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Geochemical Survey at Richborough, Kent : an assessment

James Moore[1], David Dungworth[2] and Jen Heathcote[3]

Summary

This report details the preliminary geochemical analysis of soil samples taken from Richborough, Kent. The major aims of the geochemical study were to a) evaluate the efficacy of EDXRF as an analytical technique capable of producing a data set at a suitable degree of accuracy for meaningful interpretation and b) to compare the results of geochemical, geophysical and fieldwalking evidence at the site.

The major benefit of using EDXRF is its availability in-house at the English Heritage Centre for Archaeology. However, the results indicate that a sufficient degree of accuracy and level of elemental detection cannot be achieved with current equipment. Therefore, in order to address the second project aim, i.e. the question of whether there is any correlation between the evidence for archaeological activity indicated by geophysical, geochemical and fieldwalking data, an alternative analytical technique will be required.

Keywords

Soil / Sediment

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Introduction

The use of geochemical survey as a prospection technique for the identification and delimitation of archaeological sites has increased over the past decade (*e.g.* Clogg and Ferrell 1991; Bintliff, *et al*. 1992; Entwistle and Abrahams 1997; Aston, *et al*. 1998a) though its utilisation is still far from common in the U.K. Typically, the chemical species employed for geochemical survey are phosphorus and heavy metals, used either individually (*e.g.* phosphorus survey - Clogg and Ferrell 1991; heavy metal survey - Bintliff, *et al*. 1992) or in conjunction (*e.g.* Aston, *et al*. 1998a; Aston, *et al*. 1998b; Jackson 2001).

Archaeological soil phosphorus analysis is based on the principle that human activity acts to redistribute naturally occurring soil phosphorus, increasing the levels in some areas through concentrated deposition of materials such as excreta, food remains or organic building materials. Alternatively, soil phosphorus levels may decrease where, for example, arable cultivation and harvesting without manuring is practised. The reason that this activity is potentially detectable in the archaeological record is due to the fact that phosphorus is relatively stable compared to other elements within the soil system and is largely resistant to leaching (Proudfoot 1976).

The overall chemical composition of soil is influenced predominantly by the nature of the underlying geology upon which the soil has developed. However, human activities associated with agricultural, settlement and industrial practices may also affect the elemental composition creating anomalous, localised accumulations of trace elements and heavy metals with respect to the background composition of a soil in a particular locality. These anomalies are potentially identifiable in the archaeological record as the elements can be present in compounds that are resistant to leaching (Bintliff *et al*. 1992).

Rationale for the survey

Geophysical survey at Richborough (Martin, 2001; 2002) has already illustrated the extent and layout of the site, including the amphitheatre and the settlement surrounding the Saxon Shore fort. Therefore, the use of geochemical analysis for the preliminary identification of the site (thus acting as a prospective tool as suggested, for example, by Aston *et al*. 1998a) was unnecessary in this instance. However, it is worth mentioning that its use may allow the detection of a ‘halo’ pattern as noted by Bintliff *et al.* (1992: 15) that can be interpreted as traces of human activity beyond the physical evidence of settlement.

The geochemical survey reported here was conducted as a methodological trial over part of the area covered by the geophysical (magnetometer) survey (Fig.1). It was conducted in order to address two main issues:-

1) To establish the efficacy of analytical procedure (EDXRF) that was available within the Centre for Archaeology for the quantification of chemical elements across a site: of particular concern was whether the equipment available could operate at the levels of detection required for meaningful interpretation of archaeological data sets (Wilmott *et al*. 2001).

2) To compare the results of geochemical concentration patterns with geophysical anomalies identified through the magnetometer survey and, eventually, to the distribution of archaeological activity determined from fieldwalking.

Fig. 1 Magnetometer surveys conducted at Richborough, Kent in 2001 (Martin 2002).

Methodology

Field**:** samples of c.500g were collected at 30m intervals along six transects (Transects A-F). These transects were positioned running approximately NNE-SSW and utilised the 30m grid used for the geophysical survey (Fig. 2). Because of the disturbance and possible contamination from Bushe-Foxe's excavations of the 1920's, samples were not taken from within the Saxon Shore fort or its ditches. This resulted in a set of 140 samples. In addition, an area measuring 30x40m was selected arbitrarily for sampling at a higher resolution to assess the degree to which chemical anomalies occurred over short distances. An additional 41 samples, taken at 5m intervals resulted from this exercise.

Fig. 2 Location of geophysical surveys, 2001 at Richborough, Kent: samples for geochemical analysis were removed from the intersections of this 30m grid (Martin 2002).

Samples were taken using a hand auger. The upper 23cm of soil was discarded, as this material was lying within the Ap horizon (or plough zone), and the soil sample for chemical analysis was taken from the undisturbed sub-soil horizon at a depth of between 23-33cm. The auger head was thoroughly cleaned between samples. Each sample was stored in a sealed plastic bag labelled with the sample's unique grid co-ordinates.

Laboratory**:** samples were air dried for approximately 72 hours, crushed and homogenised by pestle-and-mortar, then screened through 2 mm mesh to remove pebbles and inclusions such as roots. All inclusions *e.g.* ceramics, bone, shell *etc*. were recorded before being discarded and the sub-2mm fraction was retained and re-bagged. It is hoped that the results of these records of micro-artefact (>2 mm size) distributions across the site can be compared to the distribution of macro-artefacts determined by fieldwalking.

As total soil phosphorus (P) was to be calculated, it was necessary to convert organic P to inorganic P prior to EDXRF (energy dispersive x-ray fluorescence) analysis; this was achieved by igniting the samples. Approximately 9g of each air-dry sample was weighed and placed in individual, labelled crucibles. These sub-samples were heated to 600°C for two hours in a muffle furnace. A by-product of the process was that it was possible to calculate the percentage organic matter content of each sample (see Appendix 1), providing an additional set of data whose distribution across the site may be of some interpretative value (Jackson 2001).

Multi-elemental analysis by EDXRF**:** an initial run of 25 samples was submitted to test the ability of EDXRF to detect small amounts of metals believed to be present in the samples. The sample set comprised those collected from one complete transect together with a number of samples selected from positions with a) particularly clear geophysical anomalies and b) in which geophysical anomalies were absent.

EDXRF is widely used in archaeology as it is able to simultaneously detect a wide range of elements (Na–U), it does not require elaborate sample preparation, is relatively fast and is a non-destructive analytical technique. A primary x-ray beam is directed onto the sample. These x-rays displace electrons from the inner shells of atoms in the sample. The vacant shells are filled by the movement of electrons from outer shells to inner shells, and these transitions lead to the emission of secondary x-rays. The energies of these secondary x-rays depend on the atomic number of the atom(s) involved. A typical EDXRF spectrum consists of a series of characteristic peaks, regarded as significant only if they are greater than three times the background variation. In addition, an EDXRF spectrum may contain other peaks (diffraction peaks, sum peaks, escape peaks, etc.) that can make the quantification of trace elements difficult. For this reason, EDXRF has relatively high detection limits compared to some other techniques (*e.g*. ICP-AES and ICP-MS) and the initial run of samples was examined to determine if any metals could be detected.

Results and discussion

Previous geochemical surveys (*e.g*. Aston *et al.* 1998a; Bintliff *et al.* 1992) have identified a number of key elements that can be associated with past human activity. The elements identified as important for the survey at Richborough include copper (Cu), lead (Pb), zinc (Zn), chromium (Cr), iron (Fe), manganese (Mg), calcium (Ca), potassium (K) and phosphorus (P), which have been typically used in the interpretation of geochemical signatures of archaeological sites. However, with the exception of iron (Fe) and phosphorus (P), in the trial samples, these elements were only detected at very low levels (typically 0.05wt%, or 500ppm) and are in many cases almost indistinguishable from the background levels. In order to check the reliability of the EDXRF results, eight samples were analysed by ICP-AES following aqua regia digestion. These analyses were conducted at the NERC Geochemical Research Facility, Royal Holloway College, University of London. The ICP-AES analysis showed that all of the elements of interest were present at relatively low levels (<150ppm; see Table 1). As such, the identification of elements from these samples using EDXRF is considered unreliable due to methodological limitations of the equipment.

Table 1. Comparison of results obtained by EDXRF and ICP-AES analysis (wt%).

Results obtained by EDXRF

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G	Sample H
Na_2O	<1	<1	<1	<1	<1	<1	<1	<1
MgO	<1	<1	<1	<1	<1	<1	<1	<1
Al_2O_3	5.7	7.5	6.8	7.0	6.6	6.5	6.7	6.6
SiO_2	86.6	89.4	88.7	86.3	87.6	84.9	86.7	84.8
P_2O_5	0.3	0.4	0.3	0.3	0.4	0.2	0.3	0.6
K_2O	1.6	1.7	1.7	1.6	1.7	1.5	1.8	1.6
CaO	1.0	1.0	1.0	0.9	1.1	1.2	1.1	1.6
TiO_2	0.4	0.5	0.5	0.5	0.4	0.6	0.4	0.5
V_2O_5	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Cr_2O_5	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
MnO	0.01	0.06	0.06	0.03	0.09	0.06	0.06	0.08
Fe_2O_3	2.9	3.5	3.1	3.3	3.9	3.4	3.1	3.3
CoO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
NiO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CuO	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
ZnO	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
PbO	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04

Results obtained by ICP-AES

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G	Sample H
Na_2O	0.34	0.43	0.44	0.36	0.43	0.41	0.43	0.44
MgO	0.45	0.53	0.55	0.51	0.53	0.55	0.54	0.50
Al_2O_3	5.01	5.91	5.99	5.34	5.84	5.93	5.89	5.59
SiO_2	-	-	-	-	-	-	-	-
P_2O_5	0.23	0.29	0.40	0.25	0.50	0.24	0.25	0.40
K_2O	1.39	1.59	1.64	1.48	1.54	1.55	1.53	1.51
CaO	0.88	0.81	0.98	0.70	1.11	0.87	1.34	1.23
TiO_2	0.43	0.48	0.50	0.45	0.48	0.48	0.48	0.46
V_2O_5	0.0047	0.0053	0.0054	0.0055	0.0051	0.0053	0.0050	0.0047
Cr_2O_5	0.0068	0.0049	0.0052	0.0054	0.0054	0.0050	0.0050	0.0036
MnO	0.04	0.06	0.06	0.05	0.06	0.06	0.05	0.06
Fe_2O_3	2.65	2.97	3.31	2.99	3.10	3.12	2.92	2.82
CoO	0.0005	0.0006	0.0006	0.0005	0.0005	0.0006	0.0005	0.0006
NiO	0.0015	0.0017	0.0018	0.0015	0.0016	0.0017	0.0016	0.0015
CuO	0.0022	0.0026	0.0030	0.0022	0.0032	0.0027	0.0026	0.0026
ZnO	0.0051	0.0060	0.0066	0.0052	0.0059	0.0056	0.0053	0.0055
PbO	0.0052	0.0063	0.0055	0.0047	0.0062	0.0066	0.0056	0.0057

Conclusion

The low levels of the target elements and the consequent inaccuracy of the EDXRF results indicates that the method is not appropriate in this instance and an alternative means of analysis is required that can provide lower limits of detection. Possible techniques for consideration are alternative XRF equipment where the use of copper filters will allow lower levels of elements to be detected, or ICP-MS or ICP-AES. None of these facilities are currently available within Fort Cumberland and their use would necessitate buying the analysis from another laboratory.

Until the full sample set has been analysed for selected geochemical properties, it will not be possible to address the second project aim presented at the beginning of this document. That is, whether there is any correlation between evidence for archaeological activity in the immediate vicinity of the fort indicated by geophysical, geochemical and fieldwalking data.

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Appendix 1: Loss-on-Ignition methodology

1. A weighed, empty crucible was filled approximately ¾ full with air-dried sample and re-weighed. The weight of air-dried soil was then calculated by subtracting the weight of crucible from the total weight, and recorded (W_1).

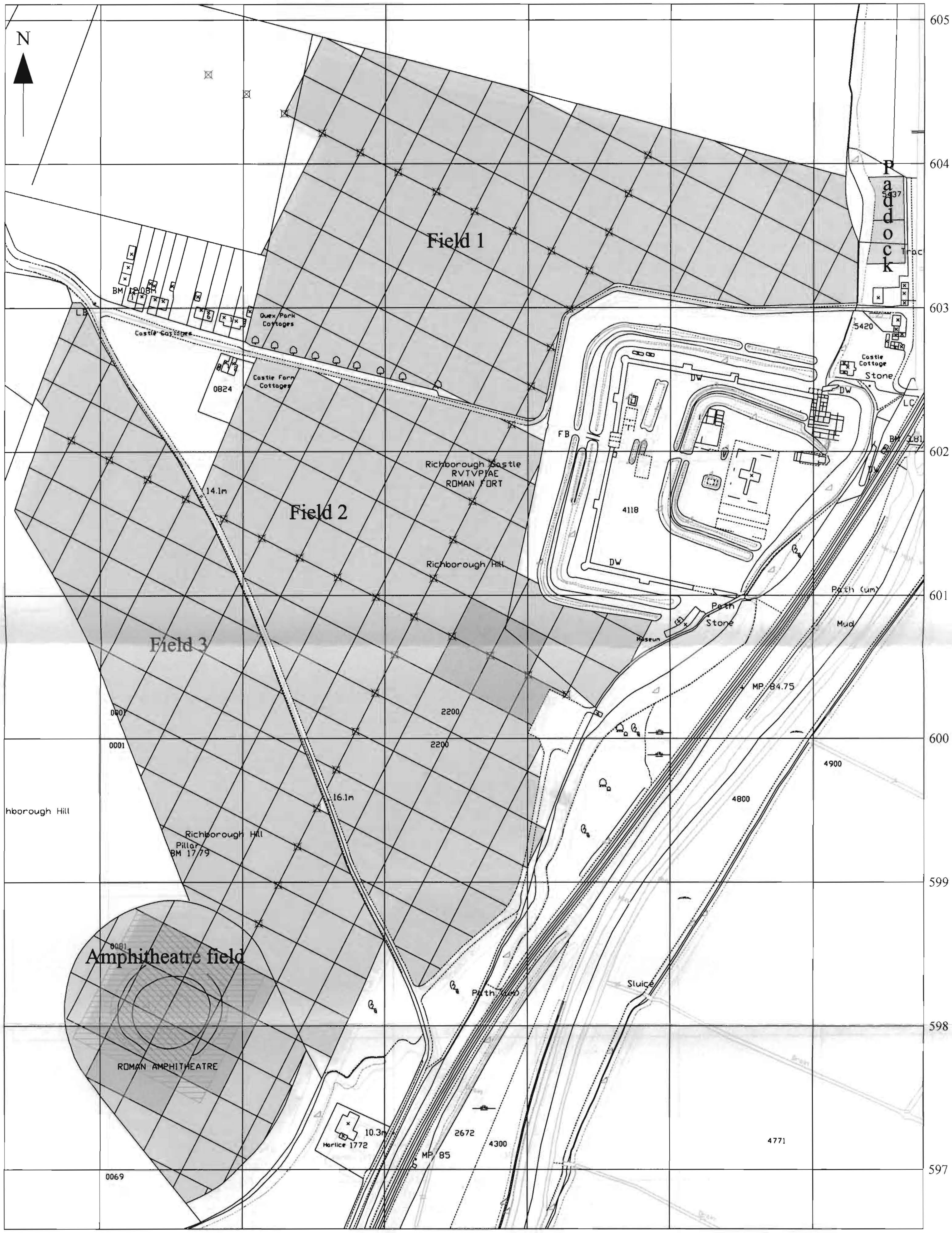
2. The samples were ignited at 600°C for 2 hours in a muffle furnace. At the end of 2 hours they were removed from the furnace and placed in a dessiccator to cool. Samples were then reweighed, and the weight of the crucible was subtracted in order to give a weight of ignited soil for each sample (W_2).

3. Loss-on-ignition (%) = $((W_1 – W_2)/W_2)*100$. This figure is taken to be equivalent to the organic matter content of the soil.

FIGURE 1

RICHBOROUGH, KENT.
Location of geophysical surveys, 2001.

TR3260



0 ▬▬▬ 90m

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- ▢ Fluxgate gradiometer survey.
- ▤ GPR survey.
- ☒ Magnetic susceptibility transect.
- ■ Earth resistance survey.
- ▨ Electromagnetic survey.

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RICHBOROUGH, KENT.
Magnetometer surveys, 2001.

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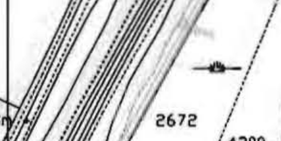

▨ After Cunliffe 1968, fig 25.

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