INTRODUCTION

The detritus produced by the activities of man and his domestic animals is rich in phosphorus (P), which is not easily dispersed by soil action - even over long periods of time. Consequently soil testing for the presence of P offers the possibility of locating ancient settlements and studying the composition of archaeological deposits. This has been recognised and a considerable body of work has been built up relating to archaeological soil P. No attempt is made to review this work here, as this has been done by others in numerous articles (eg Schwarz, 1967; Provon, 1971; Eidt, 1973; Proudfoot, 1976; Woods, 1977; Eidt, 1977).

Workers in this field have been much concerned with methods of analysing soils for P and various field and laboratory methods have been devised. Initially methods were borrowed directly from soil science (eg Chang and Jackson, 1957), which is more concerned with the agricultural, rather than archaeological, implications of P concentrations in soils. However, a number of workers have produced methods of soil P analysis for archaeological purposes, with an emphasis on rapid testing in the field rather than relatively time-consuming laboratory methods.

The work of Lorch (1939, 1940) and Gundlach (1961) provided a basis for the development of a simplified field test for P by Schwarz (1967) in Switzerland, as follows:- about 50 mg of soil are placed on a filter paper; 2 drops of solutions A and B are added. Solution A consists of 5 g ammonium molybdate dissolved in 100 mls of cold distilled water, to which 35 mls of concentrated nitric acid (HNO_3) is added. Solution B is a 0.5% solution of ascorbic acid in water. In the presence of P a blue colour develops around the sample, the intensity indicating the relative amount of P in the soil. Obviously, this is a qualitative method but it enables the archaeologist to focus his interest on a particular area.

P analysis has been widely used in Scandinavian archaeology, Arrhenius being one of the first to notice the relationship between P in the soil and sites of human occupation and successfully locating ancient settlements (Provon, 1971). An acid extraction has been used, ie 2N hydrochloric acid (HCl added to the soil sample, boiled for one hour, filtered and P determined colourimetrically, and tests carried out (a) prior to excavation to define the location and boundaries of a settlement and (b) to find out how buildings were used, intensity of occupation, etc (Provon, 1971).

In the USA the field test of Schwarz (1967) was further modified (Eidt, 1973) and found useful not only for mapping horizontal P distribution (eg settlement boundaries) but also for ascertaining the vertical extent, ie the relative duration of settlement activities. Eidt (1973) found that HCl gave better results than HNO_3 and suggested that this is because certain compounds formed from HNO_3 interfere with the reduction of molybdic acid. Consequently 5N HCl is used instead of concentrated HNO_3.

P testing of soils as a prospecting method has not found a great deal of favour in British archaeology, possibly because it is much slower than geophysical prospection and may, if laboratory work is involved, cause delay in initiation of excavation. However, it was found useful at Grime's Graves, Suffolk (Sieveking et al, 1973), where the 93 acre site could, obviously, not be totally excavated and P analysis was used to locate the occupation debris of the prehistoric flint miners. A method of P analysis for soil was developed (Sieveking et al, 1973) which provided data more quantitative than that produced by the earlier field tests of Schwarz and Eidt, ie 1g ($\pm$ 0.1g) of soil is weighed into a glass vial, 5 mls of 2N HCl added and allowed to stand for 10 minutes. A 0.2 ml aliquot is then transferred to a 25 ml volumetric flask, molybdenum blue reagent added and the solution diluted to volumes. Initially visual comparison of the blue colour with a set of standards was carried out but a colourimeter was used in later work. The "background" P level in soil was estimated as well as "archaeological" P, in order to rule out confusion which could arise from the presence of animal manure and artificial fertilizers of recent origin. It was found (Sieveking et al 1973) that, using this method, a relatively large number of samples could be dealt with in the field.

P analysis of soil may also be used to reveal variations in intensity of site occupation. Total P was measured in deposits of a tell at Sitagroi (NE Greece), the tell having 11 m depth, 180 m diameter and representing 5 major occupation phases with a time-span of about 5,400 to 2,200 calendar years BC. (Davidson, 1973). In this case total P was measured colourimetrically after fusion with sodium carbonate ($Na_2 Co_3$). Samples from the tell contained much more P than surrounding soils and concentrations were higher in later deposits, indicating an increase in intensity of occupation.

More recently, attempts have been made to use fractionation techniques to distinguish human P deposition from natural soil P and to identify types of features and land use (Woods, 1977; Eidt, 1977). Eidt (1977) suggested that his rapid field test should be used initially to identify settlement areas, followed by a P fractionation method, based on that of Chang and Jackson (1957), on selected samples. This method is supposed to distinguish between "natural" P and "human" P, and conclusions relating to land use are drawn from the distribution of P in the various fractions.

However in Britain a wide range of methods are used to determine soil P and the search for the "ideal" technique continues. Clark (1977) compared magnetic susceptibility and P analysis (using the method of Sieveking et al, 1973) for prospection at Tadworth, Surrey, on an Iron Age 'banjo' site (chalk bedrock). Both surveys revealed areas of enhancement largely coincident with the enclosure but were almost mutually exclusive, in that susceptibility was associated with the central living area (burning) and P with the annexe - presumably where animals were kept and their excreta accummulated - indicating that electromagnetic and P surveying are complementary rather than interchangeable.

SOME RECENT WORK ON ARCHAEOLOGICAL SITES IN GREAT BRITAIN AND PERU

(A) Field Testing for P

Over a period of about 8 years I have used the P spot test (Schwarz, 1967) routinely during soil investigations at archaeological excavations, with varying degrees of success, as follows:-

(a) Successes

i. Nornour, Isles of Scilly (Iron Age) - relatively high P levels against a background of low P, allowed differentiation of occupation deposits from natural soil horizons to be made in vertical sections (Keeley, 1972).

ii. Samson, Isles of Scilly (Early Christian) - as at Nornour, P tests enabled occupation deposits to be differentiated from natural soil horizons (Keeley, 1973).

iii. Trethurgy, Cornwall (Roman) - high P concentrations were associated with an enclosure, implying that it was used for domestic stock (Keeley, 1974).

iv. Watch Hill, St Austell, Cornwall (Bronze Age barrows) - high P levels of surrounding soils indicated the location of an inhumation in a situation where bone was not preserved (due to extreme soil acidity) (Keeley, 1975).

v. Hereford (Saxon, Medieval) - enhanced P levels - indicated occupation levels (including a possible garden soil) when compared to low P in natural soil horizons (Keeley, 1976).

vi. St Peter's Street, Northampton (Saxon, Norman, Medieval) - determination of enhanced P levels was used as an indication of occupation deposits of natural soil horizons (Keeley et al, 1976).

vii. Moel y Gaer, Rhosemor, Choyd (Prehistoric) - as at Watch Hill, it was possible to locate the position of an inhumation, where the bone had disappeared, by delineating P enhancement in the soil (Keeley, 1976a).

viii. Trefignath, Anglesey (Neolithic chambered tomb) - enhancement of P was found in the chamber of surrounding soils, indicating the presence of an inhumation (Keeley, 1977).

ix. Little Bay, St Martins, Isles of Scilly (Bronze Age) - as at Nornour and Samson, P testing successfully differentiated occupation deposits (high P) from natural soil horizons (low P).

x. Foxhole Cave, Derbys (Palaeolithic) - low P and pH in the upper cave deposits indicated intense leaching of these sediments of underlying deposits.

(b) <u>Partial Successes</u>

i. Denny Abbey, Cambs (Medieval) - slight enhancement of P in a deposit, of associated soil horizons, allowed tentative interpretation as an old ground surface (Keeley and Keepax, 1976).

ii. Shaugh Moor, Devon (Bronze Age) - enhancement of P was found in soils of one of the huts but, in general, soil P appeared to be below the detection level of the spot test (Keeley, 1976b).

iii. Holyhead Mountain Circle, Anglesey (Iron Age) - higher P concentrations of surrounding soils were found to be associated with better preserved areas of flooring in one of the huts but it was not possible to delineate activity areas, etc (Elmhurst and Keeley, 1978).

iv. Huillca Raccay, Cusichaca Valley, Peru (Inca) - P spot testing has been carried out extensively, within buildings and associated open spaces, during excavation of this Inca fort. Although high P levels have been found to be associated with occupation deposits, it has not been possible to delineate areas of activity (Slack, 1978 pers comm; Straker, 1979 pers comm).

(c) <u>Failures</u>

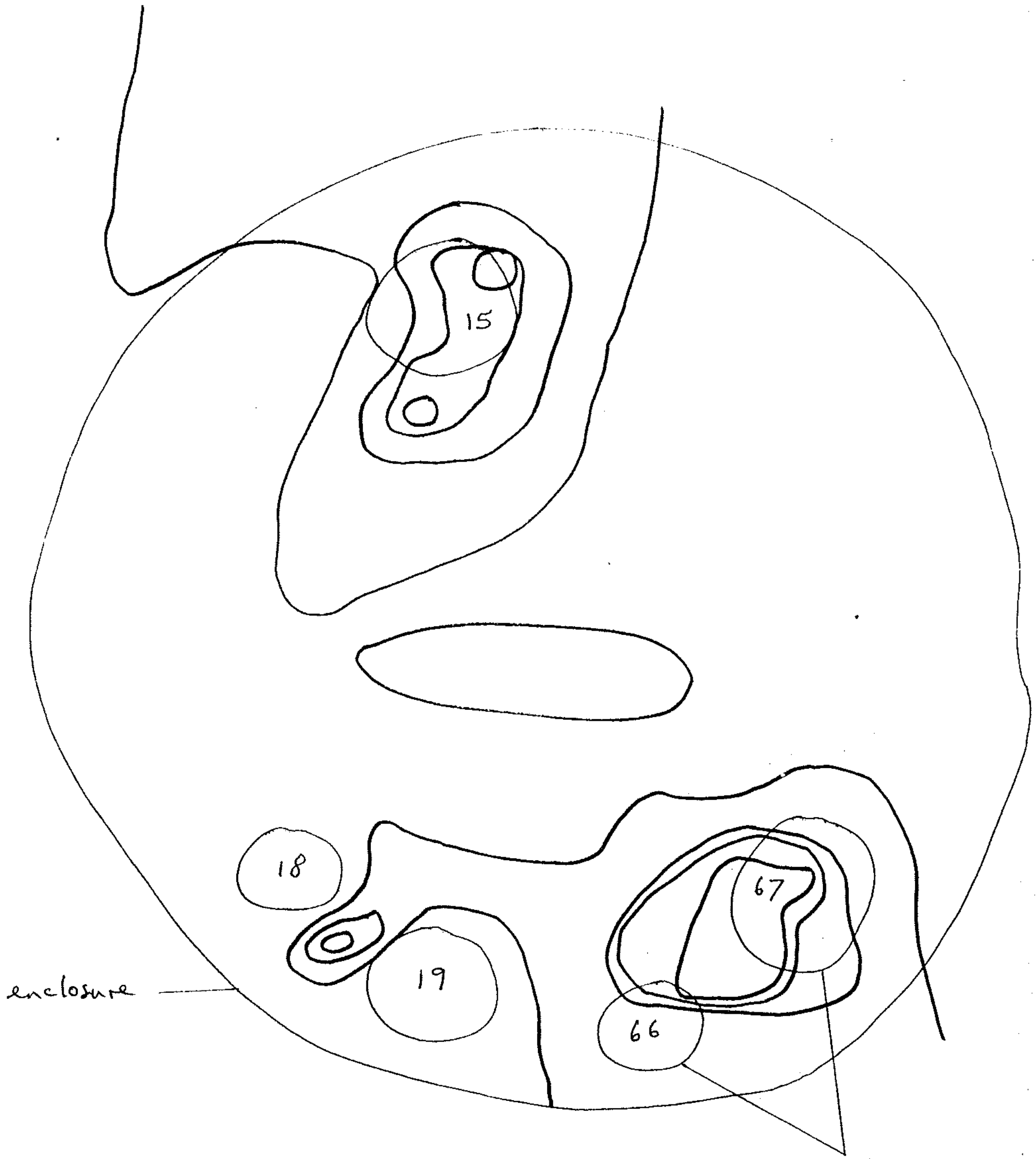
i. Wilderspool, Warrington, Lancs (Romano-British) - no relationship was found between soil P concentrations and archaeological features (Keeley, 1977a).

ii. Andover Harroway, Hants (near Iron Age/Romano-British site) - soil marks visible on aerial photographs could not be defined by the P spot test.

iii. Kirkhead Cavern, Cumbria (Palaeolithic) - the P spot test failed to differentiate natural cave sediments from supposed human occupation deposits.

iv. Kelverdon, Essex (Iron Age) - in a situation where bone did not survive (due to low soil pH), the P spot test did not indicate locations of inhumations in features

FIGURE 1. PHOSPHORUS DISTRIBUTION IN SOILS OF A PREHISTORIC ENCLOSURE – SHAUGH MOOR, DARTMOOR, DEVO



P concentrations :-

1) Outside huts 202 – 1142 μg/g (mean 481)
2) Inside huts 790 – 7520 μg/g (mean 3282)
3) Enclosure 555 – 4480 μg/g (mean 1537)

thought to be graves. This may have been due to interference from recently-applied P fertilizer, since high values were obtained for "natural" control samples.

v. Seamer Carr, Yorks (Bronze Age) - P levels were low on this site and occupation deposits did not show enhanced P concentrations.

vi. Holyhead Mountain Circle, Anglesey (Iron Age) - during the 1979 excavations P testing did not delineate activity areas, possibly because levels in features investigated were below the detection limit.

(B) Quantitative Laboratory Soil P Analysis

High concentrations of P, of surrounding soils, were found in samples of body stains from the site of Mucking, Essex (Saxon cemetery) (Keeley et al, 1977). Subsequently total P analysis (for some samples by X-ray fluorescence, for others by wet chemical digestion followed by colourimetric determination) was used to located the presence of inhumations within graves at Spong Hill, Norfolk (Pagon Saxon cemetery) - bone had disappeared due to low soil pH and only dubious stains remained (Keeley, 1979).

Because of the unpleasant aspects of using perchloric acid (ie the unsafeness of boiling $HClO_4$) during the preparation of soil samples, workers in the Ancient Monuments Laboratory have recently turned to the method of Dick and Tabatabai (1977), which was initially developed for determination of total P in soils and lake sediments. A mixture of soil and sodium hypobromite solution is boiled to dryness in a sand bath (260-280°C), the total amount of orthophosphate extracted with 1N sulphuric acid (H_2SO_4) and determined colourimetrically by the molybdenum blue method. Dick and Tabatabai (1977) found that this method gives similar results to $HClO_4$, only 4% lower than $Na_2\ Co_3$ fusion and allows rapid analysis of large numbers of samples.

Following the failure to delineate areas of activity on Shaugh Moor, Dartmoor, mentioned previously, using a spot test for P, the DOE Central Excavation Unit have carried out quantitative P analysis on samples from a prehistoric enclosure containing several huts, using a modified form of the Dick and Tabatabai (1977) method (Balaam, pers comm 1980). The results are shown in Figure 1.

During the analysis measured quantities of reagents and water have been added at the final stage, rather than making the volume up to 25 mls. Test tubes are used at this point rather than volumetric flasks as they are cheaper and easier to wash. Centrifuging has been eliminated in favour of allowing the flasks to stand for about an hour - during this time other material can be prepared and the use of an extra set of glassware is avoided. These modifications introduce additional errors which have not been quantified but it is thought that these are insignificant (Balaam, pers comm 1980). At least 200 samples a day may be processed, assuming that the initial sample drying and grinding are done in advance.

This method has been found to be much simpler and safer than perchloric acid digestion. The results are more readily reproducible and iron staining is eliminated from sample solutions. It is suggested (Balaam, pers comm 1980) that this method (excluding initial sample preparation) is at least as fast as that used at Grime's Graves (Sieveking et al, 1973) and is particularly useful on soils, such as those on Dartmoor, which have inherently low P contents. Consequently it will be used on a routine basis in future P surveys.

Conclusions

Use of a field spot test for soil P during investigations of archaeological sites has proved reasonably (but not consistently) successful in providing indications of human activity. However, it is clear that a quantitative method of total P determination is needed for detailed follow-up work, particularly on sites where P levels in soils are too low to be detected by the spot test or too high to allow meaningful interpretation. The method of Dick and Tabatabai (1977) appeared to offer a suitable analytical technique for this purpose, since it enables rapid determinations to be carried out on large numbers of samples. Modifications of the method carried out during investigations of samples from the prehistoric settlement site on Shaugh Moor, Dartmoor, enable the potential number of samples to be processed daily to be increased still further.

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