Identifying ancient manuring: traditional phosphate vs. multi-element analysis of archaeological soil

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ABSTRACT

Elevated soil phosphorus levels are often used as indicators for prehistoric manuring. However, in this article it is argued that though P is indeed a good anthropogenic marker, multi-element analyses can provide more insight into former fertilisation practices and land use.

Here, we compare the ability of both traditional total P analysis and multi-element analysis by ICP-MS to identify prehistoric manuring on soil samples from a well-preserved prehistoric Celtic field system in Denmark. The ICP-MS data set of 58 soil samples was furthermore analysed by multivariate analysis (PCA). Results show that the stronger extraction for the multi-element analysis releases significantly more P than the traditional analysis but similar archaeological interpretations based on relative P enrichments can be made. Among the 42 analysed elements, 11 were significantly ($P < 0.01$) enhanced in the fields relative to a reference soil, namely Na, P, K, Ca, Mn and Sr and the rare earth elements (REE's), Nd, Sm, Eu, Gd and Dy. Cobalt was the only element which was depleted within the field system. Enhanced P levels show that manuring was practiced, while elevated concentrations of Sr indicate that not only animal manure but also bones/domestic waste was added. Furthermore, the enhancement pattern of some major and minor elements indicate that unweathered subsoil was incorporated into the topsoil — probably through tillage erosion until approximately 2000 years ago. The study also indicates that the banks demarcating the individual fields were made of the same material as the field plough-layers, which makes within-field soil relocation the most likely cause of the banks.

1. Introduction

Manuring practices are important for understanding prehistoric agriculture and prehistoric cultures in general. This is first of all because manuring improves crop yields and helps in preventing soil deterioration, but also since the practice of manuring — in combination with fallowing — enables more permanent field systems, require byres or enclosures for collecting the manure, and is a very labour intensive practice, which therefore influenced people's daily lives. Prehistoric manuring has accordingly been the subject of many archaeological studies during the last decades focussing on when it was introduced, what kind of manure was used, and the intensity of manuring (e.g. Bakels, 1997; Guttmann et al., 2005, 2006). The practice of manuring is usually inferred archaeologically on the basis of ceramics, charcoal, bone, etc. found on prehistoric fields, but soil micromorphology and analysis of soil lipids have also proven very useful (Guttmann et al., 2005). However, the two latter approaches rely on good preservation conditions and time consuming laboratory investigations.

Analyses of the essential plant-nutrient soil phosphorous — usually reported as phosphate (PO_4^{3-}) — have been used since the 1930s with great success in archaeology as it is fast and applicable in a wide range of settings (Holliday and Gartner, 2007). Animal dung, bones, food remains, etc. are highly enriched in P and when deposited, the largest fraction of the added P is usually irreversibly bound to the minerals and soil organic matter while only a smaller fraction is removed with crops (Blume et al., 2010). The relatively simple analytical determination of P has facilitated its widespread use in archaeology, but extractions and determination techniques have varied greatly in time and among researchers, which makes it difficult to compare results in absolute terms (Holliday and Gartner, 2007). Thus phosphate has long been considered a good proxy for human activity, although P accumulation patterns should always be interpreted cautiously.

In the 1950s it was recognized that elements other than P can be useful in archaeological contexts (e.g. Lutz, 1951). Within archaeology, multi-element analyses have increasingly been applied for identifying

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Fig. 1. Location of the study site Øster Lem Hede, Denmark. Originally the prehistoric field system stretched further to the north where there are now modern fields and to the east where there is now a plantation. The location of the four excavated trenches (T1–T4) and the reference soil are marked on a map of the Celtic fields based on Hatt (1949).

different activity areas in connection with settlements as reviewed by Holliday et al. (2010). This is driven by recent technical developments, especially inductively coupled plasma-mass spectrometers (ICP-MS) with superior detection capabilities that can carry out simultaneous analyses of multiple elements at ultra-low concentrations. Based on ICP techniques, the elements most often found to be associated with human settlements are P, K, Ca, Mn, Cu, Zn, Sr, Ba and Pb, but elements such as Mg, Rb, Cs and Th have also proven useful in some instances (Entwistle et al., 2000; Oonk et al., 2009; Wilson et al., 2005, 2008, 2009). Ancient fields have hitherto received less attention in multi-element analysis although some studies of historical sites have indicated that elements other than P can be useful. For instance, Sr and Ca − probably deriving from shell sand, bones or fish refuse − were found in fields in a study from Isle of Skye (Entwistle et al., 2000), while Ba, P and to some degree Ca, Zn and Sr were enhanced in a study in Scotland (Wilson et al., 2005). Element enhancement in fields will naturally vary with manuring practices and it will generally be much less pronounced compared to settlements.

Understanding what the enhancement of certain elements in soils represents is still problematic (Walkington, 2010), and interpretation of multi-elemental data is complicated by the fact that one has to take into consideration factors such as length and intensity of human activity, topography, parent material shifts and natural and cultural post-depositional processes (e.g. Woodruff et al., 2009). Nevertheless, each group of elements has unique vertical distributions in undisturbed soils depending on soil types (e.g. Tyler, 2004), which may be used to trace possible anthropogenic disturbances or additions. In some studies it has been

possible to ascribe particular elements to specific anthropogenic features, but these elements usually vary from site to site and generally it is varying concentrations that reflect different activity areas at a given site (e.g. Wilson et al., 2005).

The aim of this paper is to evaluate and compare how both traditional total P analysis and multi-element analysis of abandoned ancient fields can be used to identify prehistoric manuring strategies. This will be done by examining a well-known Danish prehistoric field system where manuring is indicated by e.g. ceramics, charcoal and allochthonous soil particles. A Principal Component Analysis (PCA) is applied for multivariate data description and structure exploration, allowing us to discover grouping of samples and/or variables which may otherwise be obscured by individual sampling and analytical errors (Esbensen, 2010).

2. Material and methods

2.1. Site description

The site investigated is the Celtic fields at Øster Lem Hede (56° 3′ N, 8° 27′ E) partly situated in a protected heathland in Western Jutland, Denmark (Fig. 1) (Hatt, 1949). The field system dates from the late Bronze Age and the Pre-Roman Iron Age (ca. 800 BC−AD 1). It is > 1 km² and one of the best preserved Danish prehistoric field systems − the low earthen banks and lynchets demarcating the individual fields can still clearly be seen. The area has subsequently been used for extensive grazing, but only minor areas within the protected area have been physically disturbed by later activities.

The landscape in the northern part of the field system is flat (inclinations ≤1°), while the south-western part has slopes of up to 20° (Christiansen, 1996). The climate today is temperate Atlantic, average annual precipitation is 780 mm, and average temperature is 7.7 °C with a monthly maximum of 15.7 °C (July) and minimum of −0.4 °C (February). The parent material is loamy sand to sandy loam. The vegetation is dominated by heather (*Calluna vulgaris*), crowberry (*Empetrum nigrum*), purple moor grass (*Molinia caerulea*) and other heathland plants. The soil types outside the field system but still within the protected heathland are Podzols, while the soil within the field system only shows weak morphological traces of podzolisation and are Arenosols or Luvisols as seen at other prehistoric fields in Denmark (Kristiansen, 2001).

2.2. Field work

In 2001 and 2007 sampling for geoarchaeological investigations of the natural preconditions of the site, land use history, date of the field system and formation processes of the field boundaries was undertaken. Four trenches, T1-T4, with lengths of 10–28 m were dug through five banks and one lynchet as well as part of the adjacent fields (Fig. 1). No clear archaeological traces of human activities predating the Celtic fields were found in T1-T3 while a few older pits and artefacts were found next to one of the banks in T4. Duplicate soil samples were taken in profiles in the banks, the lynchet and in the fields. Reference samples were taken from a representative, well-developed, undisturbed soil profile typical of the heathland just outside the prehistoric field system, where subsequent impacts from grazing animals, air pollution, etc. are expected to be similar to the sampled field system.

2.3. Stratigraphy

The general stratigraphy in the four trenches, T1-T4, at the Celtic fields of Øster Lem Hede is very similar. In the top, a weakly developed Podzol is present, which consists of an up to 10 cm thick mor layer (O horizon), followed by a 2–9 cm thick weekly developed E horizon (or in a few cases an A2-horizon) and an up to 20 cm thick illuvial Bh/Bs/Bhs horizon. Where the trenches cut through prehistoric banks a brown to greyish brown layer making up the core of the banks is present below the upper Podzol. This horizon − here denoted Apb with a suffix "b" for buried − either represents an old plough layer or material, which has been deposited at the field boundary. Generally the Apb horizons differ from other horizons by their colour and their content of charred plant material. It is also primarily in Apb horizons in addition to any overlying horizons that fragments of ceramics dating from the Late Bronze Age/Early Iron Age are found. Probably the brownish fill originally went all the way to the top of the bank, but today a secondary podzolisation has changed the soil morphology. Below the core of the banks either a buried A horizon (Ab) or a truncated Bhs/Bs horizon are present − the latter where the lower part of the bank were made up of a plough soil. In trench T2, which cuts through a lynchet, the lower Apb horizon appears to be resting directly on a BC horizon. Outside the banks, i.e. within the areas considered as fields, no Ap horizon could be recognized due to the secondary podzolisation. Thus, no layers were visible between the illuvial B horizons and the BC and C horizons. The reference soil consists of a well developed Haplic Podzol with an O, A, E, Bh, Bs and C horizon as typically found in this part of Denmark.

2.4. Soil analysis

Analyses were carried out on air dried, <2 mm sieved, milled earth samples. Total P was extracted from 42 samples after using a traditional weak extraction method with a diluted acid (1 M HCl)

after ignition at 550 °C, and was determined by spectrophotometry (Svendsen et al., 1993). Phosphorous extracted by this weak agent is denoted "HCl-extractable". For the multi-element analysis 58 samples were analysed. Extraction for major, minor and trace element analysis on ICP-MS was done with a strong HNO_3–HF procedure as some resistant minerals will not dissolve in weaker agents. Here, 0.1 g material was twice treated with HF and HNO_3 in closed Savillex vessels at 130 °C. HNO_3 and water were added, boiled at 130 °C for >12 h and diluted to 50 ml before analysis. Elements extracted by this strong agent is denoted "HNO_3–HF-extractable".

For calibration of the ICP instrument certified solutions of international and internal reference materials and two blanks were measured on a PerkinElmer Elan 6100DRC ICP-MS instrument and quantitatively analysed (Merck VI standards). Potentially volatile elements used as internal standards, elements insufficiently dissolved during laboratory pretreatment, and elements below detection limits were not included in subsequent data analysis. A total of 42 elements were included. Standard deviation between triplicates of an internal standard soil sample was <12% for all the included elements.

2.5. Statistics and multivariate data analysis

As a first data exploration the multi-elemental data were plotted in separate concentration−depth diagrams for each element. A Shapiro−Wilk test of normality suggested that 22 of the 42 elements were not normally distributed. Thus, a Mann−Whitney nonparametric test was performed to compare means of the reference soil and field samples and banks vs. field samples. The software XLStat was used (XLStat Version 2013.3).

A multivariate Principal Component Analysis (PCA) was thereafter run on the ICP-MS dataset to explore the overall data structure. The PCA dataset consists of 42 elements (variables) for 58 samples (objects) of which five are reference samples. Concentrations on a mass basis (mg kg^{-1} dry soil) were used, as a conversion of the concentrations to mass per area (mg m^{-2}) introduced more uncertainty due to inclusion of bulk density measurements. The quartz dilution/compositional data effect (Bern, 2009) was not accounted for as the site has a very homogenous parent material (X-Ray Fluorescence data: 82–94% SiO_2 with only major differences between surface and subsoil B and C horizons; See Inline Supplementary Table S1). A free add-in to Microsoft Excel, CAPCA version 2.0 (Madsen, 2007) was used for PCA. The PCA was based on correlations matrix, whereby the dataset was standardized and normalized (by subtracting mean values of each element from the value of the element and then taking 1/STD of the element multiplied with $\sqrt{(N-1)}$).

Inline Supplementary Table S1 can be found online at http://dx.doi.org/10.1016/j.jas.2013.11.013.

A PCA was run on untransformed data as well as on log-transformed data, which is recommended for closed data-sets, but as the two analyses produced very similar results regarding distribution and clustering of objects and variables, it was decided to use the PCA on untransformed data, as transformed data can be more complex to interpret (see e.g. Reimann et al. (2012)). As a first step a PCA of the full dataset was included to explore the overall data structure, with focus on delineating objective groupings and data clusters. A strong influence of the reference samples could be understood fairly well and it was therefore decided to exclude the reference samples from the final PCA, as the main objective of the analysis was to understand the elemental concentrations within the field system. Several PCA models were then run on the reduced dataset (without reference samples), but the most informative

pattern of sample and element distribution was obtained by including all elements and all samples from the field system.

3. Results

3.1. Total P determined by traditional phosphate analysis and by ICP-MS

Since both traditional phosphate analysis and ICP-MS analysis were carried out on 42 of the same samples from Øster Lem Hede it was possible to compare P values from the two extraction and determination methods. As can be seen in Fig. 2, there is generally a good correlation between the P concentrations determined by the two different methods ($R^2 = 0.87$). However, as expected the results do not follow the 1:1 line, for instance the maximum $HNO_3–HF$-extractable P (determined by ICP-MS) value is 640 mg kg^{-1} soil, while maximum HCl-extractable P (determined by spectrophotometry) is < 400 mg kg^{-1} soil (full dataset can be seen in Inline Supplementary Table S2). The overall tendency is nevertheless the same: increasing P concentrations from the reference soil to subsoil (BC and C horizons), and again to the above lying A, E and Bh/Bs/Bhs horizons within the field system. Exceptions to this are the Bh horizon from the reference soil, which is situated among the upper horizons (the triangle among the dots on Fig. 2), and an E horizon from the field system, which plots among the BC and C horizon samples (dot among the triangles on Fig. 2). P concentrations in the upper horizons within the field system (excluding the above-mentioned E horizon) vary between 210 and 640 mg P kg^{-1} soil in the $HNO_3–HF$-extractable fraction.

Inline Supplementary Table S2 can be found online at http://dx. doi.org/10.1016/j.jas.2013.11.013.

3.2. Enriched elements

Based on the Mann–Whitney test a total of 11 elements showing significantly ($P < 0.01$) enhanced concentrations in the fields relative to the reference soil were identified: Na, P, K, Ca, Mn and Sr and the rare earth elements (REE's), Nd, Sm, Eu, Gd and Dy. All of these have concentrations in the upper (and in some cases all) horizons well above the uncultivated reference soil. Additionally, seven elements were significantly ($P < 0.05$) enriched in the Celtic fields but generally not in all horizons as seen from the visual inspection: Ba, Y, La, Pr, Tb, Ho and U. Only Co had significantly

Fig. 2. Comparison of soil total P measured on an HCl-extraction by spectrophotometry and a $HNO_3–HF$-extraction by ICP-MS from the Celtic fields at Øster Lem Hede, Denmark. "Topsoil" here refers to all E, A and Bh/Bs/Bhs horizons, while "subsoil" refers BC and C horizons.

($P < 0.05$) lower concentrations in the field system compared to the natural reference soil, respectively 2–150 vs. 90–250 mg kg^{-1} soil (see Inline Supplementary Fig. S1).

Inline Supplementary Fig. S1 can be found online at http://dx. doi.org/10.1016/j.jas.2013.11.013.

In Fig. 3, nine diagrams of selected elements are shown. Na, P, K, Ca, Mn, and Sr are depicted as they are clearly enhanced within the field system and they represent elements that have previously been associated with past human activity areas; La is selected as representing one of the enriched REE's. Furthermore, the figure includes Co as it is the only depleted element in the field system and Zr as its vertical concentration pattern can reflect the degree of weathering in the soil (Blume et al., 2010). The upper horizons such as the E- and Bh- horizons are generally at the same depth, but since material has been added where banks are present, the BC/C-horizon is at a greater depth in these. The pattern of elemental enhancement down through the soil profiles varies with each element and sometimes with location. Generally, concentrations of elements like Na, K, Ca, Ba, and many of the REE's increase with depth. Other elements have higher concentrations in certain locations, for instance the highest $HNO_3–HF$-extractable P concentrations are found in T4, the highest concentrations of Sr are found in T4 and to some degree T2, and the highest concentrations of Mn are found in T1 and T4. Other elements such as V show no significant site differences (see Inline Supplementary Fig. S1 and Inline Supplementary Table S2).

Regarding Zr high concentrations are seen in the A and E horizon of the reference soil, while this peak is absent in the soils within the field system; here the Zr concentrations have a uniform or irregular vertical distribution as typically seen in physically disturbed soils.

None of the heavy metals are generally enhanced in the field system, one exception being a buried Apb horizon in a bank in trench T4. In this horizon Zn was enhanced by approximately 60 mg kg^{-1} soil compared to the highest value measured in the reference samples, while Pb was enhanced by approximately 10 mg kg^{-1} soil (see Inline Supplementary Table S2).

While there are differences among sample sites, generally no clear division in elemental enrichment between samples taken from banks and fields can be identified (Fig. 3). Only Co is significant enriched ($P < 0.01$) in banks vs. fields with respectively 1.82 vs. 1.68 mg Co kg^{-1} soil (Fig. 3).

3.3. Multivariate data analysis

The PCA model revealed moderate low-dimensional structures as the first principal component (PC1) explained 45%, PC2 15%, and PC3 8%, i.e. the first three PCs explain 68% of the total variance in the dataset (elemental loadings on PC1, PC2 and PC3 can be seen in Inline Supplementary Table S3). This model is considered well suited for studying the correlations between the key variables of interest; higher PCs did not reflect any clearly distinguishable effects and are not discussed further. Fig. 4 shows the elemental distribution on PC1 and PC2 where the elements are divided into three groups. Group 1 consists of the REE's Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu, in addition to U, Th and Zr originating mainly from highly insoluble minerals such as zircon. Group 2 consists of the metals Li, Na, Mg, Al, K, Ca, Sc, V, Cr, Fe, Ni, Ga, Rb, Cs, Ba, and Tl. Group 3 is situated to the left in the diagram and the elements in this group are generally more scattered compared to the elements in the two other groups. This latter group consists of P, Mn, Co, Cu, Zn, Sr, Nb, Ta and Pb. The distribution of the elements on PC1 vs. PC3 produced no clear pattern.

Inline Supplementary Table S3 can be found online at http://dx. doi.org/10.1016/j.jas.2013.11.013.
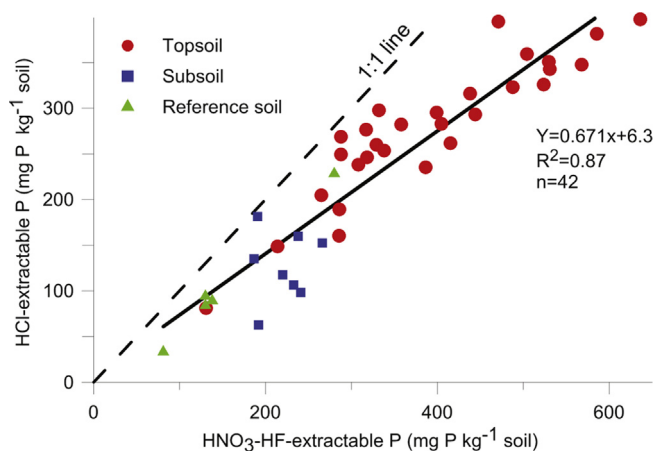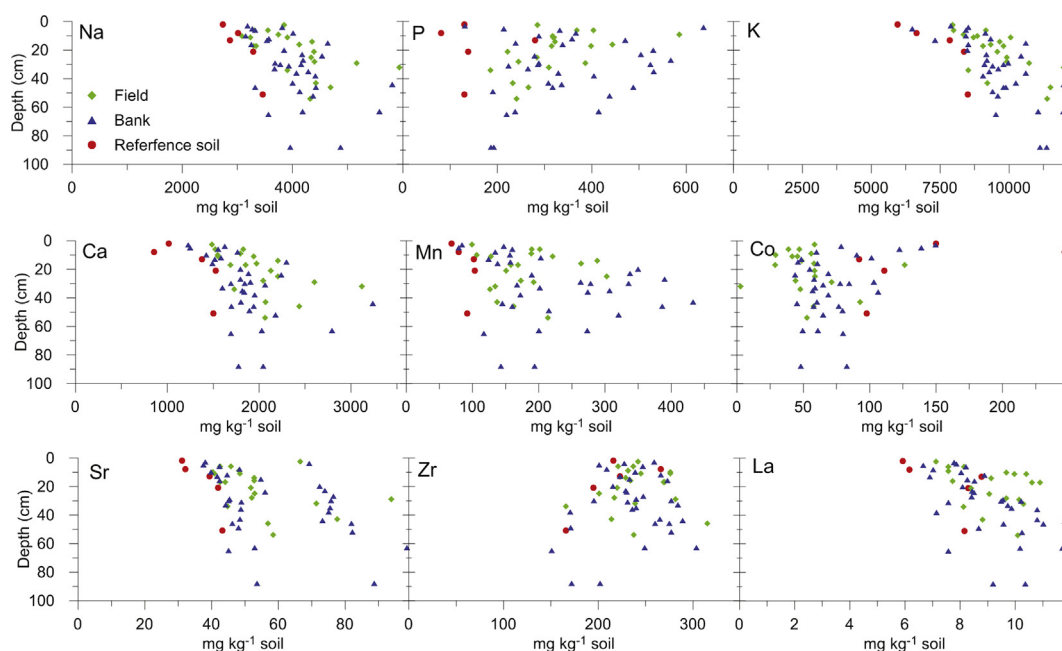
Fig. 3. Depth–concentration plots of selected elements showing the elemental concentrations in the reference soil and the fields and banks of the field system at Øster Lem Hede, Denmark.

On Fig. 4 each element is depicted with a signature according to whether the concentration of the element in the field system is not significantly different from the reference soil, or whether it is significantly enriched or depleted. As seen on the figure, elements with enhanced concentrations are found in all the three groups of elements indicating that the explanation for the enrichment varies among the elements.

Fig. 5 shows the distribution of the samples on PC1 and PC2 which are arranged in three somewhat overlapping groups – especially group 1 and 2 are not completely separated. The first group comprises the top horizons, i.e. A-, E- or Bh-horizons. The A- and E-horizons, which are the samples taken closest to the soil surface, are situated furthest away from group 2. This group 2 encompasses deeper lying soil horizons such as Apb horizons as well
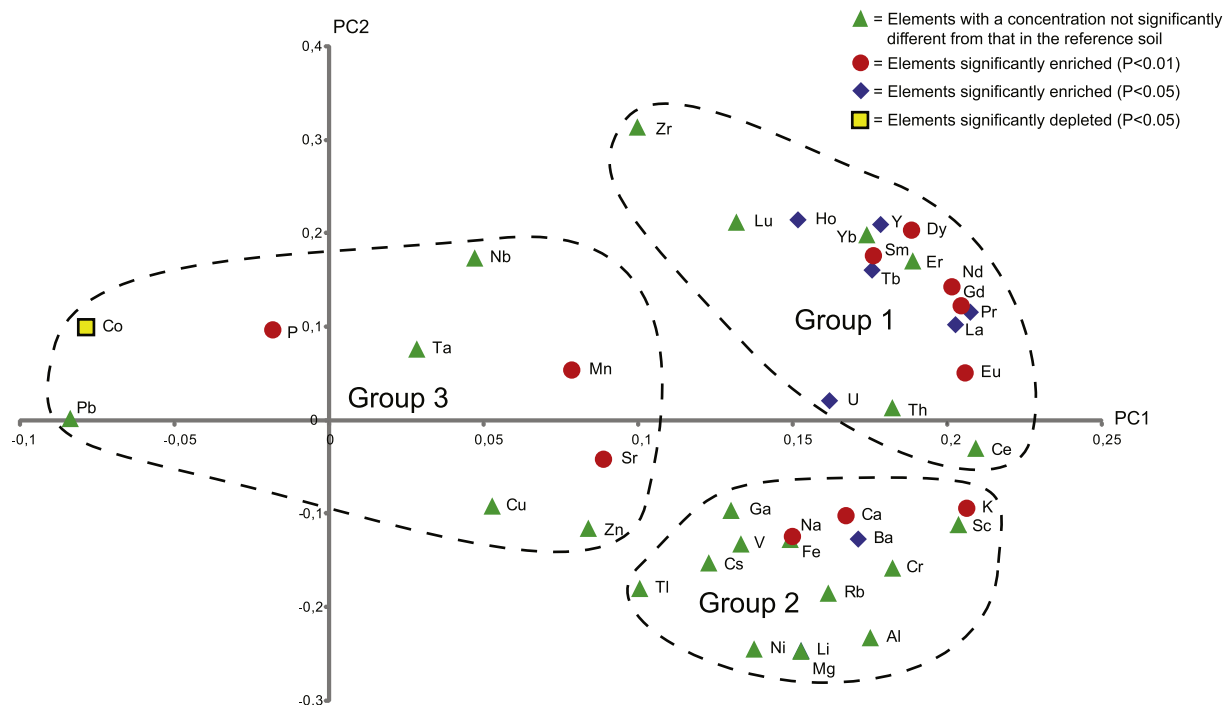

Fig. 4. Plot of variables (elements) from a multivariate principal component analysis (PCA) for PC1 vs. PC2 of the analysed elements from the Celtic fields at Øster Lem Hede, Denmark. On the figure it is marked whether the concentrations of the individual elements are not significantly different in the field system compared to the reference soil, or whether the elements are either significantly enriched or depleted.
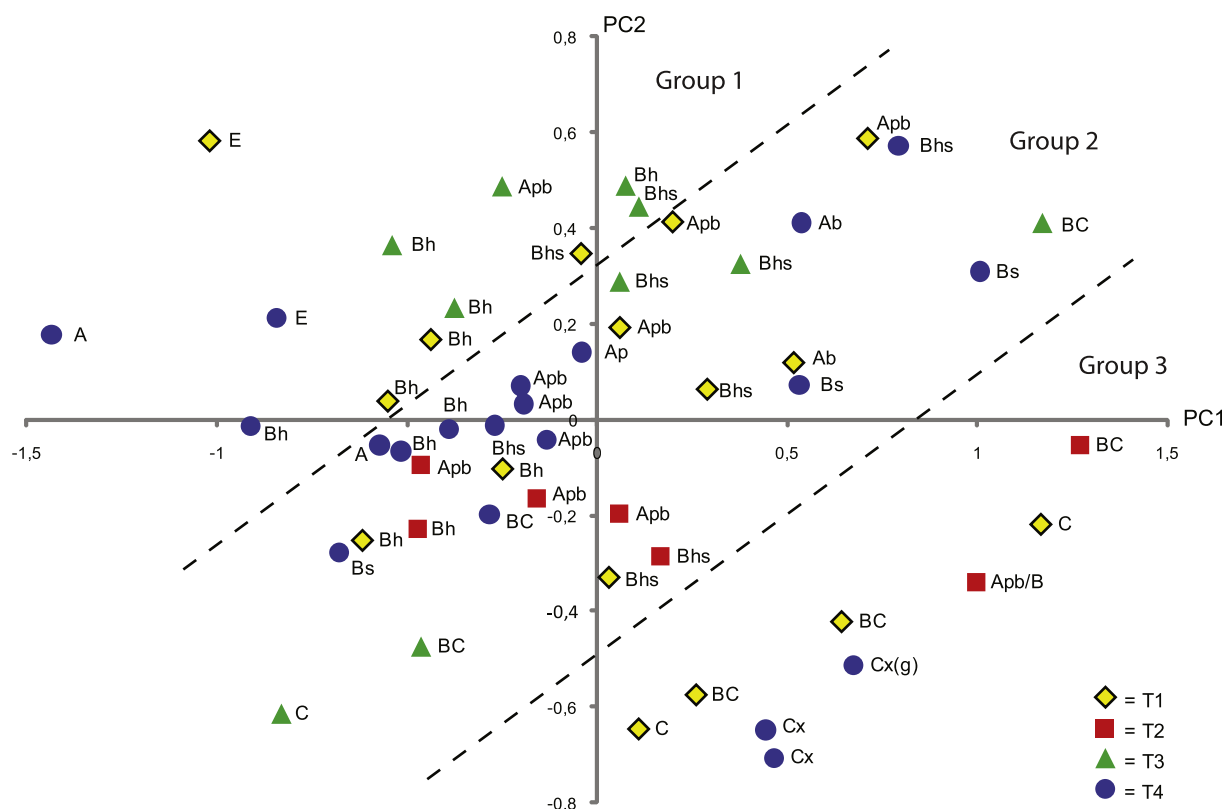
Fig. 5. Plot of objects (soil samples) from a multivariate principal component analysis (PCA) for PC1 vs. PC2 of soil samples from the Celtic fields at Øster Lem Hede, Denmark.

as Bh/Bhs/Bs horizons not included in group 1. Group 3 consists of samples from BC and C horizons, i.e. parent material which has undergone no or only slight pedogenic modifications. Outliers to this pattern are one sample denoted Apb/B, which is found in group 3, and four samples from BC/C horizons found in group 2 – three of them from trench T3, one from T4.

Fig. 6 depicts the distribution of soil samples on PC1 and PC3, where a clear grouping according to trenches is seen. At the positive part of the PC3, samples from trenches T1 and T3 are present, while samples from T2 and T4 are found on the negative part of PC3. Outliers are two Cx-horizons from trench T4 and a Bh-horizon from T2 with positive PC3 loadings, and an Apb horizon in T3 with negative PC3 loading. Despite these four outliers the PCA clearly indicates marked differences between the trenches based on elemental concentrations.

4. Discussion

4.1. Comparison of the two methods for determining P

Since total soil P was determined by spectrophotometry on the HCl extraction as well as by ICP-MS on the HNO_3-HF extraction, it was possible to compare not only P yields but also archaeological interpretations based on the two methods. As expected, the stronger HNO_3-HF extraction agent generally released considerably more P than the HCl extraction due to the different ability to dissolve strongly bound P in minerals and soil organic matter (Holliday and Gartner, 2007). However, recent findings suggest that the additionally extracted and measured P derives not only from primarily minerals, but also from archaeologically relevant sources as a significant part of added P is irreversibly bound to soil minerals with time. This anthropogenic P is not extracted through the weak acid digestion that is often recommended (Wilson et al., 2006).

Despite the discrepancies between P concentrations determined by the two methods, the overall trends are the same, and in our case the archaeological interpretation, i.e. that manuring was practiced, would therefore be similar regardless of the extraction method used. Since P analysis is the most common geochemical analysis within archaeology (Holliday and Gartner, 2007), it is worth considering whether total P analysis in some cases (e.g. related to manuring practices) could be carried out as part of a multi-element analysis by a strong extraction agent whereby not only P is determined by ICP-MS but also a range of other potentially informative elements. The HNO_3-HF extraction used in this study has the advantage that all silicates and most oxides are dissolved (Blume et al., 2010) whereby signals from additions of refractory earth materials can also be elucidated.

4.2. Anthropogenic impact reflected by elemental groups and enhancement patterns

Based on the PCA of the ICP-MS data it was possible to divide the elements into three different groups (Fig. 4). The first group comprises REE's in addition to U, Th and Zr; the second group primarily consists of metals of which Na, K, Ca and Ba are enriched ($P < 0.05$) inside the fields. These two groups, which are both situated to the right in the diagram, seem to represent elements from refractory minerals which are not the result of anthropogenic enrichment but merely are positioned differently in the diagram due to pedological and physical reworking processes. The third group is more heterogeneous and includes P, Cu, Zn, Sr, Mn, Pb, Co, Ta and Nb which except for the heavy metals are significantly ($p < 0.01$) enriched, or depleted in the case of Co, inside the field system. The first six elements are accumulated in animals or plants and have been identified as indicators for human activity in other studies (see section 4.2.1). Co, Cu, Zn and Pb are sometimes associated with
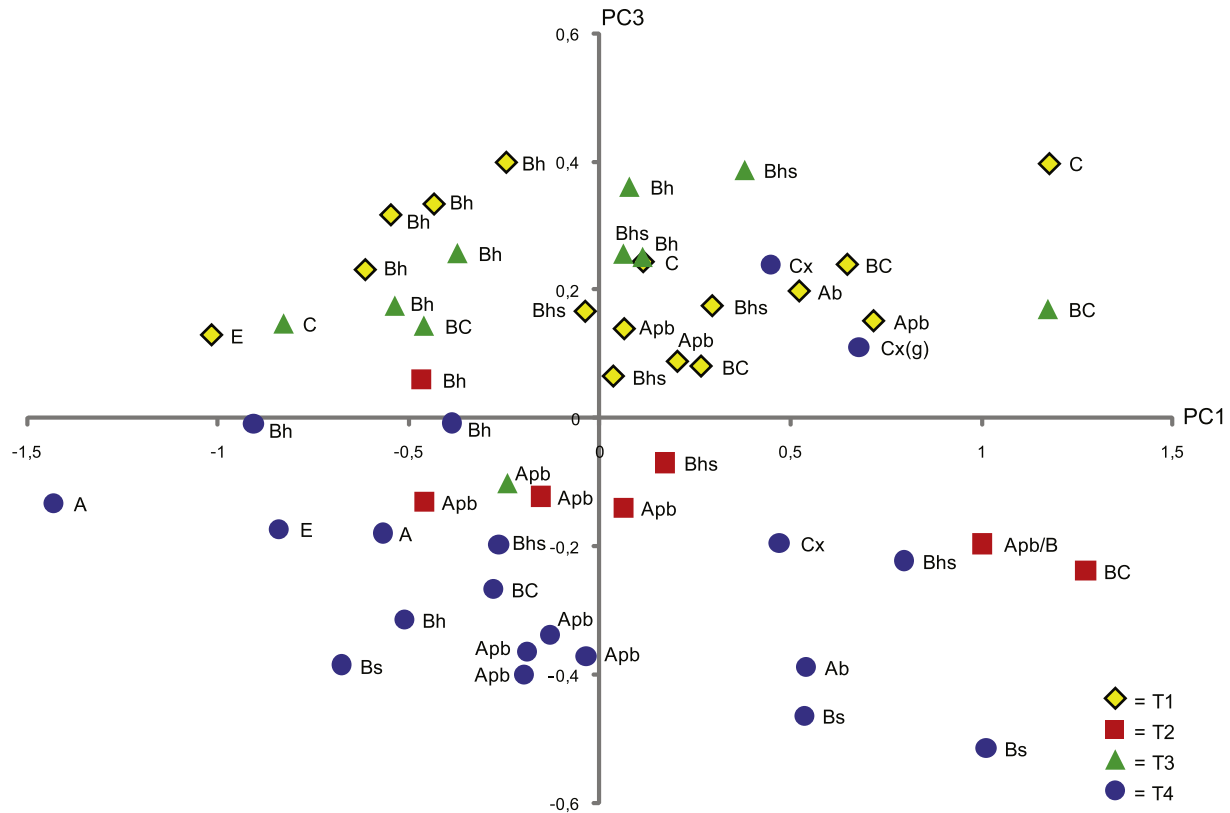
Fig. 6. Plot of a multivariate principal component analysis (PCA) for PC2 vs. PC3 of soil samples from the Celtic fields at Øster Lem Hede, Denmark.

modern-day diffuse air pollution (Reimann et al., 2007), but when compared with the reference soil there is strong evidence that the enhancement pattern seen at Øster Lem Hede is due to prehistoric land-use (with the exception of the topsoil).

The elements Nb and Ta are primarily found together in some very rare minerals such as columbite-tantalite, but also as trace elements in other minerals. Why Nb and Ta cluster together with well-known anthropogenic indicators is not clear.

The elements in this "anthropogenic influenced" group 3 are more scattered in the diagram (Fig. 6) than groups 1 and 2, which fit with the interpretation of their concentrations as being primarily the result of spatially-dependent anthropogenic processes.

No obvious analytical errors or explanations are found for the statistical significant Co ($p < 0.01$) depletion in the field soils and the contrast between Co and the other analysed elements (see Inline Supplementary Fig. S1). Cobalt deficit in soils could have been problematic for raising especially cattle in prehistory as too low Co intake from fodder results in cobalt deficiency among the animals. Already in 1951 it was suggested that Co depletion by prehistoric agriculture might have been a problem for animal welfare on strongly acidic and leached sandy soils such as in western Jutland, Denmark (Glob, 1951). Hence, in theory Co could have had adverse effects on prehistoric societies, but more research on prehistoric field systems involving multi-elemental analyses is needed to determine whether the depletion of Co was a general phenomenon and how widespread the problem was.

4.2.1. Indicators of prehistoric manuring

The enriched elements in group 3 (Fig. 4) seem to provide good evidence of prehistoric manuring and other human additions to the soil. The higher P levels within the field system compared to the reference soil clearly indicate that manuring was practiced at Øster Lem Hede. Although P is present in most domestic waste, it is especially concentrated in animal dung, which was probably the primary source of P here. However, considering the size of the fields and their possibly long use in relation to the P concentrations, the manuring may not have been that intensive.

Strontium is also considered a good anthropogenic marker deriving from e.g. bones and material from the coast such as shell sand (Entwistle et al., 1998, 2000). Wilson et al. (2005, 2008) found Sr to be present especially in hearths and houses followed by the byre and sparingly in arable fields. The significantly enhanced levels ($P < 0.01$) within the field system at Øster Lem Hede support the idea that Sr can be used for identifying areas of human activity on abandoned fields. The highest Sr levels are clearly found in T4, followed by T2, but enhancement is also found in T1 and T3 (see Inline Supplementary Fig. S1) indicating that Sr rich material was added to all the investigated fields. Øster Lem Hede is situated 22 km from the coast and 9 km from the inlet of Ringkøbing Fjord whose salinity levels have varied through prehistoric and historic times. The distance to the coast makes it unlikely that large amounts of material such as shell sand have been transported to Øster Lem Hede. Strontium is excreted by animals, but since the Sr concentration in the reference soil is low, the manure from animals feeding on local fodder would also be expected to contain only little Sr. Even if animals were grazing during summer on the regions lush coastal grasslands, which perhaps could have increased the Sr concentration in the manure, most of this would be dumped *in situ* at the meadows and not brought back to the settlement. The most likely source of strontium at Øster Lem Hede therefore seems to be bone fragments, which probably were spread on the fields together with other household waste. The bones and other organic material have decayed, but fragments of e.g. ceramics and charcoal is still seen in the soil. The fact that there is no linear correlation between P and Sr ($R^2 = 0.01$) supports the interpretation that not only animal manure but also other kinds of material were spread on the fields.

Manganese is also clearly enhanced ($P < 0.01$) in the field system compared to the reference samples (see Inline Supplementary Fig. S1). Manganese has only been identified as a geochemical tracer for human activity in a few studies where it has e.g. been associated with organic matter (e.g. da Costa and Kern, 1999). However, Mn is strongly influenced by pedogenic processes such as gleying, which may relocate it in the profile and the landscape. At Øster Lem Hede pseudogley was only observed in the deepest parts of T4, which rules out waterlogging as an explanation for the enhancement pattern. Thus, the high concentrations of Mn at Øster Lem Hede likely derive from anthropogenic materials added to the fields; a conclusion also supported by the decreasing Mn concentrations with depth (Fig. 3).

Copper, Zn and Pb are all metals that have previously been associated with anthropogenic activities, for instance, the latter two have been found in ash and charred particles (Davidson et al., 2007). The three elements are not significantly enhanced throughout the field system at Øster Lem Hede, but elevated concentrations are found as outliers in some areas and specific horizons. This indicates that material enriched in Cu, Zn and Pb were added very locally or – especially regarding the Apb horizon in T4 with high concentrations of Zn and Pb – that some special human activity took place at certain spots within the field system which deposited heavy metals.

Thus all the significantly enhanced elements in group 3, Fig. 4 – in addition to Cu – can be explained as being caused by anthropogenic activities and especially fertilization of the fields; animal manure as well as bone fragments (probably as part of household waste) seem to have been spread on the fields at Øster Lem Hede as part of the manuring strategy in the Late Bronze Age/Early Iron Age.

4.2.2. Indicators of relocation of soil material

The enrichment of K, Ca, Ba and Na within the field system could in theory also be related to manuring. Although Na generally is considered less suited as an anthropogenic marker due to the lower concentration in occupation waste (Oonk et al., 2009) and its very low retention in soil when once dissolved, both Ca and K are highly concentrated in manure and K is highly enriched in plant tissue and ashes. Barium and Ca have also been found to be enhanced in historic fields (e.g. Entwistle et al., 2000; Wilson et al., 2005). However, the four elements are all found in group 2 (Fig. 4) together with clearly non-enriched metals such as Fe and Cr, and it therefore appears that at Øster Lem Hede the enhanced concentrations of K, Ca, Ba and Na probably mainly originate from incorporation of weathered feldspars into the otherwise quartz-dominated topsoils. The enhanced levels inside the field system were thus likely a result of topsoil rejuvenation where fresh, unweathered subsoil material was brought to the surface of the arable fields due to increased bioturbation and tillage erosion.

Elevated concentrations of REE's relative to adjacent reference soils have previously been observed at archaeological sites (Entwistle et al., 2000; Wilson et al., 2005), but the origin of these differences are generally poorly understood. Addition of REE's through manuring is a possibility, however, the concentration of most REE's in the field system is not only enhanced in absolute amounts but also differs from typical vertical distribution patterns in both the reference soil (Fig. 3) and similar natural sandy soils (e.g. Tyler, 2004). Furthermore, Th, U and Zr from refractory minerals are also present in group 1 (Fig. 4), and a more plausible explanation for the enhancement pattern in the field system is therefore again that unweathered B and C horizon material was incorporated into the topsoil by physical disturbances. This interpretation is also supported by the fact that the reference soil showed the expected enrichment of Zr in the topsoil (Fig. 3) due to accumulation of the weathering resistant mineral zircon (Blume et al., 2010), whereas

the infield soils have uniformly or irregular distributed Zr concentrations with depth.

Thus, although the significantly enriched elements of group 1 and 2 in Fig 4 could be interpreted as originating from manure, the PCA and the vertical distribution pattern of the elements indicates that physical soil disturbance is a better explanation for the enhancement. This could potentially be a valuable tool in investigations of ancient fields, where it is uncertain whether the soil have been ploughed or not (although the site must be in a place where it is possible to actually bring up BC and C material through tillage e.g. in a sloping terrain).

Different theories about the formation of banks and lynchets at Celtic fields have been presented through the years (Bech, 2003; Groenman- van Waateringe, 1979; Nielsen, 2008). Although geochemical analyses cannot reveal the formation process, our data showed that only Co were significant enriched ($P < 0.05$) in banks relative to field soils. Thus the banks appear to be made of top soil material from within the cultivated field, which is supported by particle size and thin section analysis (unpublished data). The lower Co concentrations in the fields compared to the banks could possibly be because Co – which is an essential plant nutrient (Blume et al., 2010) – was removed with the crops.

4.2.3. Differences in human impact between sampling sites

In Fig. 6 samples from trenches T1 and T3 group in the negative part of PC3, while samples from T2 and T4 appear on the positive part of PC3. No large differences between the parent materials in the four trenches have been observed during field work or soil analyses and the patterning is therefore most likely the result of differences in anthropogenic impact or slight differences in parent material. On PC3 it is especially Sr (elemental loading of −0.45) but also to some degree Na, Ta, Ba, P, and Ca (elemental loadings between −0.22 and −0.33), which groups in the left-hand side while Cs, V and Th (elemental loadings of 0.24−0.33) is correlated on the right-hand side (see Inline Supplementary Table S3). Since all the mentioned elements with negative loadings (with except of Ta) seem to be associated with anthropogenic activities, and Cs, V and Th probably are not, it appears that somehow the degree/character of human impact is reflected in PC3. The distribution of samples on PC3 from the different trenches therefore most likely reflects differences in the anthropogenic impact. Among other things these differences probably include the degree of household waste spread in the area (reflected in Sr concentration). The highest Sr concentrations are found in T4 followed by T2, which fits nicely with T4 samples having the most negative PC3 loadings, followed by the samples from T2. For some reason it was especially in these two areas that bones/household waste was deposited. Samples from T4 moreover have the highest P concentrations, which may also be a reason why T4 samples are situated in the negative part of PC3. Since the enhancement is further up in the profile than the deeper buried features predating the field system and since no significant upward transportation of elements are expected, it cannot be ascribed to this. Rather, the higher Sr and P concentration levels must be related to the prehistoric use of the field system. Possibly the fields in this area were used for a longer time or manured more intensively than the other.

That evidence of manure varies throughout a large field system is expectable. Usually fields closest to settlements would be more intensively manured simply because of the work load associated with transporting manure to the fields. Also it is reasonable to believe that sometimes household waste were spread on the fields – perhaps together with the animal manure – other times not. This could be due to different or changing manuring practices, but since no clear development in time can be identified at Øster Lem Hede, the variations may simply be related to the material that was available or needed to be discarded at the time when manure was brought out to the fields.

4.2.4. Soil horizons and anthropogenic layers reflected in PCA analysis

The PCA analysis provided information on how the elemental composition in samples from the four trenches clusters. PC1 and PC2 (Fig. 5), where A-, E- and upper Bh-horizons are situated furthest away from the BC/C horizons and where the central horizons are found in between these two groups, together is interpreted as reflecting depth, which is related to soil formation and possibly some anthropogenic influences. Since this pattern is a very dominant low-dimensional structure of our dataset it can provide information about the five outliers. Thus, during the field work it could not be ruled out whether a horizon denoted Apb/B (in trench T1) represented a buried plough layer or was natural. However, Apb/B cluster among the subsoils in group 3 which suggests that it is a natural B or BC horizon. Furthermore, the presence of the three BC and C horizons in group 2 (i.e. in the group with the Apb and illuvial B horizons) could indicate that the area of trench T3 and T4 where the samples were taken may have been influenced by unrecognized human activities prior to the formation of the Celtic fields. A multi-variate analysis based on ICP data thereby also helped improve the archaeological understanding of some horizons that was otherwise difficult to allocate to natural or anthropogenic processes, and proved overall to be a very valuable tool.

5. Conclusion

This study demonstrates that P analysis based on a strong extraction agent results in similar, relative within site trends as a traditional and weaker extraction method typically applied in archaeological investigations. However, a stronger extraction method facilitate analysis of multiple elements by ICP-MS, which in this study has proven to offer greater insight into manuring strategies and prehistoric land use than P-analysis alone – especially when combined with multivariate data analysis.

While P evidently remains the strongest anthropogenic marker in ancient soils, Sr proved in this study to be valuable for determining that not only animal manure but also bone fragments/household waste was added to the fields. Differences in manure composition and probably intensity/length of use at the different fields were furthermore reflected in the PCA analysis. In addition, the multi-element analysis revealed that unweathered subsoil material had been incorporated into the prehistoric topsoil by physical disturbances. Thus, based on our findings we recommend using multi-element geochemical investigations in future studies of ancient fields. In order to fully utilise the potential of the method, more research on what the enhancement – or depletion – of different elements represents at archaeological sites is needed.

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