

## SOIL/SEDIMENT ANALYSIS: BACKGROUND TO ANALYTICAL METHODS

This document provides background information on the principal types of soil/sediment analysis undertaken by UWLAS and presents details of the analytical methods employed:

1. Phosphate
2. Magnetic susceptibility (including fractional conversion)
3. Heavy metals (Cu, Pb and Zn)
4. Loss-on-ignition
5. pH
6. Particle size
7. Carbonate
8. Soil micromorphology

### 1. Phosphate

#### Background and applications

Phosphates are present in all organic material (plant tissue, excreta, bone, etc.). As they are released by organic decomposition processes, they tend to form insoluble compounds and thus become 'fixed' within the mineral fraction of soils and sediments. Many forms of human activity lead to phosphate enrichment and, under favourable conditions, this may remain detectable for  $10^2$ - $10^3$  years (see reviews by Bethel and Máté, 1989; Crowther, 1997; Heron, 2001). Phosphate analysis therefore potentially provides valuable insight into the nature and origins of individual contexts on archaeological sites (e.g. floor surfaces, midden deposits, fills of post holes and pits, etc.); spatial patterns of human activity across a known site (through analysis of samples taken on a regular grid or along transect lines from old ground surfaces); and temporal sequences of activity (through analysis of samples taken through vertical sections of deposits – e.g. enclosed depressions in limestone landscapes, cave earths, hillslope colluvium, ditches, moats, etc.). It can also be effective as a 'reconnaissance tool', e.g.: (1) at the assessment/pre-excavation stage of a project (as with geophysical techniques) – to help target areas for detailed evaluation/excavation; and (2) at the assessment stage in the investigation of trial cores through deep Quaternary and Holocene sedimentary sequences – to help identify zones of likely human activity for more concentrated coring.

#### Analytical methods employed

It is standard procedure to determine phosphate-P (total phosphate), though separate analyses of the inorganic (phosphate-P<sub>i</sub>) and organic (phosphate-P<sub>o</sub>) fractions may be appropriate for more detailed investigations of individual contexts. Alternatively, just phosphate-P<sub>i</sub> may be determined. The latter is particularly recommended for large numbers of samples (e.g. from extensive spatial surveys or deep sediment cores).

Determination of phosphate-P<sub>i</sub> is cheaper than phosphate-P, and work undertaken in our laboratories on samples from a range of sites for which both phosphate-P and phosphate-P<sub>i</sub> have been determined have revealed an extremely strong correlation between the two (Fig. 1) – i.e. variation in phosphate-P<sub>i</sub> very closely mirrors that of phosphate-P. It should be noted that these samples display somewhat greater variability in phosphate concentration than is often encountered within a single study area, and further work is currently being undertaken to confirm that satisfactory results can be obtained from a single extensive spatial survey of phosphate in topsoils.

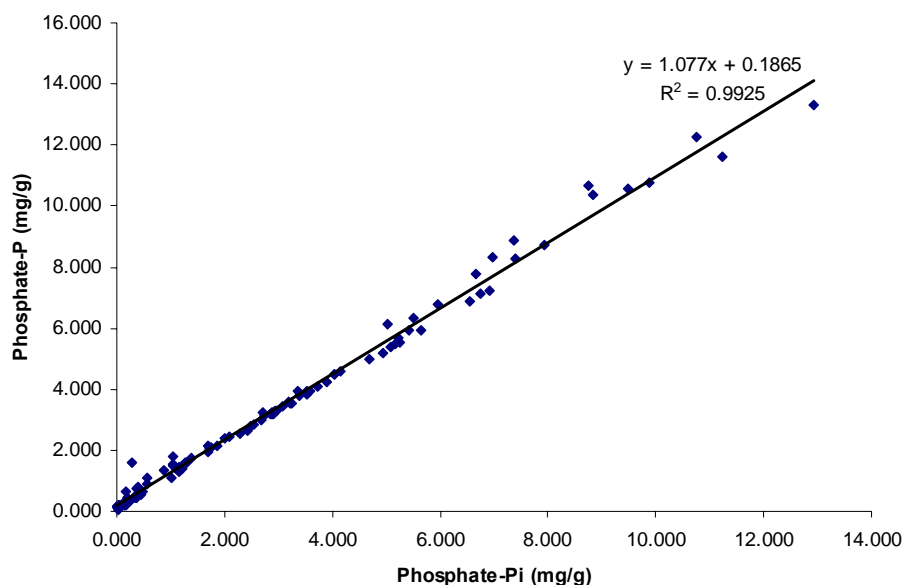


Fig. 1: Plot comparing phosphate-P<sub>i</sub> and phosphate-P determinations made on 104 samples from various archaeological sites using the standard methods described in the text

It should be noted that the methods we employ use strong acids which are capable of extracting a very high proportion of the phosphate present (and probably all of the 'archaeological phosphate'), and that all analyses are undertaken in a controlled analytical laboratory environment. The results generated are far more meaningful from an archaeological viewpoint than those produced using weaker extractants – many of which only extract a very small proportion of the phosphate present (the 'readily available' soluble and 'labile' fractions). The Mehlich II extractant, for example, which has been used in a number of phosphate surveys, effectively only provides a measure of 'plant-available' P, which on average accounts for only 1.8% of the total phosphate present (Terry *et al.*, 2000). As such, it does not provide a direct measure of the 'archaeological phosphate' present.

**Standard methods:** Analysis is undertaken on finely ground, air-dried samples of the fine-earth (<2 mm) fraction and the results corrected for moisture content. Phosphate-P (total phosphate) is determined following alkaline oxidation of the sample with NaOBr, using the procedure described by Dick and Tabatabai (1977). Phosphate-P<sub>i</sub> (inorganic phosphate) and phosphate-P<sub>o</sub> (organic phosphate) are determined using a two-stage adaptation of this procedure in which the phosphate concentration of a sample is measured first without oxidation of organic matter (phosphate-P<sub>i</sub>), using 1N HCl as the extractant; and then on the residue following alkaline oxidation with sodium hypobromite

(phosphate-P<sub>o</sub>), using 1N H<sub>2</sub>SO<sub>4</sub> as the extractant. Phosphate concentrations in the resulting extracts are determined by colorimetry.

**Alternative methods for large numbers of samples ( $n \geq 100$ ) – e.g. for extensive spatial surveys or closely-spaced samples from deep sediment cores:** Such investigations can be prohibitively expensive when using standard methods of analysis. Experimental investigations undertaken in our laboratories on 40 samples (with a wide range of phosphate concentrations) from several different archaeological sites have demonstrated that considerable savings can be achieved, with relatively little loss of accuracy and reproducibility (see Fig. 2), by eliminating the labour-intensive steps of sieving and grinding (in sample preparation) and centrifuging/filtering (during colorimetry) from the standard procedures outlined above. It should be noted that very occasionally with certain soils determination of phosphate-P<sub>i</sub> proves problematic because of brown humic substances released from organic matter during the acid extraction that interfere with the colorimetry. In these cases inorganic phosphate may not be very reliable and it may be necessary to revert to total phosphate. In such cases the number of samples analysed can be reduced at the time of analysis in order to stay within budget.

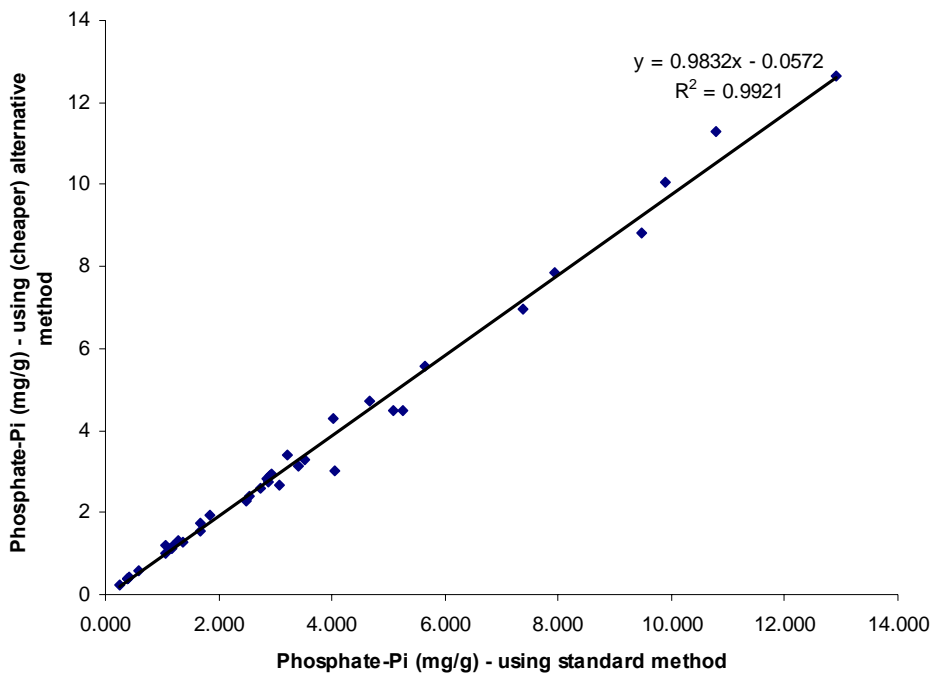


Fig. 2: Plot comparing phosphate-Pi determinations made on 40 samples from various archaeological sites using the standard method and the alternative method described in the text

### References

- Bethell, P. and Máté, I. (1989) The use of phosphate analysis in archaeology: a critique. Pp. 1-29 in *Scientific Analysis in Archaeology* (J. Henderson, ed.), Oxford University Committee for Archaeology, Monograph, 19.
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## 2. Magnetic susceptibility

### Background and applications

$\chi$  (low frequency mass-specific magnetic susceptibility) in soils and sediments largely reflects the presence of magnetic forms of iron oxide (e.g. maghaemite) – this being dependent upon the presence of iron (Fe) and occurrence of alternating reduction-oxidation conditions that favour the formation of magnetic minerals. Enhancement is particularly associated with burning (hence its archaeological significance), though it is also caused by microbial activity in topsoils (see reviews by Clark, 1996; Scollar *et al.*, 1990).  $\chi_{\max}$  is a measure of maximum potential magnetic susceptibility, determined by subjecting a sample to optimum conditions for susceptibility enhancement in the laboratory. In general this will tend to reflect the overall iron concentration of a sample.  $\chi_{\text{conv}}$  (fractional conversion), which is expressed as a percentage, is a measure of the extent to which this potential susceptibility has been achieved in the original sample, viz:  $(\chi/\chi_{\max}) \times 100.0$  (Tite, 1972; Scollar *et al.*, 1990). In many respects this is a better indicator of magnetic susceptibility enhancement than raw  $\chi$  data, particularly in cases where soils or sediments have widely differing  $\chi_{\max}$  values (Crowther and Barker, 1995; Crowther, 2003).

Ideally,  $\chi_{\max}$  and  $\chi_{\text{conv}}$  would be determined for each sample analysed (English Heritage, 1995), but this may not be cost-effective for very large sample sets. Where the sample size exceeds 20 it is recommended that  $\chi$  is determined on each, and that  $\chi_{\max}$  and  $\chi_{\text{conv}}$  are then determined on a subset of 20 comprising the 10 samples with the highest  $\chi$  values recorded and 10 chosen at random from the remaining samples. In this way it is possible to establish the extent to which variations in  $\chi$  are attributable to variations in magnetic susceptibility enhancement ( $\chi_{\text{conv}}$ ), rather than in  $\chi_{\max}$ . Such an approach has proved extremely valuable in the interpretation of data from routine field magnetic susceptibility surveys (Crowther, 2003).

### Analytical methods employed

Analysis is undertaken on air-dried samples of the fine-earth (<2 mm) fraction and the results corrected for moisture content. Measurements are made using a Bartington MS2 meter.  $\chi_{\max}$  is determined by heating samples at 650°C in reducing conditions for 1 hour, followed by oxidising conditions for 45 minutes (Clark 1996). Approximately 5% by weight of household flour is mixed with the soils and lids placed on the crucibles to create the reducing environment (Graham and Scollar, 1976).

### References

- Clark, A.J. (1996) *Seeing beneath the soil*, 2<sup>nd</sup> edition. Batsford, London.
- Crowther, J. (2003) Potential magnetic susceptibility and fractional conversion studies of archaeological soils and sediments. *Archaeometry*, 45, 685-701.

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- Tite, M.S. (1972) The influence of geology on the magnetic susceptibility of soils on archaeological sites. *Archaeometry*, 14, 229-236.

### **3. Heavy metals – Cu (copper), Pb (lead) and Zn (zinc)**

#### **Background and applications**

Heavy metals occur naturally in most soils and sediments, but concentrations tend to become enriched through various form of human activity. Heavy metal concentrations may provide specific insight into mining/metal working activities and, more generally, into overall levels of technological development or 'industrialisation'.

#### **Analytical methods employed**

Analysis is undertaken on air-dried samples of the fine-earth (<2 mm) fraction and the results corrected for moisture content. Pb, Zn and Cu are extracted from the soil/sediment by boiling with 'aqua regia' (1:3 ratio of concentrated HNO<sub>3</sub> and HCl). This procedure breaks down most of the organic matter present and extracts all the heavy metals, apart from those contained within the matrices of rock minerals (which are of little archaeological interest). Concentrations of Cu, Pb and Zn are determined using a Pye Unicam PU9100 atomic absorption spectrophotometer.

### **4. Loss-on-ignition (LOI)**

#### **Background and applications**

LOI provides a cost-effective means of estimating organic matter concentration, which is an important diagnostic property of all soils and sediments. Higher concentrations of organic matter are indicative of inputs of organic rich materials (topsoil, plant material, excreta, etc.) and/or conditions in which organic decomposition is inhibited (e.g. waterlogged or very acidic environments). Even quite small variations in organic matter concentrations up through a sequence of deposits (colluvium, ditch fills, estuarine sediments, etc.) can provide evidence of hiatuses in minerogenic sediment accumulation and associated periods of soil/proto-soil development.

#### **Analytical method employed**

Analysis is undertaken on oven-dried samples of the fine-earth (<2 mm) fraction. Samples are ignited at 375°C for 16 hours (Ball, 1964). This temperature is sufficient to burn off most organic matter, but does not lead to significant breakdown of carbonates or clay minerals.

#### **Reference**

- Ball, D.F. (1964) Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils. *Journal of Soil Science*, 15, 84-92.

## 5. pH

### Background and applications

The pH of a soil/sediment is critically important in terms of the preservation of various natural materials and artifacts (e.g. bone, mollusca and many metals rapidly decompose in acidic conditions), and also affects the retention of phosphate. It is important therefore to have some knowledge of the pH of soils and specific contexts on archaeological sites.

### Analytical method employed

pH is determined on a 1:2.5 (air-dry soil weight:volume of water) soil suspension using a pH meter with pH probe (combined glass electrode and calomel half cells) (Bascomb, 1974).

### Reference

Bascomb, C.L. (1974) Physical and chemical analyses of <2 mm samples. Pp. 14-41 in *Soil Survey Laboratory Methods* (Avery, B.W. and Bascomb, C.L., eds). Soil Survey Tech. Monog., 6.

## 6. Carbonate

### Background and applications

While calcium and magnesium carbonate occur naturally in some soils and sediments, notably on calcareous lithologies and where the shell fragments are present (estuarine deposits, coastal dunes, etc.), their presence may also be the result of human activity. Mortar and other lime-based building materials, for example, are rich in carbonate, and in some cases ash deposits may contain significant amounts of carbonate. Often it sufficient to establish whether carbonates are present and gain a broad indication of their concentration.

### Analytical methods employed

Quantitative analysis is undertaken on air-dried samples of the fine-earth (<2 mm) fraction and the results corrected for moisture content. Where only traces of carbonate are present, determinations are made using a calcimeter (Bascomb, 1974). Otherwise, the carbonate concentration is determined by dissolution of carbonates in an excess of 1N HCl, followed by back titration of the remaining acid using 1N NaOH (Rowell, 1994). Alternatively, a semi-quantitative estimate of carbonate content is obtained by observing the reaction when 10% HCl is added to the soil (Hodgson, 1974).

### References

Bascomb, C.L. (1974) Physical and chemical analyses of <2 mm samples. Pp. 14-41 in *Soil Survey Laboratory Methods* (Avery, B.W. and Bascomb, C.L., eds). Soil Survey Tech. Monog., 6.  
Hodgson, J.M. (ed.) (1974) *Soil Survey Field Handbook*. Soil Survey Tech. Monog., 5.  
Rowell, D.L. (1994) *Soil science: methods and applications*. Longman: Harlow.

## 7. Particle size

### Background and applications

Particle size distribution (of the mineral fraction) is a fundamental characteristic of any soil or sediment. It can provide valuable insight into the origins of particular archaeological contexts; is especially useful in the characterisation of sedimentary sequences (e.g. in establishing changes in the energy of the depositional environment within estuarine sequences); and is an important factor affecting the retention of phosphate (Crowther, 1997).

### **Analytical methods employed**

Particle size analysis is undertaken using the pipette method on <2 mm, peroxide-treated (to remove organic matter) soil (Bascomb, 1974).

### **References**

- Bascomb, C.L. (1974) Physical and chemical analyses of <2 mm samples. Pp. 14-41 in *Soil Survey Laboratory Methods* (Avery, B.W. and Bascomb, C.L., eds). Soil Survey Tech. Monog., 6.
- Crowther, J. (1997) Soil phosphate surveys: critical approaches to sampling, analysis and interpretation. *Archaeological Prospection*, 4, 93-102.

## **8. Soil micromorphology**

### **Background and applications**

Micromorphology (the investigation of thin sections of soils and sediments under the microscope) is widely used in archaeological site investigation as a means of recording, characterising and interpreting individual contexts (see Courty *et al.* 1989, Macphail *et al.* 1990). The technique has proved extremely effective when complemented by the chemical and magnetic susceptibility analysis of bulk samples – as for example in work undertaken on the British Association Experimental Earthworks at Overton Down and Wareham (Crowther *et al.* 1996, Macphail *et al.* 2003), the Butser Ancient Farm Project (Macphail *et al.* 2004), the Privy Garden Hampton Court Palace (Macphail *et al.* 1995), and the Tower of London Moat (Macphail *et al.* 2004).

### **Methods employed**

Undisturbed samples of soil/sediment are taken using Kubiena or monolith sampling tins. Samples are impregnated with a cystic resin mixture and, when cured, cut into blocks for thin section manufacture (Murphy, 1986). Thin sections are studied at magnifications from x 1 to x 400 under plane polarized light (PPL), crossed polarized light (XPL), oblique incident light (OIL) and fluorescence microscopy (blue light), and described according to Bullock *et al.* (1985) and other authorities.

### **References**

- Bullock, P., Federoff, N., Jongerius, A., Stoops, G. and Tursina, T. (1985) *Handbook for Soil Thin Section Description*. Waine Research Publications, Wolverhampton.
- Courty, M.A., Goldberg, P. and Macphail, R.I. (1989) *Soils, Micromorphology and Archaeology*. Cambridge University Press.
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