et al., 2010; Dreibrodt et al., 2013b; Entwistle, 2000; Entwistle et al., 1998; Gaus et al., 2013, Lubos et al., 2013; Middleton, 2004; Wilson et al., 2009), and even consideration of ancient population dynamics (e.g. Nowaczinski et al., 2013). Whereas early studies used AAS measurements (e.g. Bintliff et al., 1988; Ottaway and Matthews, 1988), in more recent investigations ICP-OES/MS analysis were used as the main analytical techniques (e.g. Entwistle, 2000; Entwistle et al., 1998; Middleton, 2004; Wilson et al., 2009). ICP measurements require wet extraction protocols and thus provide results from only selected fractions. They are assumed to deliver data in high precision. On the other hand, XRF -measurements were usually applied on the bulk of the <2 mm fraction of a soil/sediment sample, embedded in fused glass disks ($Li_2B_4O_7$). Measured with

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the wavelength dispersive (wd) technique, the results provided precise quantitative data of total elemental contents. With technical improvements (e.g. Garrison, 2003) of the instruments, energy dispersive (ed) spectroscopy became more precise than before. More chemical elements became measurable, and, within the last decades, ed-XRF devices became available in a portable form for field measurements (e.g. Gaus et al., 2013, Higueras et al., 2012; Hunt and Speakman, 2015; Kalnicky and Singhvi, 2001; Lubos et al., 2016; Speakman et al., 2011). Compared to conventional wd-xrf measurements, the sample preparation for p-ed-XRF is much easier and less time consuming. These devices are much cheaper to acquire and service than conventional wd-xrf devices, and are operable in the field as well as in an office or laboratory without the help of a laboratory assistant. Furthermore, the measurement time and modus (xray-frequency spectrum) can be easily adapted to the research task: in the field, p-ed-xrf devices can be used to detect anomalies qualitatively, ensuring purposeful sampling – the same device can then be calibrated to quantitatively measure these anomalies in the office or laboratory.

We evaluated the precision of quantitative measurements of a portable Niton XL3t900-ed-XRF-device via a comparison with data acquired with a conventional quantitative wd-XRF device (Philips PW1480). As a case study, the elemental contents of the ditch fill of a Linear Pottery House at Vráble-Ve'lke Lehemby were measured with the p-ed-XRF device. The implication of the results for the reconstruction of a potential number of inhabitants of a Linear Pottery House using a model applied at a close-by Bronze Age site (Gaus et al., 2013) are discussed. Since the measured P contents resulted in calculated population sizes for the Linear Pottery Houses too small to be reasonable, the duration of inhabitation of the houses, the potential functions of the ditches, as well as post-depositional processes are reconsidered.

2. Material and methods

2.1. Evaluation of p-XRF laboratory measurements

74 samples were selected for a comparison of p-ed-XRF and wd-XRF measurements. The samples were collected from profiles of alluvial and colluvial layers, from the multilayered settlement sites of Donje Môstre (Dreibrodt et al., 2013a, 2013b; Hofmann and Müller-Scheeßel, 2013) and Jagnilo (Schroedter et al., 2013) in Bosnia-Herzegovina, and from Arslantepe, Turkey (Dreibrodt et al., 2014; Frangipane and Palmieri, 1983). All samples were dried for 1 week at 40 °C and sieved to separate the <2 mm fraction. This fraction was subsequently pulverized to a grain size <60 μm in an Agate mill.

Wd-XRF measurements of major and minor element concentrations were carried out on fused glass discs using a sample to flux ($Li_2B_4O_7$) ratio of 1:6 in a Philips PW1480 X-ray fluorescence device. Quantitative contents of the measured elements were calculated considering the Loss-on-Ignition values of the samples at 1050 °C.

P-ed-XRF laboratory measurements were carried out by a NITON XL3t 900-series-device (Thermo Scientific Niton Analyzers). Samples were transferred into plastic tubes that were covered with a thin (4 μm) film. Measurements were performed under standardized conditions using a lead-mantled measurement chamber and He-flotation in the detector unit of the device. The measurement mode 'mining Cu/Zn' was applied. This mode includes measurements in 4 'filters' reflecting different spectral intervals of xray-fluorescence. The following filter modes were used: main filter- 40 kV, 50 μA, high filter: 50 kV, 40 μA, low filter: 20 kV, 100 μA, light filter: 6 kV, 100 μA. Given appropriate concentrations, it is quoted that the device measures the content of 35 main and trace elements and additionally calculates the amount of unmeasured residues ('bal'). Based on calibration with internal standards, the NITON XL3t 900-series-device also gives an estimation of measurement errors for each element. For the wd-ed-comparison, we considered only elements measured with relative standard errors of ~10% or less. A total measurement time of 300 s (main filter- 60 s, high filter– 60 s, low filter – 60 s, light filter- 120 s) was chosen based on a consideration of the ratio of effort and outcome. The number of comparable elements increased very little when the measurement time was doubled (600 s, one additional element). By bisecting or quartering the measurement times the number of comparable elements decreased by one and two additional elements respectively.

Three replicates were measured using the p-ed-XRF for each sample. Afterwards mean values and standard deviations were calculated for each element. The mean values were used for comparison of the wd- and ed-xrf measurements. . A certified standard sample (GBW07411) was measured regularly to check the reproducibility of the measurements.

The results of the wd-XRF measurements are considered here to reflect the real chemical composition of the samples, since it is a standard quantitative geochemical method proven for its precision (e.g. Hunt and Speakman, 2015). The statistically considered data set of chemical elements was limited to the elements measured with both techniques. Thus, 14 elements (Fe, Mn, Ti, Ca, K, Si, Al, P, Mg, Zr, V, Cr, Sr, Rb) were used for a statistical comparison of wd-XRF and p-ed-XRF measurements.

2.2. The Neolithic Linear Pottery house at Vráble-Ve'lke Lehemby (Slovakia)

The Neolithic Linear Pottery settlement of Vráble-Ve'lke Lehemby is situated at 48°13′33 N, 18°18′50 E at an elevation 150 m a.s.l., close to the city of Vrablé, southeastern Slovakia (Furholt et al., 2014) (Fig. 1). The geology of the studied site is characterized by Tertiary sediments, covered with Pleistocene Loess and Holocene deposits of the river Žitava. Gentle slopes incline to the adjacent creek Kováčovský potok and the river Žitava exposing a low relief gradient of about 10 m. The investigated Linear Pottery house remnants are situated on a small plateau that inclines with less than 1° towards the creek (Fig. 1). The lower part of the ca. 200 m long slope inclines ca. 1.6°. An auger core transect through the slope revealed that Holocene soil erosion was negligible at the site. Chernozems and Cambisols formed within the Loess deposits during the Holocene (Miklós and Hrnčiarová, 2012). The climate at Vráble is classified as cold-temperate (Köppen-Geiger Dfb) with an annual mean temperature of 9.9 °C and an annual sum of precipitation of 593 mm for the period 1982–2012 (www.climate-data.org). According to Walter and Straka (1970) the potential natural vegetation forms of the region are mixed woodlands with a dominance of beech and oak. In the recent past and today the site has been covered by agricultural fields.

Three distinctive settlement areas of the Neolithic Linear Pottery period were discovered at Vrable during an extensive geomagnetic prospection close to the small creek Kováčovský potok that flows into the Žitava river ca. 1000 m eastwards (Furholt et al., 2014; Gaus et al., 2013). Twenty radiocarbon dates from ditch fills of these Linear Pottery settlements date occupation of the site to the period of ca. 5250- 4900 cal BC (Furholt et al., 2014). The preserved archaeological traces reflect the typical situation for LBK long houses: filled ditches that framed the long sides of the houses, and postholes in the interior area of the former houses (Fig. 1). The preservation depth of the posthole remnants (about 120 to 100 cm from the recent surface) indicates that only a small portion of the archaeological profile might be missing, indicating negligible post Linear Pottery soil erosion. The excavation and dating of intersecting house structures indicates a house occupation length of <50

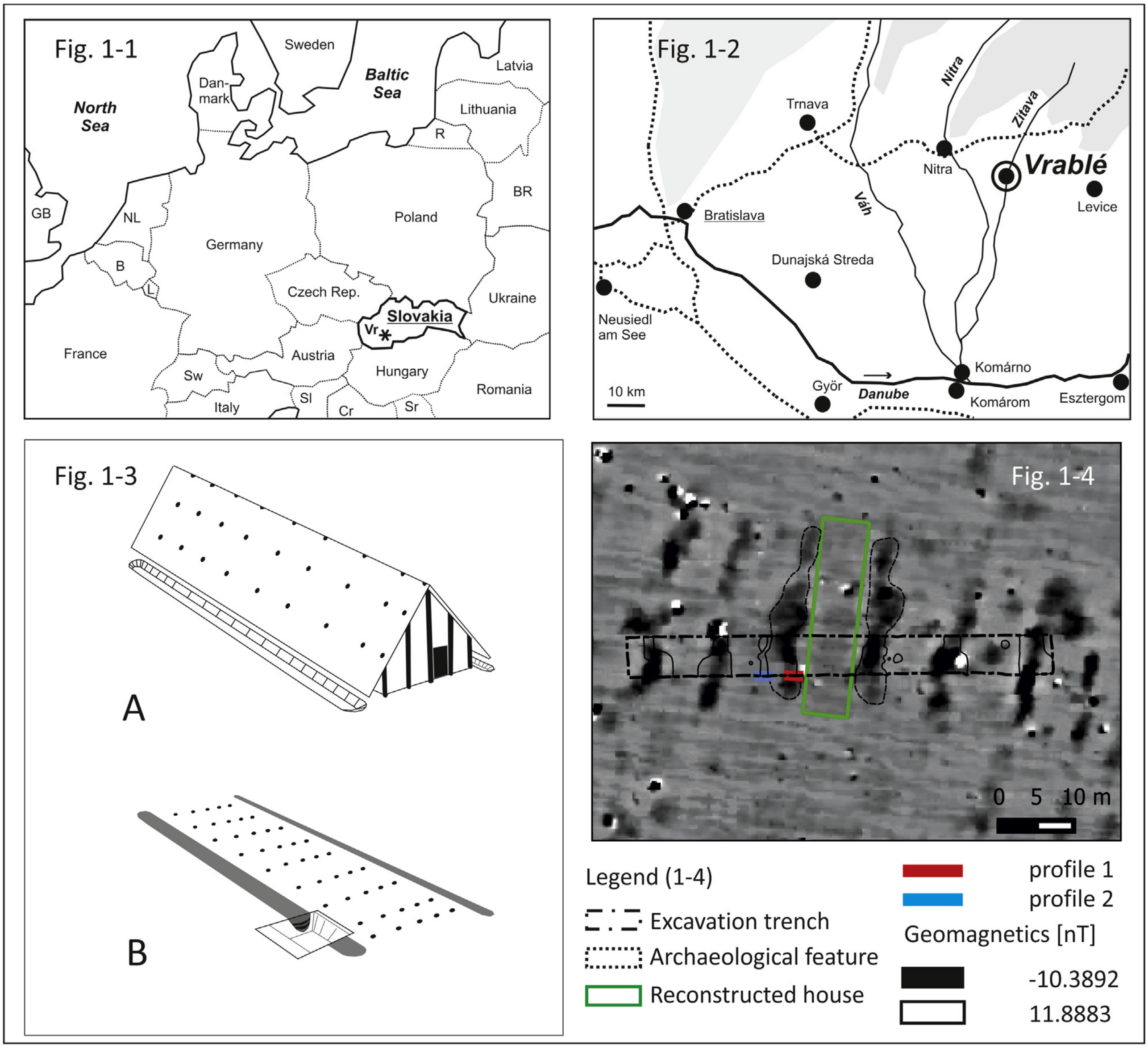

Fig. 1. Research Location 1.1 Slovakia in eastern central Europe 1.2 Vráble in the Zitava valley 1.3 Reconstruction of a Linear Pottery house (A) and sampling situation (B) 1.4 right: geomagnetic map of the studied row of Linear Pottery Houses.

years which is in accordance with reconstructions from other sites (25 years in the Merzbach valley, western Germany, Stehli, 1989; Zimmermann, 2012). The sampled context is a house remnant of a dimension of 26 × 6 m with accompanying ditches of a width of 3–5 m (Figs. 1–3). There, two profiles were dug down through the house structure and the accompanying ditches to the underlying Loess deposit. The profiles were documented in scaled drawings and photographs and described with usual pedological field methods (Boden, 2005; Munsell soil color charts, 1992). Soils were classified according to the WRB (FAO, 1998).

Fig. 2 illustrates the sampling conditions. Both profiles were free of stones. Within the freshly cleaned profiles a gradient of water content was present with less water in the upper part (in particular the upper ca. 40 cm) and increasing water content towards the base of the profiles. Profile 1 (Fig. 2-1) is a cross section through the fill of the ditch accompanying the house. At the base of the exposure, yellowish (2,5 YR 8/4) calcareous Loess was exposed. In the upper part of the calcareous, silty Loess a zone (ca. 20 cm) of pedogenic calcite concretions (Loesskindel) was present. This upper part (ca. 30 cm) of the Loess was altered (Bw1 horizon) and had a light brown color (10 YR 5/6). The ditch that accompanied the long sidewall of the Linear Pottery house was dug into the Loess. The profile of the ditch reveals two infill phases. The lower ca. 50 cm of the silty fill contained no artifacts or charcoal. The color of the lower fill resembles the light brown color of the upper part of the Loess but has a lower bulk density. The upper fill (ca. 25 cm) is more humic and of a darker brown color compared to the lower part (10 YR 4/2). The central part of the ditch the upper fill contains a high concentration of daub and charcoal (ca. 10 cm). According to these characteristics, it is possible to suggest that the lower part the fill likely reflects the inhabitation phase of the house, whereas the upper part (containing concentrations of remnants of the former architecture-namely daub) probably reflects the phase of destruction of the house. Above the ditch fill a ca. 20 cm thick denser silty layer of a dark brown color (10 YR 4/2) was present (Bw2 (Bt) -horizon). The presence of slickensides indicates a higher clay

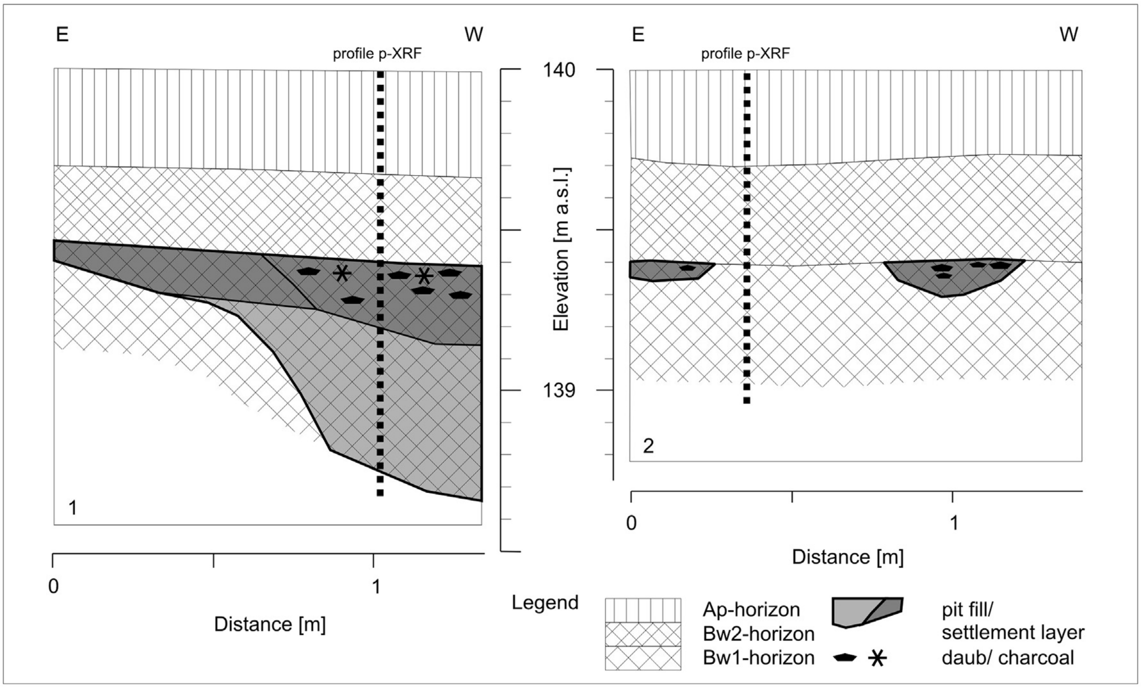

Fig. 2. Investigated profiles left: profile 1 filled ditch, right: profile 2 outside of the ditch.

content in this layer. Finally, the profile is capped with the recent, paler grayish brown (10 YR 6/2) plow horizon (upper 35 cm).

Profile 2 is situated ca. 3 m west of profile 1 and exposes the setting outside of the former ditch. At the base the yellowish (2,5 YR 8/4), calcareous Loess was again exposed. In the upper 30 cm, the altered light brown Loess (Bw1) was present (10 YR 5/6). Instead of a ditch fill, thin (ca. 10–15 cm) patchy remnants of an archaeo-sediment were preserved. They contained some daub pieces and resembled the color of the upper ditch fill (10 YR 4/2) from profile 1 and might reflect the base of a former pit or the base of filled postholes. The wavy lower border of the layer indicates some post-depositional bioturbation. Above, a denser silty horizon of ca. 20 cm thickness of dark brown color (10 YR 4/2) that contained more clay was present (Bw2 (Bt)). The recent plow horizon (Ap) (upper 35 cm) is of paler grayish brown color (10 YR 6/2).

All layers and horizons had a similar bulk density. The Bw2 (Bt) -horizon was classified to Ld3 (1.55 to < 1.80 g*cm^3) whereas the rest of the layers and horizons were classified to Ld2 (1.30 to < 1.55 g*cm^3) according to the field survey instructions of Boden (2005).

Since the Linear Pottery pit fill was altered by pedogenesis, and the Bw1-horizon clearly follows the archaeological structure, the soil formation must be younger than the archaeological record. The same is true for the Bw2 (Bt)-horizon that overlays the pit fill. Thus, a post-depositional multiphase soil formation occurred after the abandonment of the Linear Pottery settlement at the site. Phases of Cambisol (to incipient Luvisol) formation were interrupted by phases of agricultural field use (with haploidization instead of horizonation processes) at the studied site.

Each of these profiles was sampled in 5 cm depth-increments. (Figs. 1 and 2). The samples were prepared as described for the wd-/ed-xrf-comparison above. Threes replicated were measured for every sample. The correction factors deduced by linear regression in the wd-/ed-xrf-comparison were applied to convert the p-ed-xrf-measurement results into quantitative data.

To check the reliability of the results, a model used by Nowaczinski et al. (2013) to estimate the paleo-demography of the nearby Bronze Age site Fidvár on the basis of its P-content geochemical record was applied to Vráble-Ve′lke Lehemby. Nowaczinski et al. (2013) divided their amounts of P within the settlement layers by the inhabitation time and two different P-values representing the amount of phosphorous excreted by an individual. According to a caloric demand of ca. 2750 kcal/day (FAO, 1998) the authors assumed that P contents of 1116 g*P*a^{-1} would reflect an annual nutrition of a diet rich in meat, whereas an amount of 1047 g*P*a^{-1} was assumed for a diet less rich in meat. To finesse their model, Nowaczinski et al. (2013) included similar additional data about phosphorus in animal excrements and firewood. By applying this method to the ditches associated with the sampled LBK house at Vráble-Ve′lke Lehemby it was possible to test if reliable numbers of inhabitants of Linear Pottery houses could be deduced from the preserved geochemical record.

From the geomagnetic measurements and exposed profiles/plana we calculated the volume and mass of the ditch fill assumed to reflect the inhabitation period of the investigated Linear Pottery house (Table 1). After subtraction of the background P content of the calcareous Loess (measured in profile 2), the mass of P preserved in the ditch fill was calculated. In a first scenario, the mean P content [a] of the fill was used to calculate the mass of phosphorus that is preserved in the lower ditch fill. For a second scenario, the maximum content [b] was assumed to reflect the initial P content, whereas the decrease to the upper part of the pit fill was considered to be a result of loss of initial P content due to weathering or leaching. Finally, as a third scenario, the detected amount of leached phosphorus within the Loess below the ditch fill [c] was calculated and added to the values from the first two scenarios ([a+c], [b+c]). For all of these scenarios, the calculated amounts of P were then divided by the P content of the two nutritional models from Nowaczinski et al. (2013) and different estimated lengths of house occupation.

There is an ongoing discussion about the average numbers of inhabitants in the large Linear Pottery houses; based on

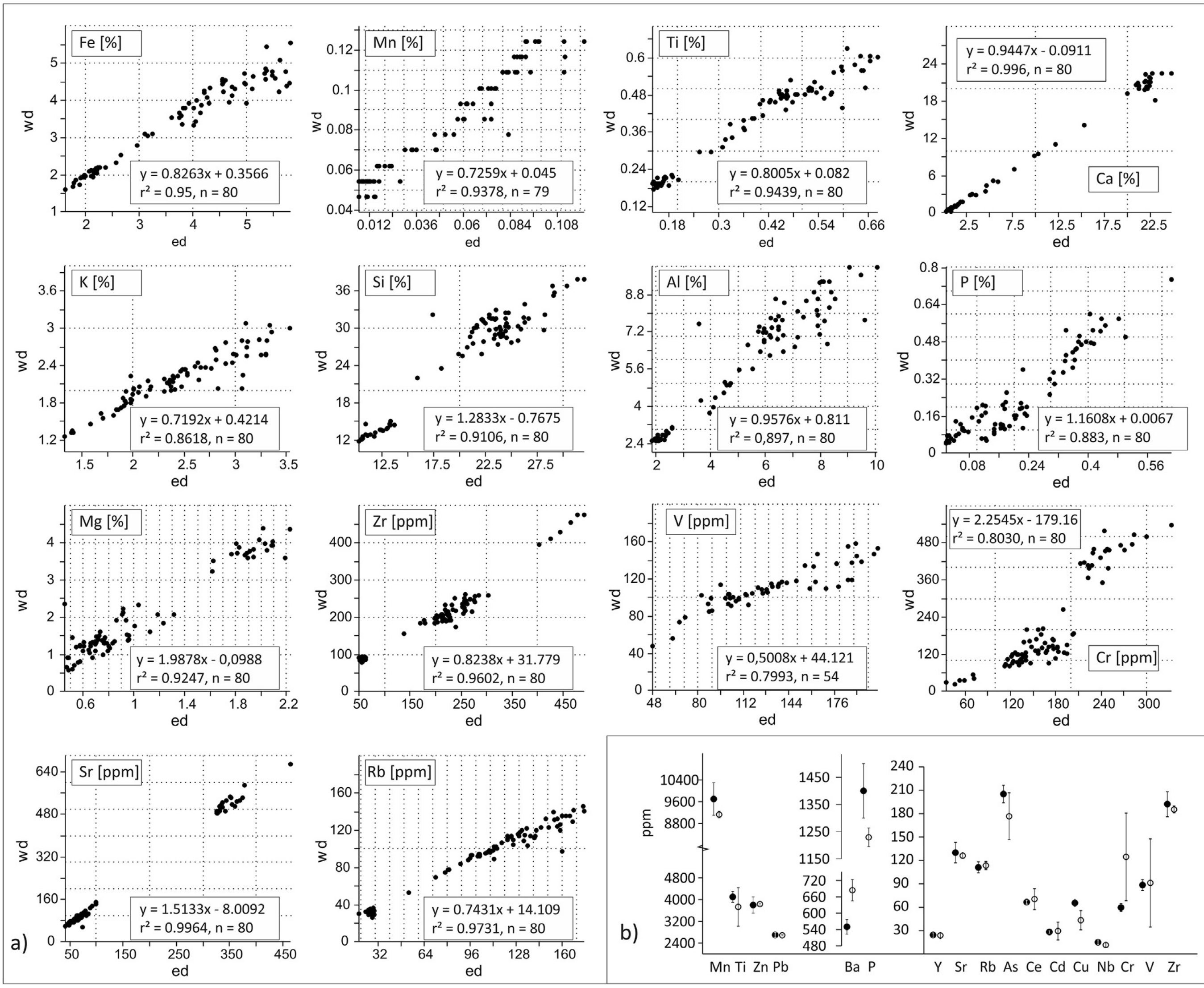

Fig. 3. a) Linear regression of p-ed-XRF and wd-XRF measurements on identical samples, n = 74, b) p-ed-XRF measurements of the standard sample GBW07411. Filled circles-reference data with standard deviation, open circles-measured data with standard deviation (n = 5).

comparisons of house-numbers and connected burials per generation in Western German LBK settlement areas, Zimmermann (2012) argues that 5–10 persons - probably one nuclear family, or extended nuclear family - represents the most probable number of inhabitants of a typical Linear Pottery house (see also Zimmermann et al., 2004). Biermann (2009) and Rück (2012) have argued for a much larger number of inhabitants using different ethnographical records, resulting in about 20–40 people per house (Biermann, 2009). Most archaeologists assume that the ditches, which are associated with LBK-houses, were used by the inhabitants to dispose of everyday waste (see comprehensively, Stäuble, 1997). To test whether different inhabitation periods could explain the observed geochemical record from the ditch fill of the Linear Pottery house at Vráble- Ve'lke Lehemby, three scenarios (15 a, 25 a, 50 a) were calculated separately.

3. Results

3.1. Evaluation of the p-ed-XRF measurements

The comparison of the content of 14 elements measured via p-ed-XRF and wd-XRF shows that there are very good linear regressions for the values of Fe, Mn, Ti, Ca, K, Si, Al, P, Mg, Zr, Sr, Rb, and good regressions for V and Cr (Fig. 3a). As the wd-XRF technique is a well-established method for determining the quantitative amounts of different elements, these regressions show that the p-ed-XRF under-estimates the quantity of certain elements and over-estimates that of others. A slight overestimation is observed for K, Al, Zr, Rb, Fe, Mn, Ti, and Ca, V is strongly overestimated, Si, Sr, and P are slightly underestimated, and Mg and Cr are strongly underestimated. With the exception of Cr and V, the quantity of all elements measured with the portable XRF device could be corrected by multiplying the results by the relevant coefficients from the wd-XRF:p-ed-XRF regression equations.

A comparison of the quantities of the different elements present in the standard sample (GBW07411) measured by both the wd-XRF and p-ed-XRF also show that quantitative data related to most elements is relatively precisely recorded by the portable device (Fig. 3 b). Larger aberrations are only visible for Pb, Cu and in particular for Cr. Whereas the relative standard error is about ± 7.5% for Pb and ± 33.7% for Cu – a high, but acceptable amount - it is about ± 108.7% for Cr indicating that the latter element is not

Table 1
Dimension of the investigated ditch fill, its surplus phosphorus content and calculations of inhabitants. Conversion of volume into mass by multiplication with 1.5 g*cm^3. Anthropogenic P contents adjusted to the background P contents of the parent material (320 ppm). Inhabitation duration according to Ebersbach, 2010 (15 a), Zimmermann 2012 (25 a), and the radiocarbon dates from Vráble (50 a). Model a and b P in human nutrition/excrements according to Nowaczinski et al., 2013.

Dimension of the ditch fill				
Ditch length [m]	Ditch width [m]	Thickness of fill [m]	Volume of fill [m^3]	Mass of ditch fill [kg]
26	1.5	0.35	13.7 Two ditch fills:	20.5 41
Modelling nr. of inhabitants based on P contents of ditch fills			Adult inhabitants	
P surplus [%]	Mass P surplus [kg]	Inhabitation duration [a]	Model a (1047 g/a)	Model b (1116 g/a)
[a] Mean- 0.043	17.6	15 25 50	1.2 0.7 0.3	1.0 0.6 0.3
[b] Max- 0.059	24.2	15 25 50	1.5 0.9 0.5	1.4 0.9 0.4
[c] leached P- 0.046	16.4	15 25 50	2.2 ([a]+[c])/2.6 ([a]+[b]) 1.3 ([a]+[c])/1.5 ([a]+[b]) 0.6 ([a]+[c])/0.8 ([a]+[b])	2.0 ([a]+[c])/2.4 ([a]+[b]) 1.2 ([a]+[c])/1.4 ([a]+[b]) 0.6 ([a]+[c])/0.7 ([a]+[b])

measured with appropriate precision by the p-ed-XRF device. As the P-content is discussed extensively in the remainder of this paper, it is worth noting that the p-ed-xrf consistently underestimates P-values. However, after applying the correction factor from the linear-regression of p-ed- and wd-XRF measurements, the certified value of 0.14 ± 0.01% P present in the standard sample results.

3.2. Measurements on the Linear Pottery house

Results of measurements from the two studied profiles at Vráble-Ve'lke Lehemby are given in Fig. 4. All results were adjusted with the correction factors of the different elements deduced from linear regression (Fig. 3). Fig. 4-1 gives values for the pit fill studied in profile one. As visible in the Ca content, the whole profile above the Loess (117.5–127.5 cm) is decalcified. The lower part of the pit fill contains twice as much phosphorus (ca. 750–800 ppm) than the covering layers and horizons (ca. 300–350 ppm). Within the pit fill, the phosphorus content increases with depth, reaching its maximum at the base of the pit fill (107.5 cm). The pit fill considered to reflect the inhabitation interval of the investigated Linear Pottery house contains a mean P content of 750 ppm with a maximum of 900 ppm. At 720 ppm, the underlying Loess samples (117.5–127.5 cm) have enhanced phosphorus values as well. When compared with the mean P content of 320 ppm from the Loess in profile 2, that outside of the habitation zone, this elevated phosphorous in the Loess of profile 1 suggests leaching occurred.

The ratios of Fe, Al, and K to Si, all indicating pedogenic enrichment (brunification, clay formation/translocation) of the former elements, show a similar distribution within the profile. In the Ap horizon all ratios had the lowest values. In the Bw2 horizon larger ratios could be recognized. Excluding the Ap horizon, Fe, Al, K, and Si generally all occurred in higher concentrations in the upper parts of profile than in the underlying Loess. A similar pattern is visible in the Rb/Sr ratio with lower values in the Ap, higher values in the Bw2, medium values in the Bw1 (pit fill), and lowest values in the Loess. This same pattern of element distribution is present in profile 2 (Fig. 4-2), supporting the pedological horizonation established based on field properties in Section 2.2.

4. Discussion

4.1. Evaluation of p-XRF measurements

By the application of a number of pretreatment steps, He-flotation, and a minimum measurement time of 300 s with the measurement modus 'mining-Cu/Zn', the portable ed-XRF device produced quantitative data with little aberrations (over- and underestimations) for the compared set of elements.

In contrast to the findings of Hunt and Speakman (2015), phosphorus is measured with a good precision by the p-ed-XRF device. The coefficient of the linear regression between wd- and p-ed-XRF measurements equals 0.88 and the p content of the certified standard sample is perfectly met after the application of the correction factor of 1.1608. Moreover, the Ca contents of the compared samples were measured in an even better quality ($r^2 = 0.996$). Since the samples used in this comparison contained a different amount of calcium than amount of phosphorous, the effect of the escape peaks of Ca, which is considered by Hunt and Speakman (2015) as a main source of error and overestimation of phosphorus content, has been solved by the software of the device. Instead, we observed a systematical underestimation of P contents by the p-ed-xrf device. For the compared elements, only the results of V and Cr contents largely deviated from a good linear regression. Different speciation of Cr in the sub-sets of data measured differently in wd-XRF and p-ed-XRF or problems of overlying fluorescence spectra (e.g. V Kβ - Cr Kα) as discussed in Hunt and Speakman (2015) could explain the observed aberration.

While the one week long drying step (at 40 °C) is necessary as it ensures comparable water content for all measured samples, the remainder of the sample preparation for p-ed-XRF measurement is relatively non-time intensive. Sieving through a 2 mm mesh requires 10 min per sample including careful cleaning of the sieves after each sample. Pulverizing (<60 μm) in a mechanical Agate mill requires another ~5 min (30 s for the milling process plus inserting and removing of the sample, and careful cleaning of the equipment). These two homogenization steps ensure that measurements result in representative mean contents of the respective elements, allowing the portable ed-XRF to provide a reliable quantitative data set for a large number of elements. These time requirements are small in comparison to wd-XRF measurements (all mentioned pretreatment steps plus preparation of fused glass disks and LOI at 1040 °C), or to wet chemical measurements (ICP/AAS measurements after extractions) and no toxic chemicals are needed.

Our successful results imply that, in contrast to Hunt and Speakman (2015), preparation of pressed pellets is not necessary to acquire precise measurements with a p-ed-XRF device. Measurements on pulverized samples (<~60 μm), using He-flotation and appropriate long measurements times at low voltage/high amperage spectra to measure the lighter elements (here 120 s at

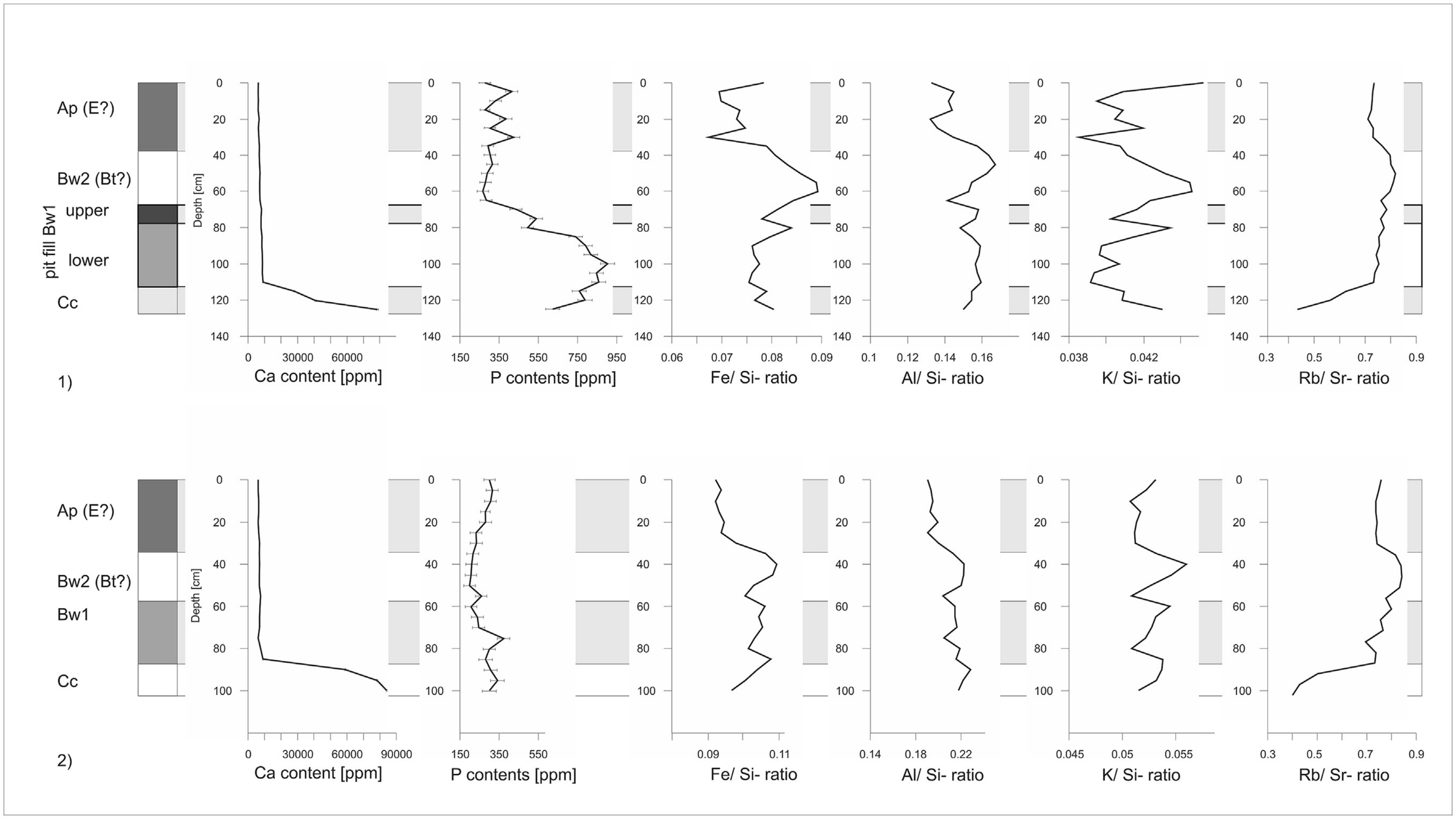

Fig. 4. Selected elemental results or ratios from measurements on the profile with ditch fill 1) and 2) without ditch fill.

6 kV, 100 μA) results in quantitative data comparable with wd-XRF measurements.

4.2. Results of p-ed-XRF measurements at the site Vráble-Ve'lke Lehemby

In the following section, the markedly increased P content of the lower pit fill which is most likely reflecting the occupation phase of the associated house and the following multiphase soil formation at the site are discussed.

Phosphorus enrichment due to ancient human activities (subsistence economy) is relatively resistant against leaching out from soils (e.g. Wild, 1988) and often even used as geochemical signal to survey for ancient settlements (e.g. Holliday and Gartner, 2007). While leaching of P is considered negligible under usual soil surface conditions, the particularities of the case of the investigated ditch system might explain the observed leaching. Firstly, the ditch collected precipitation water from the roof of the former house and liquid garbage. Thus, more water was available than under normal conditions, promoting leaching in general throughout the ditch. Additionally, if - as archaeologists suggest - the ditch was a main dump for the inhabitants, some of the phosphorous could have entered it organically bound in a liquid solution (i.e. excrement). Under such conditions increased P leaching has been reported (e.g. Johnston and Poulton, 1976; Wild, 1959). Thus, both the fill of the respective layer of ditch fill, as well as the increased P content found within the Loess below the ditch fill were considered to reflect remains of ancient human activity (Table 1).

The calculation of numbers of inhabitants according to the amount of P as a measure of anthropogenically excreted P, results in surprisingly low values (Table 1). The maximum number of inhabitants – two – is estimated assuming an inhabitation period of 15 years and Model a (a more cereal based nutrition). This is highly in discordance with the existing archaeological interpretations of inhabitation numbers. Since all other scenarios result in even lower numbers of inhabitants, several possible explanations are now considered.

One explanation could be a house occupation period significantly shorter than expected. Such an option is virtually absent in the debates on LBK settlement (e.g. Rück, 2012; Zimmermann, 2012), where houses are commonly portrayed, almost assumed to be, continuously settled for several generations. This is partly based on the large size of the houses, which seems to indicate considerable work effort in their erection. Dieck (2014) calculated the number of necessary working hours and laborers to erect a house in a comparison of the central European Neolithic. His results of 21–28 workers laboring 5000–10,000 h each make a very short inhibition interval rather unlikely.

Nevertheless, settlements discovered in areas with other preservation conditions, like the lake-shore settlements in the regions adjacent to the Alps, are obviously often settled for 5, 10 or 15 years (e.g. Ebersbach, 2010). It should be noted, however, that these settlements were most likely erected 1500 years later than the settlement at Vrable.

Another option could be that locations other than the ditches were preferred as prehistoric toilets, although no supporting archaeological evidence has been found so far. From a geoarchaeological perspective, a sophisticated system of house-made-manure, like that of the later "night-soils" (e.g. Anderson, 1794), seems obsolete considering the fertile soils that naturally form on Loess. Long term investigations of comparable soils on Loess (e.g. Merbach et al., 2013) indicate a negligible loss of soil fertility even without the application of manure or fertilizer. Nevertheless, cultural reasons for the relocation of human excrements have to be considered, and recent publications indicate Linear Pottery manuring may have occurred (e.g. Bogaard et al., 2007; Fraser et al., 2011).

In addition to these behavioral explanations for the low P-values, we have to consider possible taphonomic issues. Firstly, it is possible that the measured part of ditch fill does not reflect the mean P values. We cannot exclude such a mismatch completely. However, the lower ditch fill measured in a continuous profile (seven samples) looks very much like what could be expected as an ancient mainly organogenic fill (no coarse material, rich in humic matter). Additionally, the sampling position of the profile is relatively close to the potential former door of the investigated house (Fig. 1c). Thus, it is positioned where we could expect the infill of waste from the house, not below-average P values.

Alternatively, the post-depositional history of the locale might explain a certain amount of phosphorus loss. Due to the presence of clear indications of the formation of a forest soil (Cambisol or incipient Luvisol) over the ditch fill, it is possible to suggest that soil formation processes under forest vegetation might have altered the elemental composition. Additionally, the site was used for agricultural during certain prehistoric periods, including most certainly the period from the medieval times until the present day. Thus, we have to consider post-depositional scenarios including phases of woodland cover and agricultural field use. The diachronous settlement history, known from intensive archaeological surveys in the surroundings of the investigated site (e.g. Gaus et al., 2013, personal communication Dr. K. Rassmann, Römisch-Germanische Kommission Frankfurt), enables an estimation of the duration of post-Linear Pottery phases that were probably characterized by agricultural field use and those probably characterized by forestation. After the termination of the Linear Pottery settlement at the site (ca. 4900 BCE), features and finds are present from the Lengyel period (duration ca. 100 a), the Baden period (ca. 100 a), the Kosihy Caka period (ca. 100 a), the Bronze Age settlement of Fidvár (ca. 1000 a), the Roman Iron Age and Roman Times (ca. 100 a), and the medieval period to the present (first written documentation of Vrablé at 1265 AD, ca. 750 a). Thus, the post-Linear Pottery phases of assumed agricultural field use sum to ca. 2150 a. Based on the assumption that forest encroached over the territory during non-agricultural phases, the forested post-Linear Pottery phases sum to ca. 4165 a.

Cambisol formation was found to have occurred within 1500–2000 years in the southern Netherlands (Bolt et al., 1980) and at different sites in Germany within ca. 2000 years (Becker and Schirmer, 1977), 2750 years (Stolz and Grunert, 2010), or ca. 3000 years (Dreibrodt et al., 2013c). This is very similar to observations from northern America, where Mollisols to Inceptisol exposing a cambic Bw horizon developed during the past 1500–1000 years in alluvial deposits (Bettis, 1992). No similar consensus exists for the length of the formation of Luvisols in the literature. The formation of clay laminae in sands is a sometimes-fast process, operating in few decades (e.g. Webb, 1939). Bork (1983, 1988), Bork and Rohdenburg (1979) report the formation of Luvisols from non-calcareous colluvial layers within 500–600 years. Semmel and Poetsch (1996a) found a Luvisol that has formed within 1000 years in non-calcareous colluvial layers, whereas the time for Luvisol formation within calcareous archaeo-sediments was equal to ca. 3000 years (Semmel and Poetsch, 1996b). Eheim and Völkel (1994) report the formation of a Luvisol in a non-calcareous man-made dam of the Celtic period within ca. 2000 years. Fickel et al. (1977) and Beckmann et al. (1978) report the formation of a Luvisol in burial mound erected from non-calcareous material within 2600 years. Becker and Schirmer (1977) found Luvisols at terraces of the River Main exposed for ca. 2000 to 2300 years. Similar ages of Luvisol formation (4000–2000 a) were found on alluvial sediments in the US by Bettis (1992). The large differences in reported Luvisol

Table 2
Calculation of potential P recycling and loss by forest, prehistorical and historical agriculture at Vrablé-Lehemby. Data of settlement history according to Gaus et al. (2013) and personal communication Dr. K. Rassmann (Römisch-Germanische Kommission). Subsoil P uptake of oaks 25% of 7.5 kg*ha^{-1}*a^{-1}; 75% of fine roots assumed in the upper 20 cm of the profile. P uptake from the Ap horizon by ears and straw of wheat according to DLG (1973). All potential P fluxes are related to the size of the investigated ditches (78 m^2).

post-Linear Pottery landscape phases		potential bio-cycling under Oak forest	potential export due to pre-industrial cereal (wheat) harvest	
phases	duration [a]	P [kg]	P [kg], yield 1 t*ha^{-1}	P [kg], yield 5 t*ha^{-1}
forested	4165	60.9	–	–
prehistoric agricultural field use	1300	–	32.4 (ears)	
historic agricultural field use	850[a]	–		121.7 (99.8 ears, 21.8 straw)

[a] Last 50 years are assumed to have been characterized by the application of synthetic fertilizers and thus P loss via harvest of crops is assumed to be negligible of negative for that period. Thus, 800 years of potential P loss by harvested crops (wheat) were applied in the model.

formation time perhaps result from issues with differentiating whether the given Luvisol underwent a phase of clay mineral neoformation first (Cambisol formation stage), and later clay translocation or if the studied profile resulted from the translocation of clay inherited from the parent material. The reported shorter time spans probably reflect the latter case only.

The geochemical record from the investigated profiles (Fig. 4) clearly backs the post-depositional alteration of the archaeological record due to forestation and agricultural identified with field methods. Horizons ascribed as Bw/t horizons expose increased ratios of Fe/Si, Al/Si, K/Si and Rb/Sr within the pit fill as well as in the adjacent natural substrate. The mentioned ratios indicate clearly an increase in pedogenic iron oxides and clay minerals (partly Illite- K/Si) in the B-horizons, and a decrease of the mentioned items in the upper (incipient E?) horizons.

Whereas mineral weathering in forest soils has been emphasized as an important process affecting archaeological findings buried in the soil (e.g. Crow, 2008), bio-cycling of elements due to nutrient uptake of plants (e.g. Duchaufour, 1976, 1982; Likens, 2001; Likens et al., 1998) has not yet been considered in archaeological research extensively.

Data on elemental contents of biomass of deciduous trees imply a certain bio-cycling of chemical elements due to biological weathering and uptake of nutrients in the rhizosphere, the incorporation of elements into the biomass of the trees, and their redeposition at the soil surface through leaf litter. Although a number of elements are biocycled, for the purpose of the present paper, we focus on phosphorous. The P content of the woody parts of deciduous trees is very low (e.g. Jacobsen et al., 2003; Shiel, 2006) and is recycled over longer periods of time (several centuries for most tree species), but the leaves of deciduous trees are recycled every year. Yearly amounts of elemental contents in broadleaf forests biomass data show that a transfer of considerable amounts of phosphorous from the subsoil to the soil surface is associated with bio-cycling. Sharpe et al. (1980) report that about 4 kg*ha^{-1}*a^{-1} of P is associated with yearly leaf fall in southern Appalachian mixed deciduous forests. Higher values are reported from Eurasian forests. Goryshina and Neshataev (1974) measured a P amount of 7.85 and 6.81 kg*ha^{-1}*a^{-1} in leaf litter of oaks from the Russian forest steppe (300/80 years old). Jacobsen et al. (2003) reports values of 7.84 kg P*ha^{-1}*a^{-1} for oak stands, 5.77 kg P*ha^{-1}*a^{-1} for beech stands, and 8.99 kg P*ha^{-1}*a^{-1} for birch stands in central Germany. Although the majority of most active fine roots are often found in the uppermost parts of the soil, e.g. 76% in the upper 20 cm (e.g. Goryshina and Neshataev, 1974), it should be noted that tree roots can reach remarkable maximum depths (e.g. Stone and Kalisz, 1991). Given unconsolidated parent materials (sediments rather than hard rock) and low water tables, Stone and Kalisz (1991) report oak roots to reach maximum depths of >20 m (mean of their listed data 5.8 m, n = 28), roots of birch trees to reach depths of up to 4 m (mean 2.4 m, n = 6), and those of beech trees up to 1.8 m. Thus, shallow buried archaeological remains are most probably subjected to nutrient uptake by tree roots during post-depositional phases of reforestation. The presence of subsoil uptake of P at Vráble-Ve'lke Lehemby is supported by the decreasing P values in the lower horizons which developed in the Loess of the investigated profile 2 (Fig. 4).

In Table 2 we calculated the potential P uptake of an oak forest – the identified likely natural vegetation at the site - on the base of P contents of the leaves of oak by applying the mean value of 7.5 kg P ha^{-1} a^{-1} from the measurements of Eurasian oak forests (Goryshina and Neshataev, 1974; Jacobsen et al., 2003). The values were related to the area of the investigated ditch fill (78 m^2, see Table 1). Further, since about 75% of the active fine roots are known to be located in the upper 20 cm, a percentage of 25% of the P uptake was assumed for deeper layers (subsoil). According to the mentioned assumptions, an uptake of 60.9 kg would be possible at the investigated ditch fill.

Given the considerable length of the post-Linear Pottery settlement use of the site for agriculture, the influence of farming on nutrient fluxes must also be considered. As Shiel (2006) points out, until the onset of application of synthetic fertilizers (after World War II) agricultural land use led to a general loss of nutrients on the fields and forests and a gain in nutrients in the vicinity of the settlement. While the invention of crop rotation systems with legumes in the 18th century changed the situation for nitrogen, this was not the case for phosphorus. Thus, potential P losses by uptake of crop roots and its transfer towards settlements post-dating archaeological finds might explain another part of post-depositional alteration of buried archaeological contexts. This is supported by diverse projects, which found that the uppermost settlement layers of multilayered settlement mounds with a long post-depositional history of agricultural field use show lower P contents (e.g. Dreibrodt et al., 2013b; Lubos et al., 2013; Ottaway and Matthews, 1988). Similarly, the upper layers of the Bronze Age settlement of Fidvár (e.g. Gaus et al., 2013) close to the studied finds have lower P contents in the youngest layers. The enhanced availability of nutrients because of former settlement activities at such sites might have resulted in higher harvest yields during subsequent field use, as has been reported for ancient pastures from other sites (e.g. Roscoe, 1960).

Since wheat and its progenitors were among the most important crops used by European farmers throughout the Holocene (e.g. Renfrew, 1973), and data about elemental contents and historical harvest yields are available, we use here wheat to illustrate the potential alteration of P contents of soils by historical field use.

An amount of 21.7 kg*ha^{-1}*a^{-1} of P uptake by wheat was recorded by Frissel (1978). Similar values are given by Stevenson and Cole (1999): 34 kg*ha^{-1}*a^{-1}. Some references give P uptake for ears and straw of wheat separately and in relation to the total harvest (DLG, 1973): ears 16 kg*ha^{-1}*a^{-1} and straw 3.5 kg*ha^{-1}*a^{-1} for a harvest of 5 t*ha^{-1}. When considering an effect of crop growth

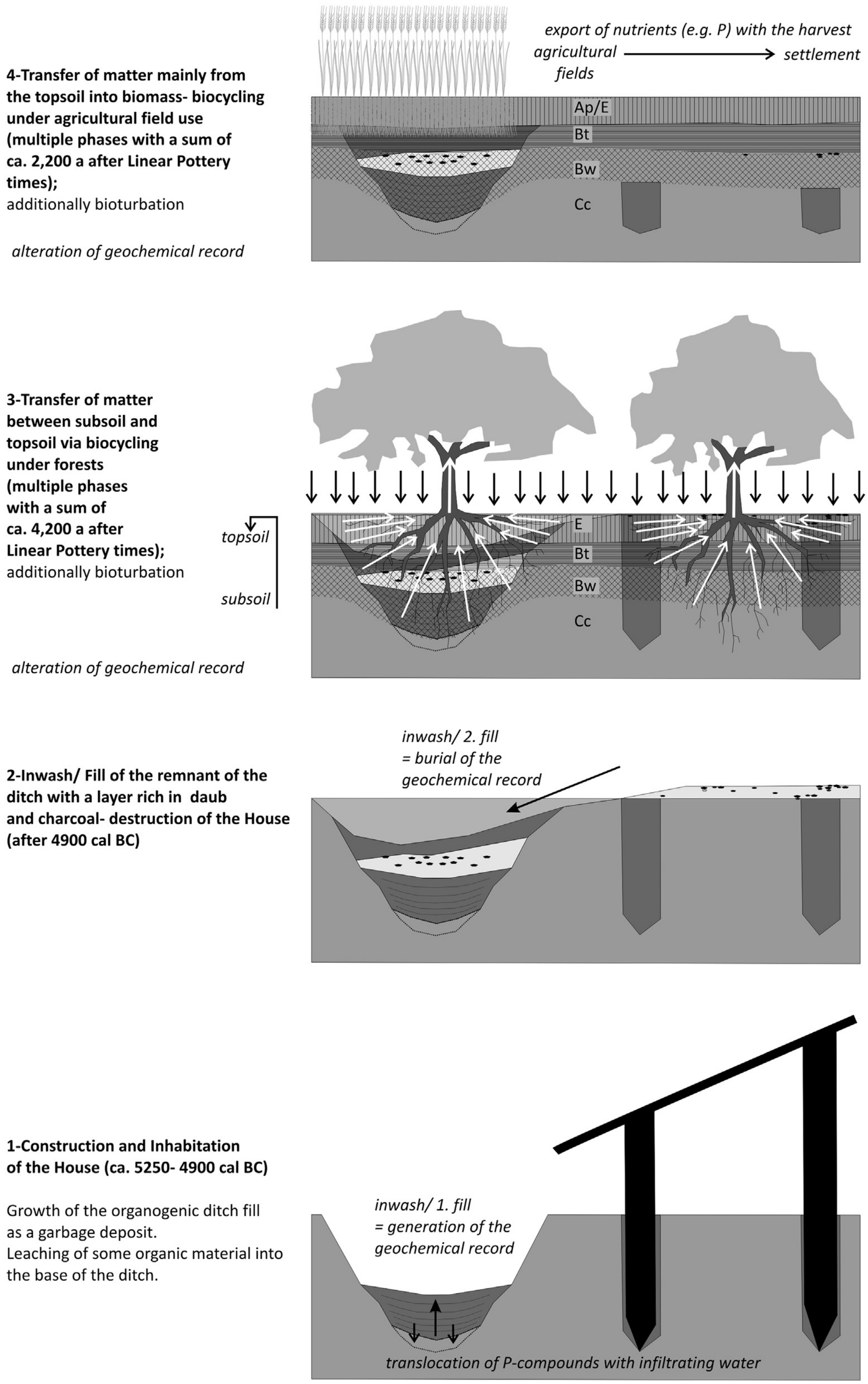

Fig. 5. Szenario of postdepositional processes at the investigated Linear Pottery House at Vráble-Ve'lké Lehemby.

on the geochemistry of archaeological sites, researchers must also account for the immense changes in harvest amounts throughout the Holocene (Evans, 1993). Zohary (1969) reports amounts of 0.5–0.8 t*ha^{-1} for wild wheat stands in Israel. Yield in Roman Times from Great Britain are estimated to about 0.6 t*ha^{-1} (Bowen, 1961). Studies of experimental archaeology in Great Britain imply higher values of 2.5 t*ha^{-1} for spelt and 3.7 t*ha^{-1} for emmer (Reynolds, 1981). For medieval times first data indicate yields as high as 5.3 $t^*ha^{-1*}a^{-1}$ (Titow, 1972). Considering the given soil conditions at Vrablé- Ve'lké Lehemby (very fertile soil on Loess), we assume mean harvest amounts of about 1 $t^*ha^{-1*}a^{-1}$ for the prehistoric period (harvest of only ears) and 5 $t^*ha^{-1*}a^{-1}$ for the historic period (harvest of ears and straw) for calculations of potential P uptake by crops in Table 2. In total, 154.1 kg of P could have been removed from the topsoil at the investigated site due to nutrient export related to cereal harvest (Table 2). Since cereals roots do not reach soil depths as large as trees, we do not consider a significant alteration of the lower pit fill associated with this p export.

The calculated 60.9 kg of phosphorus potentially recycled by tree growth (Table 2), could explain the pattern of P preservation in the ditch fill; the decreasing P-content of the upper part of the ditch fill would in this case reflect the increased density of roots towards relict forest surface (Fig. 4-1). The calculated amount of potential uptake by tree roots is larger than what was preserved in the ditch fill and measured by the XRF devices; this effect is therefore considerable (Table 2). By assuming a post-depositional reduction of the initial phosphorus content by 60.9 kg, the calculation of former inhabitants for a 25 year period excreting about 1.047 kg P each year (data from Table 1) would result in four adults, much closer to archaeological assumptions about population size of Linear Pottery houses (Zimmermann, 2012). Assuming a reduction of house occupation length to 15 years (Ebersbach, 2010), a count of up to six adults would result. Thus, the scenario of post-depositional alteration of the context by bio-cycling appears reasonable. On the other hand, we would have to expect a certain enrichment of the surface horizons as a result of the deposition of P with the leaf litter, not visible in the record of the studied profile (Fig. 4-1).

The absence of this enrichment could be explained by the subsequent agricultural field use phases. The amount of P that could have been removed with the harvest is more than twice of the amount potentially affected in the subsoil by bio-cycling of trees (Table 2). Thus, the enrichment of the topsoil might have been completely erased by the 2000 years of crop harvesting at Vráble-Ve′lke Lehemby that preceded the widespread use of artificial fertilizers.

Our data suggest the importance of careful considerations about post-depositional processes (particularly bio-cycling) when interpreting geochemical data from archaeological contexts. When evaluating the preservation of shallow buried archaeological finds and findings, enhanced biogeochemical dissolution and weathering by roots should be considered alongside physical destruction by plowing, particularly near relict and modern surface horizons where the highest concentrations of fine roots would have been found. The often-reported smaller numbers of preserved artifacts in the uppermost layers (e.g. Dreibrodt et al., 2013b; Hofmann, 2013; Medović et al., 2014) might also be an effect of this bio-degradation, in addition to destruction by plowing. Thus, while forestation might prevent the destruction of archaeological sites by erosion, the shallow buried archaeological records might be subject of chemical alteration and dissolution. Since we can exclude soil erosion due to the topographic position of the investigated site and the results of a survey for colluvial layers, the observed geochemical variability of the investigated profiles is probably a result of soil formation.

In sum, we propose that the following scenario fits best to the archaeological and geochemical record:

After the deposition of the Loess cover in Late Pleistocene, and perhaps some phases of fluvial redeposition in Early Holocene (e.g. Dreibrodt et al., 2010; Vincent et al., 2011), a Regosol to (thin) Chernozem-like A-C soil probably formed during the first millennia of the Holocene. Around 5250 cal BC the Linear Pottery settlement was founded. The investigated house and its accompanying ditch were erected and inhabited for 15–50 years (Fig. 5.1). During that time, the lower fill rich in P, probably inter alia due to its usage as an everyday dump (organic waste, excrements), was deposited. Due to the presence of excess water in the ditch and to the organic speciation of the phosphorous, parts of the P associated with the waste were leached for some cm at the base of the ditch. At ca. 4900 cal BC, the investigated house was abandoned and destroyed, perhaps by a fire. The upper thin fill rich in charcoal and daub was deposited (Fig. 5.2). For a certain time this layer might have formed the surface of the ditch fill, still exposing a small scale depression in the landscape. A humus horizon formed within the upper fill under a succession of forest, explaining the somewhat darker color of the layer. In the following Lengyel period, Baden period, Kosihy-Čaka period, Early-Middle Bronze Age (settlement of Fidvár), Roman Iron Age and Roman Times an alternation of forest clearing phases for agricultural field use and reforestation phases (Fig. 5.3 and 5.4) might be assumed At a certain time, the remaining small depression was completely filled by either natural processes (small-scale erosion/deposition, bioturbation), or human activity (leveling for agricultural field use by plowing), or a combination of both. Associated processes of bio-cycling under forests (translocation of elements from subsoil to the surface), as well as field use (transfer of elements towards the contemporary settlement sites), explain the loss of P in the lower ditch fill, as well its removal from the profile as a whole. Because subsoil bio-cycling is probable to include a large number of elements (Goryshina and Neshataev, 1974; Jacobsen et al., 2003) in addition to P, the observed enhancements of Fe, Si, Al, and K in the solum might reflect at least partly translocation of these elements from the subsoil towards the soil surface via bio-cycling of trees. Since the first written documentation of Vráble at 1265 AD, uninterrupted agricultural field use very probably took place at the site. During this period, the fill of the depression of ditch was definitely completed, and export of nutrients as P towards the village reached probably the highest intensities. This matter transfer associated with the agricultural land use system did not terminate completely until the application of synthetic fertilizers after World War II (e.g. Shiel, 2006).

As considering bio-cycling as a post-depositional process could explain the geochemical record at the Linear Pottery site of Vráble-Ve'lké Lehemby, a re-evaluation of the record presented by Gaus et al. (2013) from the nearby Bronze Age site of Fidvár is suggested. As mentioned in the sediment profiles of Fidvár, there are decreasing values of P content in the upper part (Nowaczinski et al., 2013). If there was a pedogenetic alteration (soil formation in the archaeo-sediments) after the abandonment of the Fidvár settlement mound, it has not yet studied so far.

5. Conclusions and outlook

After few preparation steps, laboratory measurements with the p-ed-XRF devices result in quantitative data of elemental contents comparable with the conventional quantitative wd-XRF method on terrestrial soil and sediment samples. Comparative analysis (interlaboratory comparison), should now be undertaken to check if the results of our investigations (correction factors for different elements) could be applied for each p-ed-XRF device of the used series and manufacturer, or if each device needs a separate calibration.

For terrestrial soils and sediments we recommend a pretreatment protocol that includes 1) continuous sampling of profiles of sediments in high resolution (here 5 cm increments), 2) drying of the samples at 40 °C for a week, 3) sieving through a 2 mm mesh, and 4) pulverizing of the sample (<60 μm). Afterwards the samples should be transferred into plastic tubes covered with a thin (4-μm) mylar-film and measured with He-floatation of the detection unit in different modes of voltage and amperage according to the research question. We found appropriate quality of quantitative results for the geo-archaeologically relevant element suite applying measurements of a total acquisition time of 300 s: 60 sec–40 kV, 50 μA, 60 sec- 50 kV, 40 μA, 60 sec- 20 kV, 100 μA, 120 sec- 6 kV, 100 μA. In particular, a long measurement time of low voltage high amperage increased the quality of the results for the lighter elements.

In addition to the inter-laboratory comparisons already mentioned, we suggest that future validation of the quantitative data from p-ed-xrf devices should include long term comparisons of the same device (aging effects) and comparison of the measurement quality with additional measurement techniques (e.g. ICP after HF dissolution of samples). Additionally, the p-ed-XRF should be tested on different types of sediments, e.g. sediments more rich in organic matter such as peat, to see if the sediment matrix effects the quality of measurements.

In this investigation, consideration of post-depositional processes was found to be necessary for a proper interpretation of geochemical records from archaeological contexts. In particular, although it has not been considered by archaeologists so far, this study discovered that bio-cycling might play an important role in post-depositional alterations of the shallow buried archaeological record. Thus, whereas the forestation of an archaeological site might prevent the record from erosion, shallow buried sites under forests are exposed to the risk of geochemical alteration associated with pedogenesis.

By integrating a thorough consideration of post-depositional processes, particularly bio-cycling of forest trees and agricultural field use systems, with quantitative analysis of geochemical data we found that the P contents of a buried ditch fill, which at first sight would indicate either a very short house usage (5–15 years), or a very small number of inhabitants (1 or 2), could actually be reconciled with the assumption of at least six inhabitants for an inhabitation period of ca. 15 years in Linear Pottery houses at Vrablé- Ve'lké Lehemby.

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