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Application of high resolution Mobile Metal Ion (MMI) soil geochemistry to archaeological investigations: an example from a Roman metal working site, Somerset, United Kingdom.

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Abstract

An innovative application of Mobile Metal Ion (MMI) partial extraction soil geochemistry is used to identify below-surface archaeological features, using a previously incompletely surveyed Roman metal-working site at St. Algar's Farm, Somerset, as a case study. Soil samples were taken and analysed for 53 elements by the MMI geochemical method. Lead, Tl, Ba and Zn were found in very high concentrations and the sensitivity of the technique also enabled Ag, Au and Sn to be measured in anomalous concentrations. Elemental maps accurately outlined known metal working areas. Principal component analysis and bivariate correlations identified two suites of associated elements: Pb, Ba, Tl, Ag, Au, Cu, Sb, the base and noble metal group (BNM), and Fe, Ti, Nb, Mn, Co, Cu, P, Li, Rb, Sc, Cs, K, Ga, P, Zr,

Th and Sn, the pegmatite (PEG) group. These were used to form indices which delineate the metal working area and areas possibly related to the processing of pegmatite containing Sn. The high sensitivity MMI data were compared with strong-acid digest results from a limited number of the MMI samples; the MMI data showed better geochemical contrast than the strong-acid results. Multi-element statistical similarity comparisons with off-site samples suggest likely sources for the Pb and Sn used at the St Algar's site. The increased sensitivity of MMI soil analysis combined with the multi-element capacity allows a more detailed archaeological interpretation.

Keywords: soil geochemistry, archaeological prospection, partial extraction, MMI, magnetic gradiometry, Roman, metal extraction.

1.0 INTRODUCTION

Geochemistry has had a small, but growing place in archaeological investigations for almost a century. Soil chemistry was first applied to archaeological questions when it was discovered that phosphate enrichment in Swedish soils was an indicator of prehistoric human occupation and could be connected with prehistoric sites and deserted mediaeval villages (Arrhenius 1931). The advent of ICP-MS presented the opportunity to analyse quickly and at relatively low cost, for a very much wider range of elements. This resulted in the analysis of soils associated with archaeological sites for an increased number of elements potentially indicative of human activity (Middleton 2004) Today, more than 20 elements have been found to be indicators of anthropogenic activity at specific sites over a wide range of archaeological contexts. These include domestic and agricultural (Davidson, Dercon et al. 2006) ,

archaeological prospection (Bintliff, Davies et al. 1992, Aston, Martin et al. 1998, Entwistle, Abrahams et al. 2000, Schlezinger and Howes 2000), interpretation of space use (Cook, Clarke et al. 2005, Cook, Kovacevich et al. 2006, Cook, Banerjea et al. 2010), middens (Beck 2007), inhumations and differentiated burial sites (Bethell and Carver 1987, Sampietto and Vattuone 2005) metal accumulation derived locally from ancient mining or mineral processing operations (Maskall, Whitehead et al. 1995, Maskall, Whitehead et al. 1996, Mighall, Grattan et al. 2002, Dunster and Dungworth 2012, Dunster, Dungworth et al. 2012, Grattan, Gilbertson et al. 2013)

The formation of anthropogenic geochemical anomalies in soils is complex. Oonk, Slomp et al. (2009) observed that retention and sequestration of elements in soils is rarely governed by a single process. Adsorption, occlusion, ion exchange, isomorphic substitution, chelation and precipitation reactions together with factors such as waste and soil composition, soil pH, redox conditions, grain and pore size can be responsible for the preservation of inorganic signals in archaeological soils. The retention and sequestration of trace elements in soils generally depends on their oxidation state, soil pH, the specific surface area, cation exchange capacity and the presence of clay minerals, Fe oxides, carbonates, phosphates, sulphides and organic matter (McBride 1989, Oonk, Slomp et al. 2009).

The detection of an anthropogenic soil geochemical signature (anomaly) is based upon the contrast between the anthropogenic signal (commonly weak) and the background. The anthropogenic contribution to the measured value may be relatively small when total or strong-acid digests are utilized because a substantial contribution to the overall analytical signal will come from dissolved lithological material. This results in a lower peak/background ratio (geochemical contrast) than would be obtained by use of a weak-acid or non-acid digest (Stanley and Noble 2008, Mann 2010). Even with the lowering of detection limits for elements, the problem of differentiating anomalies from background remains and it is only by

reducing the relative background levels that the peak/background ratio can be effectively enhanced. An acidic partial digest still dissolves part of the soil matrix whereas a non-acid partial extraction attempts to detach analytes from the soil matrix, with minimal dissolution of the matrix, thereby reducing background interference (Mann 2010). Mann (2010) also found that partial digestions and extractions appear to have the ability to discriminate in favour of the 'active' ionic (source-related) signature of the sought after material and the elements indicative of its presence, relative to their 'geochemical background', thereby improving both spatial and amplitude resolution of anomaly signals. Stanley and Noble (2008) made similar findings in their evaluation of Navan base metal deposit in Ireland. Here it was found that weak non-acid partial extractions (using solutions similar to those used in Mobile Metal Ion MMI) were far more effective in the identification of soil geochemical anomalies derived from buried base metal mineralization than were total or strong-acid digests. The reason was that the weak extractant dissolved only the material derived from the mineralization by upward transport in solution and deposition on soil clays, iron oxides etc. It dissolved negligible concentrations of elements from the soil minerals, which strong-acid digestion does, and which increase background (and thereby its detectability) by lowering the peak/noise ratio.

The Mobile Metal Ion (MMI) technique is based on a neutral-alkaline solution containing both organic and inorganic ligands (Mann, 2010). The ligands provide complexing ability, whilst the lack of an aggressive acidic (or alkaline) component ensures that during extraction the soil matrix is not dissolved. The analytical signal is most likely derived predominantly from adsorbed and loosely attached ions on the exterior of grains and grain boundaries. The amount of each element extracted is much lower than obtained by total (XRF) or by acid extraction (e.g. aqua regia) but the improved signal to noise ratio due to reduction in background has resulted in the technique being widely used in mineral exploration (Mann et

al, 1998); there is also an increased efficacy for resolution of anthropogenic anomalies (Mann et al, 2015) by discriminating against matrix material. The sampling requirements for MMI are very simple. The protocol is given in (Mann 2010). When combined with ICP-MS (capable of returning low concentrations for over 50 elements) the MMI technique provides a potentially very powerful tool for archaeological investigation.

The recently completed European Agricultural Soils (GEMAS) project (Reimann, Birke et al. 2014) analysed agricultural soils from a widely spaced sampling grid, by XRF and ICPMS after both strong-acid digestion and MMI extraction. The MMI results identified anthropogenic contributions to soil chemical composition (Sadeghi et al., 2015), some of which are potentially of archaeological interest (Mann, Reimann et al. 2014). To evaluate the use of MMI soil geochemistry in the discovery, delineation and definition of anthropogenic soil geochemical anomalies associated with archaeological sites, this study was carried out on the well documented Roman site at St. Algar's Farm, Somerset, UK. Limited strong-acid digestion investigations were included to determine whether the elemental species targeted by MMI provide more sensitive detection of archaeological anomalies than total analyses. To evaluate the use of MMI soil geochemistry in the discovery, delineation and definition of anthropogenic soil geochemical anomalies associated with archaeological sites, this study was carried out on the well documented Roman site at St. Algar's Farm, Somerset, UK. Limited strong-acid digestion investigations were included to determine whether the elemental species targeted by MMI provide more sensitive detection of archaeological anomalies than total analyses.

2.0 MATERIALS AND METHODS

2.1 Site description and sampling

An MMI geochemical soil sampling programme was undertaken on and around, the area of the Scheduled Monument centred at 51°10'31.2"N 2°18'39.0"W on St. Algar's Farm, Selwood in eastern Somerset. St. Algar's Farm is located adjacent to the Frome Road (B3092) about 2 km south of the village of West Woodland, some 6 km south of the town of Frome and about 25 km south of the city of Bath (Figure 1). The farm lies on undulating land in the valley of the River Frome and is currently under permanent pasture and used for cattle grazing. It has been subject to some ploughing in the past few decades. The site has a maximum elevation of approximately 108 m above mean sea level. It slopes gently to the east and flattens towards an irrigation channel which extends from the nearby Frome River and the farm pond, where the elevation is about 98 m above mean sea level. The soil at the site is of heavy clay and has been mapped as Soilscape 18 of the Soilscape Soil Types map of England. These soils are classified as slowly permeable, seasonally wet, loamy to clayey, commonly drainage impeded, moderately fertile, low carbon grassland soils which drain into the local stream network (Cranfield University 2015).

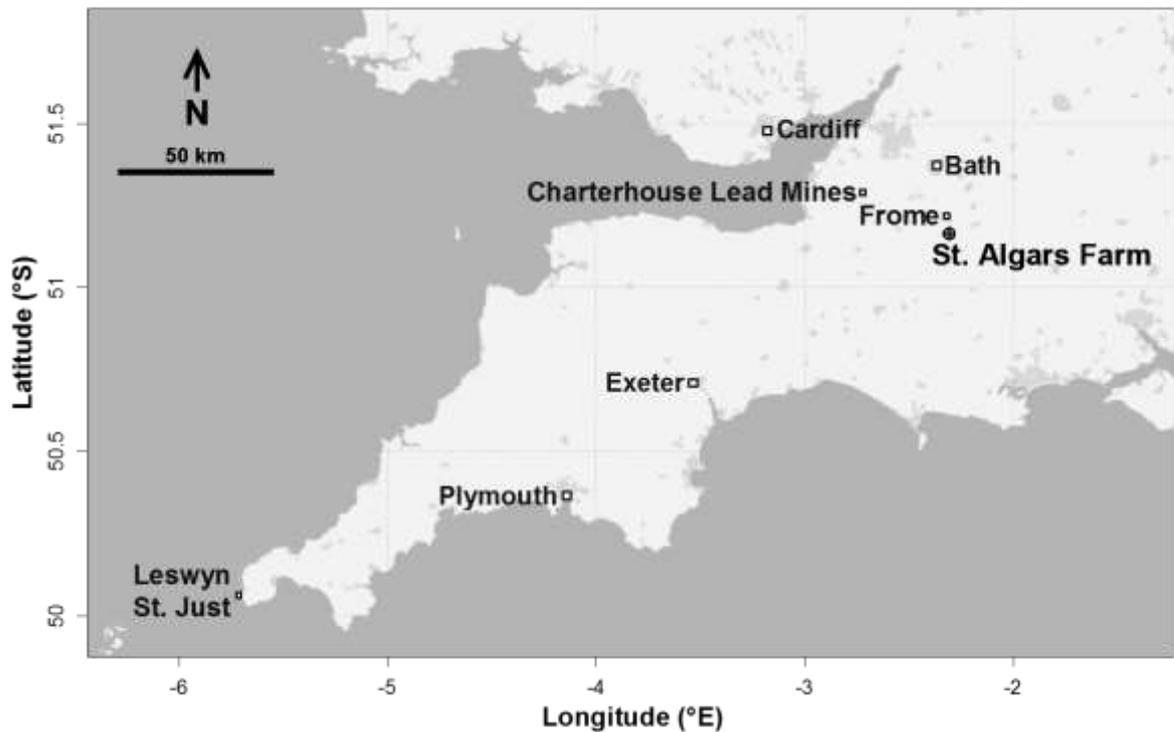


Figure 1. Map showing the location of St. Algar's Farm, reference points and other places mentioned in the text.

Archaeological investigation of the site (excavated trenches based upon geophysical results) recovered evidence of three periods of Romano-British occupation (Lambdin 2011, Lambdin and Holley 2011, Lambdin and Holley 2012, Lambdin and Holley 2012). These are 1); an early villa with internal room divisions and set within a square ditched area of 1st-2nd century CE age, 2); a winged corridor villa of likely 2nd-3rd century age and 3); a 4th century industrial site. Excavations have recovered substantial amounts of common building materials including stone rubble, roof and floor tiles, flue tiles, tesserae, fragments of painted wall plaster and a cobbled surface which has been interpreted as a yard (Lambdin and Holley 2011, Lambdin and Holley 2012). Recovered artefacts indicative of human occupation of the villa include substantial amounts of oyster shell, animal bone, glass gaming counters, local and imported

pottery, coins and a copper brooch. A considerable amount of glass and glass waste (pulled threads and trails), misshapen molten waste glass drops and small broken chunks of glass as well as crucible fragments indicative of glass working (probably 4th century) were recovered from the vicinity of the villa. No conclusive evidence of a furnace on the site was derived from the excavations. However, the discovery of cupellation products and waste, including lead and litharge are strongly indicative of Roman cupellation to produce silver from lead ore. Dipole magnetic anomalies, possibly indicative of hearth sites, are present in the geophysical survey results and strong, coincident lead anomalies obtained from pXRF surface readings may be indicative of cupellation sites (Dungworth, Comeau et al. 2013). Whilst excavation work on the site has uncovered evidence of considerable industrial activity, the timing of commencement and end dates and whether different activities were contiguous, sequential or separated in time is not well defined. Other than a calibrated ¹⁴C date of CE131-155 on cremation remains from the mausoleum, there is little in the way of secure dating evidence. Features of archaeological interest are shown on the magnetic gradiometry imagery in Figure 2.

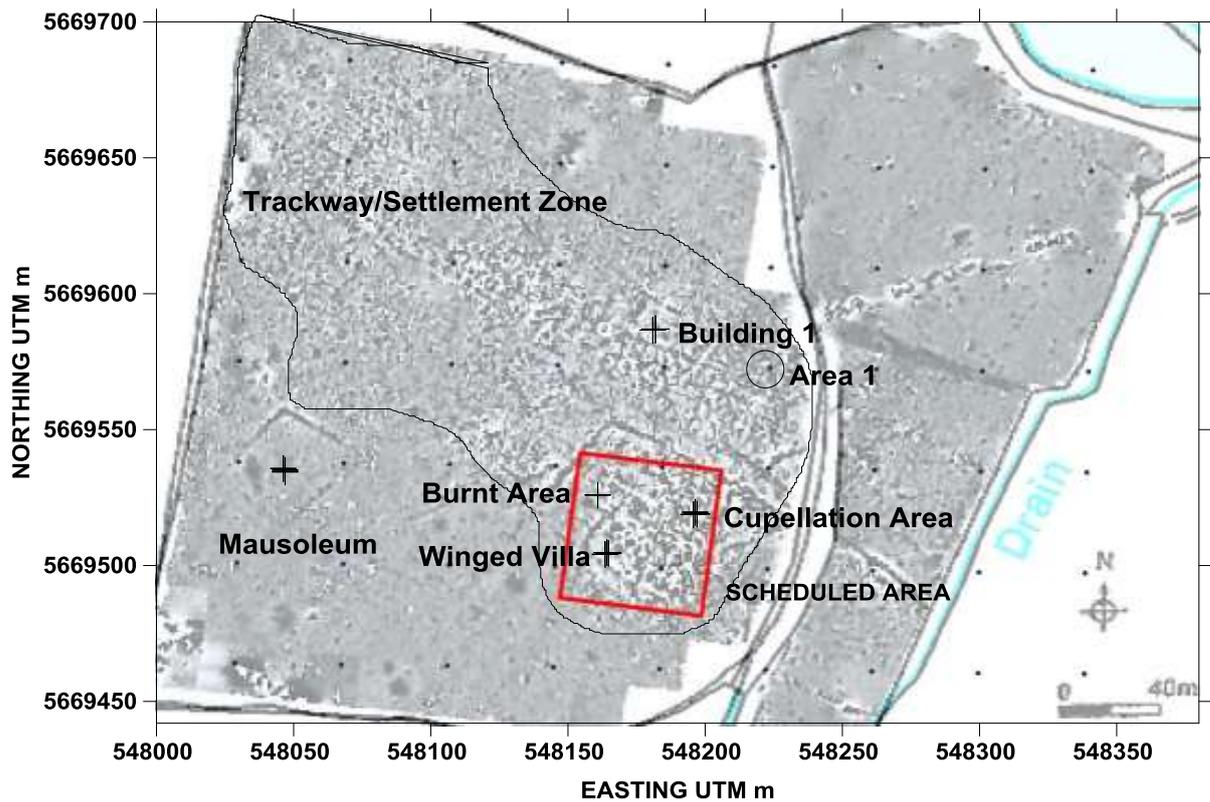


Figure 2. St. Algar's Farm magnetic gradiometry with interpreted archaeology. (magnetic gradiometry after Lambdin (2011)). The Scheduled Monument area is enclosed by the square box.

The St. Algar's soils sampled were grey in colour, appeared uniform in grainsize and texture and showed little visual variation. The site had been ploughed so there was little or no evidence of a humic material in the near surface layer. Below the grass roots most of the soils were visually unstructured and consist of a malleable, sticky clay-rich grey material. The area is underlain by Quaternary silt, sand and gravel deposited from rivers as channel fill, terrace deposits and flood plain alluvium. It is from the Quaternary flood plain alluvium that the local soil at St. Algar's Farm appears to have been developed. The basement geology consists of shallow marine calcareous sediments and limestone of Jurassic age (British Geological Survey 2015).

Sampling was undertaken using a predetermined 40 m × 40 m grid. Sampling sites were selected to test the archaeology inferred from geophysical survey and revealed by excavation. A total of 63 samples were collected over an area of 240 m × 320 m. The predetermined sample sites were located (Figure 2) using a Garmin GPS 72 GPS unit (accuracy to within 5 m). The actual sample sites were relocated with much greater accuracy (to a few cm) using a real time corrected Leica GPS900 GPS unit. At each sampling location the turf was lifted from a 20 × 20 cm area (the width of the spade used) and a pit was then dug to a nominal depth of 15 cm. Duplicate soil samples (approximately 100 g) were then taken from the pit bottom, using a plastic spoon to prevent sample contamination with metals. The sampling was thus designed to capture soil from the 10-25cm depth of the developed protocol and was noted to be coincident with the plant root zone in accordance with previous observations (Mann 2010). After sampling the excavated soil was returned to the hole and the turf sod replaced.

2.2 Chemical analysis

The samples were sent to SGS laboratories in Perth, Western Australia and were treated using the MMI-ME Mobile Metal Ion Analysis method in which 50 g of sample is subject to leaching in a known volume of “mixed lixiviants solution” (the solution’s composition is commercial in-confidence but some useful background information is given above and in Mann et al. 2012). One advantage of a relatively large sample charge and a partial extraction is reduction in the “nugget effect” when dealing with elements at low concentrations (Leduc and Itard 2003). The resultant leachate is allowed to settle and is sampled after 24 hours. A sub-sample of the clear leachate is withdrawn and presented to an Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) for elemental analysis. The ICP-MS instrumentation

was a Perkin Elmer Elan 9000 DRC II, with an argon plasma and a reaction cell with ammonia gas. The solution was analysed for the following 53 elements: Ag, Al, As, Au, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hg, K, La, Li, Mg, Mn, Mo, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, U, W, Y, Yb, Zn and Zr. Quality control and assessment (Caritat and Cooper 2011) was based on several measures: (1) analysis in a single batch, (2) insertion of blind field duplicates, (3) insertion of blind laboratory replicates, (4) insertion of laboratory standards in the analytical stream at regular intervals and (5) analysis of blank MMI®-extraction solution. Elemental values < Lower Detection Limit (LDL) were replaced in the final database with values set to $0.5 \times \text{LDL}$ (Reimann, Filzmoser et al. 2008). The elements Bi, Hg, In, Mo, Pd, Pt, Ta, Te and W were present in concentrations <LDL in all samples and were removed from the database. Four elements; As, Cr, Nb and Sn with >40% of values <LDL which would normally be removed from the database (Reimann, Filzmoser et al. 2002) were retained as they provided valuable information relevant to the goals of the study. The element deletions resulted in a final 42 element suite for this study.

2.3 Numerical and statistical analysis

Basic statistical analyses on the edited dataset were performed using Microsoft Excel®. The distributions of each variable were checked for normality using the Shapiro-Wilk test implemented in R (R Core Team 2015); skewed variables were \log_{10} -transformed prior to correlation and analyses. Numerous lead (Pb) values were above the upper detection limit (UDL; 20000 ppb); however, based on the strong linear relationship between Pb and thallium (Tl) and because Tl commonly displays geochemical behaviour similar to Pb (geochemical coherency), Pb values ≥ 20000 ppb were replaced with calculated values from the regression of

valid Pb concentrations against Tl ($r^2 = 0.75$; $p=2 \times 10^{-8}$; $\log_{10}\text{Pb} = 4.75 + 1.354 \times \log_{10}\text{Tl}$). The extrapolated Pb values (Pb_{calc}) were used to overcome the distortion caused by the large number of samples containing Pb at levels $> \text{UDL}$.

Principal components analysis (PCA) was performed in R using correlation matrix of scaled, centred-logratio transformed concentrations, with the rare earth elements (REE; in this dataset, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, and Yb) combined additively into a single variable because of their geochemical coherency and similarity in distribution. The centred logratio transformation removes any dependencies between variables due to compositional closure (Reimann, Filzmoser et al. 2008) and also corrects skewed distributions. Elements containing too many below-detection concentrations (As, Cr, Sn) were not included in the analysis.

Contour plots and background maps were generated using Sigmaplot. Interpolation of the sampling grid to calculate contours was achieved using anisotropic kriging based on linear-to-sill semivariogram models.

Distribution maps of elements in surface soils were generated from point data using simple kriging with exponential variogram models, implemented using the R package 'geoR' (Ribeiro Jr. and Diggle 2015). Variables to be predicted were log-transformed where necessary to remove skewness, and kriged predictions were made on a grid with 5 m spacings across the area sampled. Variogram models were fitted by Cressie's weighted least-squares after fitting a first-order polynomial trend surface, and with the maximum distance restricted to 40% of the greatest inter-sample distance, as recommended by Reimann et al. (2008).

3.0 RESULTS

3.1 Elemental descriptive statistics

To facilitate investigation of the relationships between the elements of potential anthropogenic significance, basic statistical data were collected and are shown in Table 1.

The local background at St. Algar's Farm is defined as being the Mean of the first quartile MMI values for each element. Geochemical contrast for each element is defined as the ratio of the Mean of the 4th quartile (4QM) to the Mean of the 1st quartile (1QM).

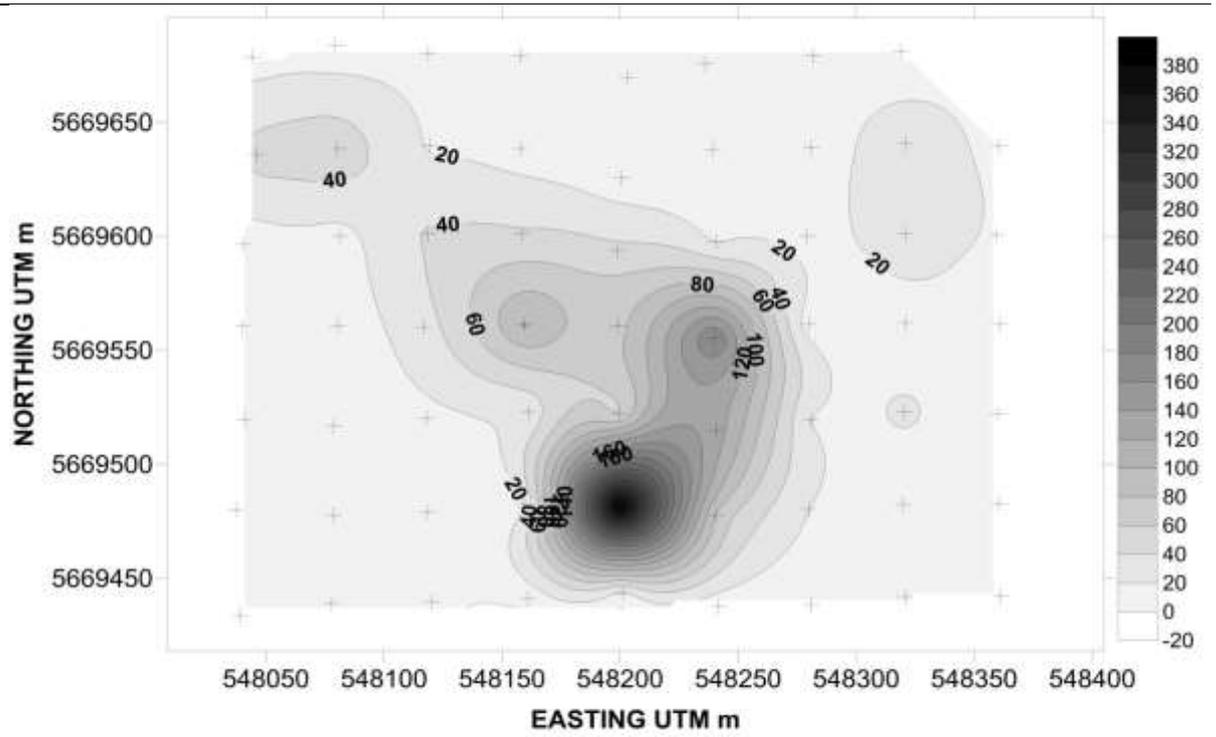
Elements of interest include those which at St. Algar's Farm show strong (>10×) and moderately strong (5-10×) 4QM/1QM geochemical contrast. Table 1 shows that Ag (19.0), Pb_{calc} (15.8), Ti (13.2), Au (12.4), Nb (10.2) and Co (10.2) show strong enrichment whilst Sb (8.4), Tl (6.8), Zn (6.5) and Sn (5.8) are moderately enriched. The enrichment of Pb_{calc}, Ag and Au is indicative of the Roman lead smelting operations at this site.

Table 1. Statistical summary for St. Algar's Farm MMI samples. Elemental concentrations are in ppb ($\mu\text{g}/\text{kg}$).

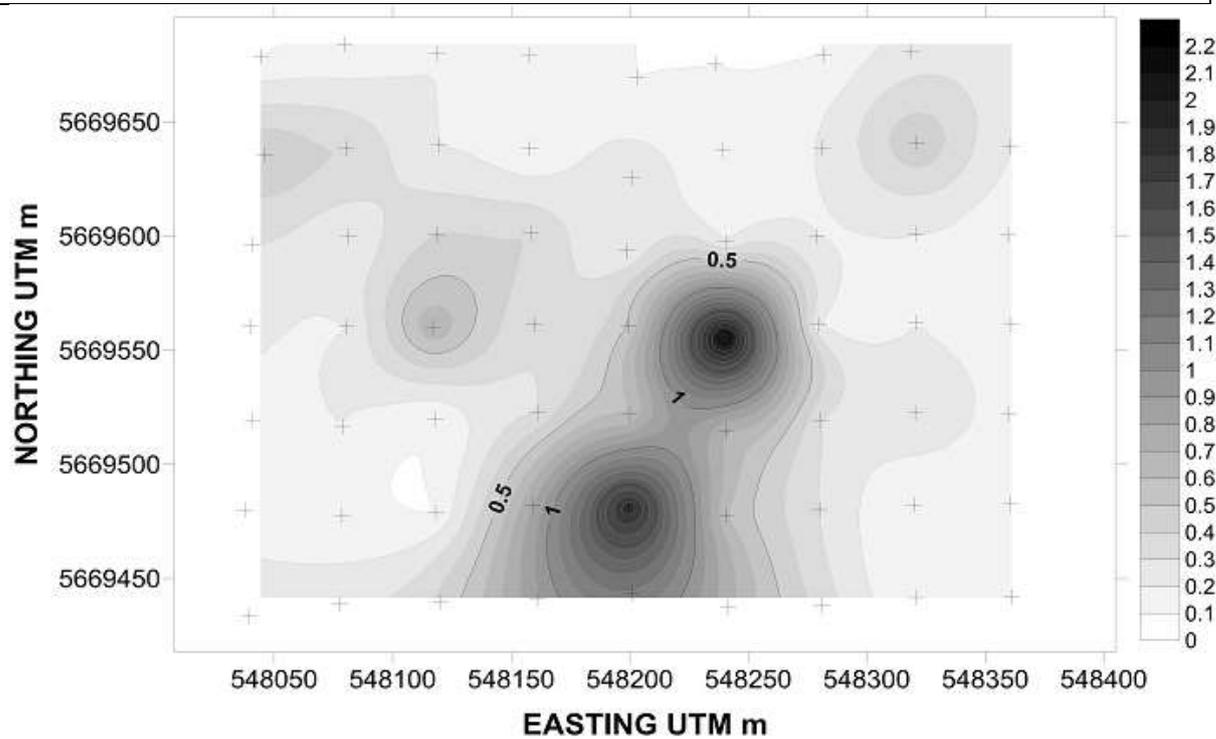
Element	Max.	Median	Mx/IQM	Mean	Std Devn.	4QMean	4Q S.D.	1QMean	1Q S.D.	4QM/IQM
Ag	398	10	83.79	29.9	57.53	90	88.81	4.75	1.26	18.95
As	20	5	2.00	16.67	5.15	10	0	10	0	1.00
Au	2.2	0.2	44.00	0.35	0.38	0.62	0.78	0.05	0	12.40
Ba	3470	920	5.01	1090	506.38	1781	534.15	693	57.96	2.57
Ca	1190000	725000	2.01	732060	125.65	894330	99.04	590938	64.62	1.51
Cd	65	38	2.95	38.4	13	54.6	4.7	22	5.14	2.48
Ce	907	315	5.93	351	188.04	595.19	140.42	153	50.26	3.89
Co	439	38	27.44	66.6	78.06	163.5	100.99	16	4.43	10.22
Cu	2770	690	6.71	901	557.22	1584.38	502.16	413	87.29	3.84
Fe	202000	39000	8.57	46490	30.8	82690	39.83	23560	6.29	3.51
Nb	6.4	0.7	25.60	1.36	1.34	2.56	1.83	0.25	0	10.24
Ni	2420	1070	3.46	1150	423.38	1772.86	348.38	700	261.25	2.53
P	1300	600	2.83	0.65	0.22	960	0.17	460	0.05	2.09
Pb	20000	20000	3.43	15878	6229.62	20000	2862.63	5829	0	3.43
Pb _{calc}	117157	43622	19.48	47515	35765.1	95112.3	2862.63	6013	0	15.82
Sb	12	2	12.77	3.27	2.51	7.9	1.87	0.94	0.17	8.40
Sn	17	0.5	34.00	1.1	2.18	2.88	3.77	0.5	0	5.76
Ti	1100	66	43.24	127.11	196.27	336.13	295.87	25.44	4.97	13.21
Tl	9.4	3.5	8.32	4.12	2.59	7.63	0.83495	1.13	0.347	6.75
Zn	2910	590	14.55	675.87	483.64	1305	495.97	200	71.24	6.53

3.2 Single element spatial distributions

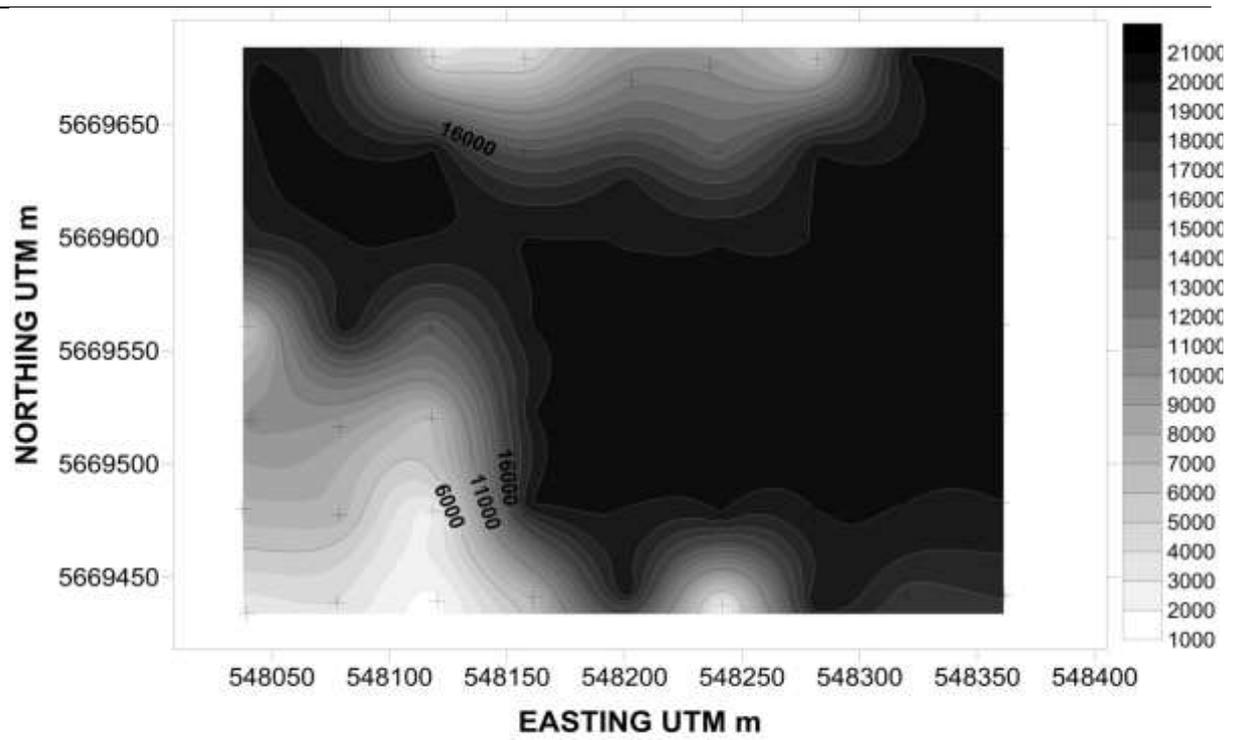
To examine the patterns of areal distribution of the elements of interest and to visualise the correspondence between elemental concentrations and archaeological features, the raw data for each element were plotted initially as Classed Post Maps (CPM) and then as contours of concentrations with an overlay of sampling locations as shown for Ag, Au, Pb, Sn and Tl in Figure 3. Contouring was chosen as the means of data presentation because it provides a clearer picture of elemental distribution. The interpolated contours conform to the known and interpreted archaeology and were generated using the kriged CPM data in Surfer[®] 12 software.



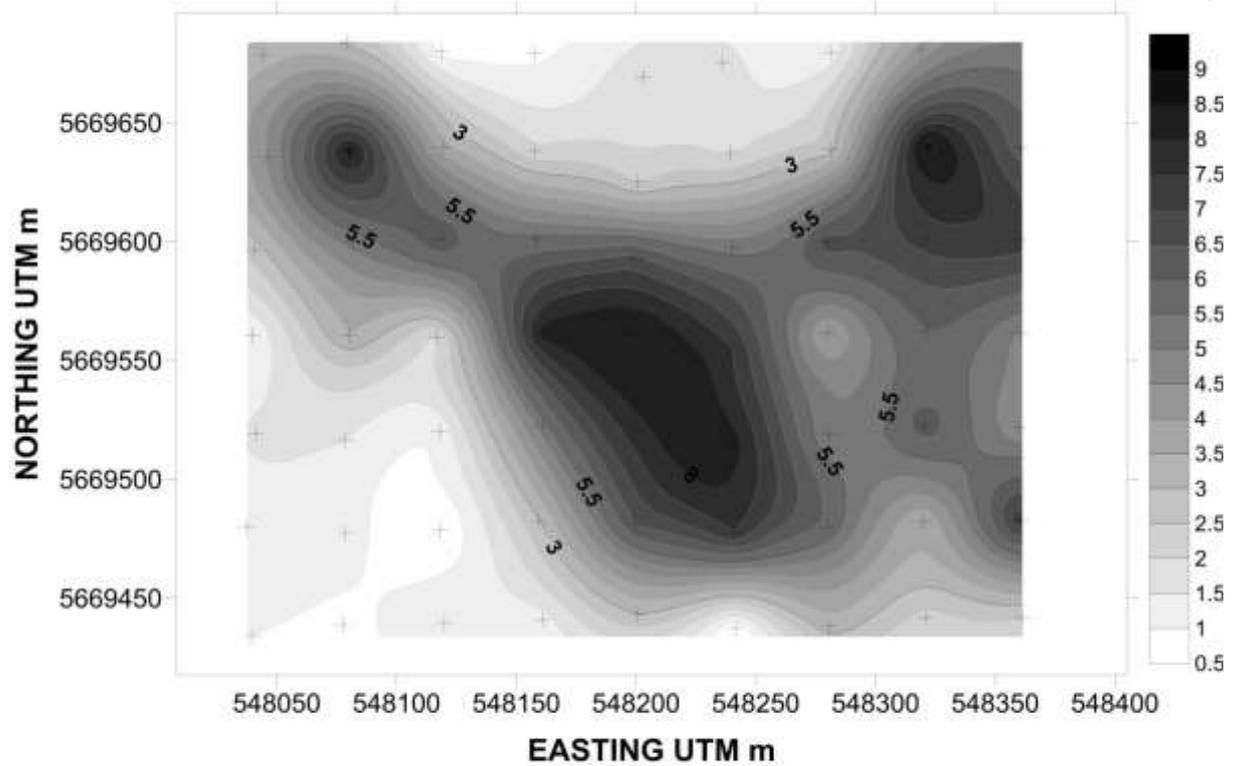
a) Silver



b) Gold



c) Lead



d) Thallium

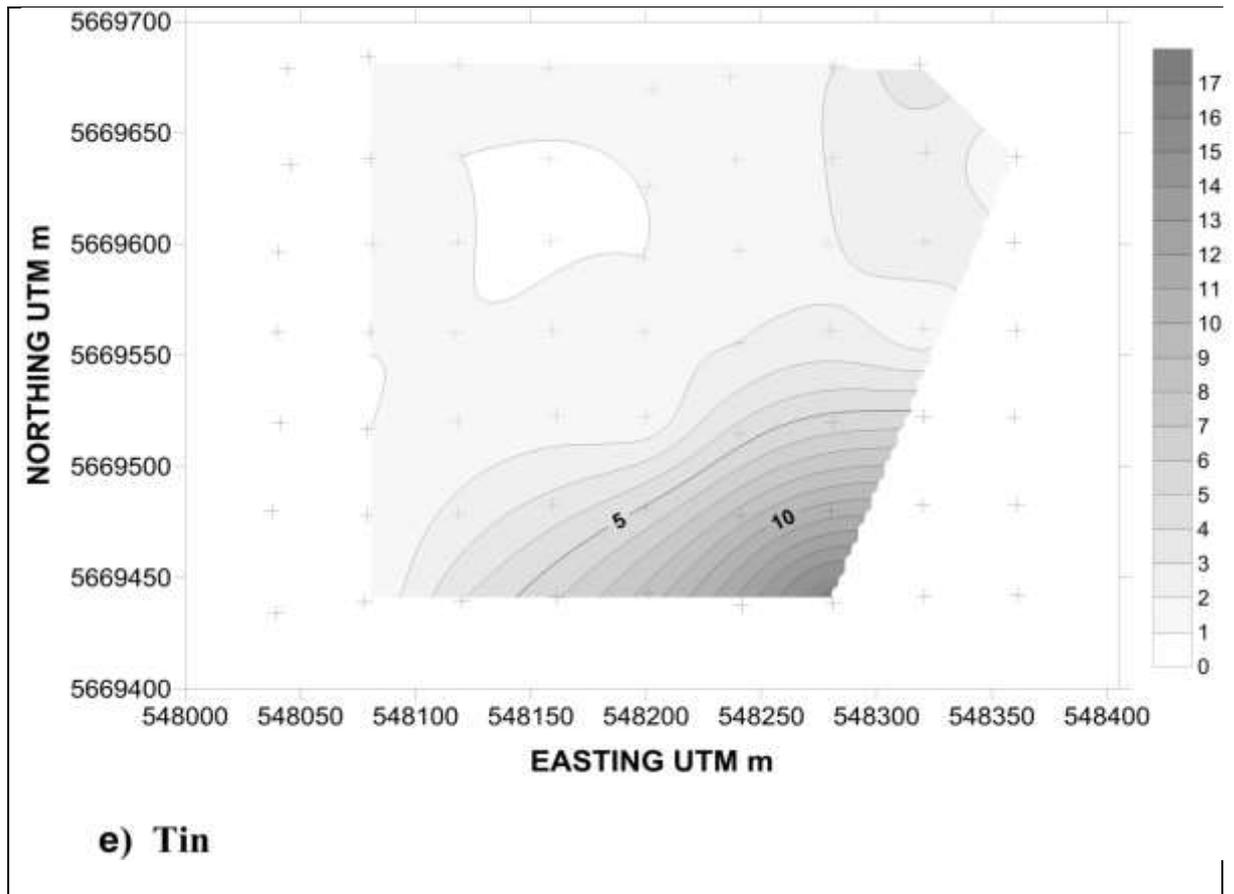


Figure 3. Contour maps for concentrations (ppb) of (a) silver, (b) gold, (c) lead, (d) thallium and e) tin in MMI extracts of soils at St Algar's Farm, Somerset. Actual sample locations are shown by + symbols. The UTM grid references are Zone 30U.

The single element diagrams (Figure 3) show that in the case of Pb and Tl large areas of anomalism exist at St Algar's Farm. For Ag and Au the zone of anomalous soils is much smaller but covers the area of Roman lead processing defined by gradiometric magnetometry (Lambdin 2011) and excavation (Lambdin and Holley 2011, Lambdin and Holley 2012). Tin is most anomalous south-east of the lead processing area but elevated concentrations extend into that area.

3.3 Correlations between elements

A summary of the correlation analyses is shown in Table 2. It includes the correlations for the 25 elements which provide the most useful information. Strong relationships (Pearson correlation coefficients > 0.8) exist between Pb and Tl, Ti and P, Fe and Zr, Zr and La and between all rare earth elements. Moderately strong (Pearson correlation coefficients $> 0.7 < 0.8$) correlations were found between Pb and Sb, Tl and Sb, Tl and Ag, Ag and Au, Ag and Cu, Nb and Fe, Ti and Nb, Fe and P, Mn and Co. These correlations and a number of those which are interesting geochemically are indicative of two elemental suites of potential anthropogenic importance. The first is a Noble and Base Metal (BNM) suite comprised of the elements Pb, Tl, Ba, Ag, Au, Cu, Sb which is most likely indicative of the lead ore and possibly other material processed on site. The second is a suite comprised of the elements Fe, Ti, Nb, Mn, Co, Cu, P, Li, Rb, Sc, Cs, K, Ga, P, Zr, Th and Sn (PEG) which may be indicative of pegmatite lithology (London and Kontak 2012) and could be reflective of the treatment of Sn bearing pegmatite on this site.

Table 2. St. Algar's Farm MMI Pearson correlation coefficients (r) for Elements of Interest

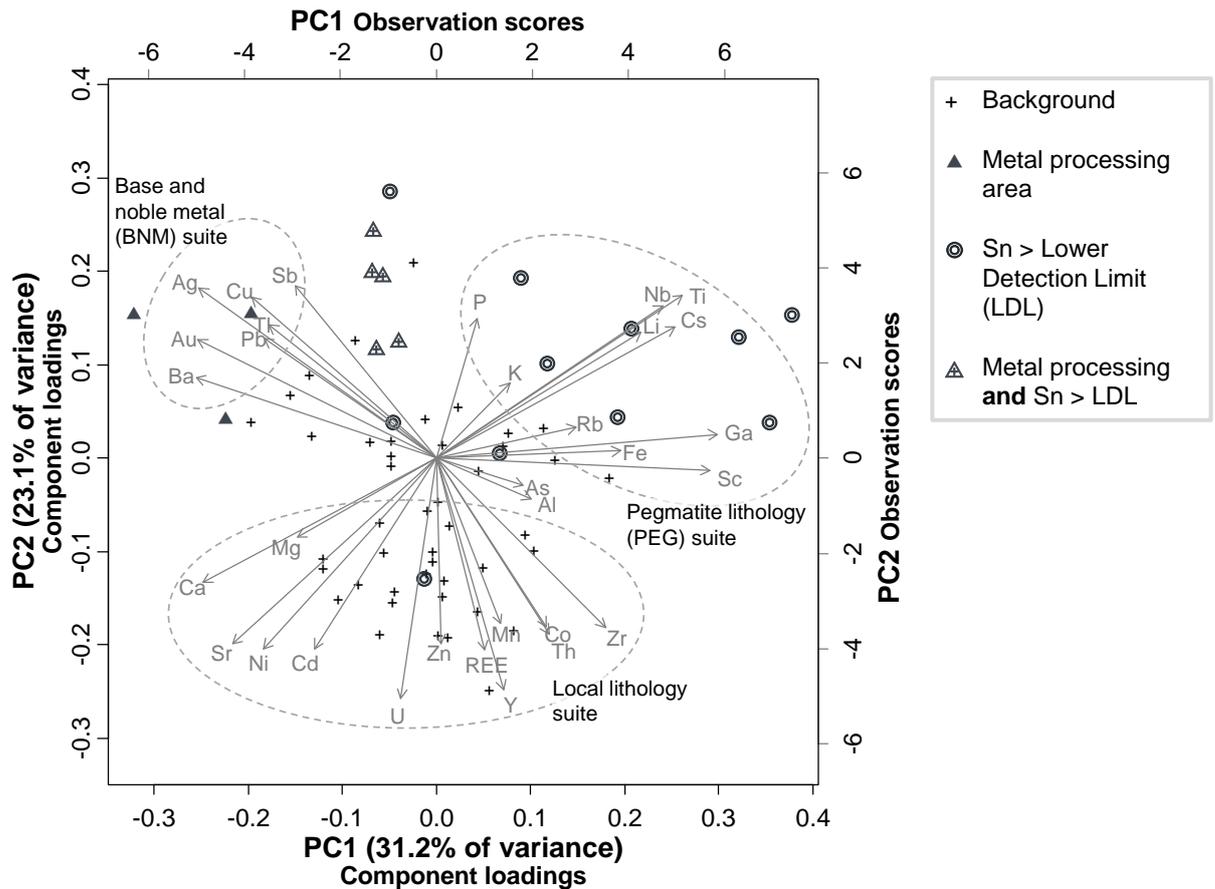


Figure 4. Biplot for principal components analysis (PCA) of MMI compositional data for soil samples from St Algar's Farm, Somerset, UK.

Figure 4 shows a number of interesting features. Observation scores for soil sampled from the known metal processing areas (▲,▲) coincide with the component loadings for the BNM element suite. Similarly, observation scores for soil samples having MMI Sn concentrations > LDL (⊙) coincide with the component loadings for the PEG suite. Local lithology (+) is characterised in PC1-PC2 space by an association of REE (including Y), refractory elements (Th, Zr), elements which can be associated with carbonates (Ca, Mg, Sr, Cd, U, Zn) and elements commonly co-occurring with Mn (Mn, Co, Ni). The presence of Ca, Mg and Sr in the local lithology suite and relatively high Ca values (Table 2) confirm the underlying bedrock has a high component of limestone. The elements Pb, Ba, Tl, Cu, Ag and Au also

show a high degree of similarity and are marked as the Base and Noble Metal (BNM) suite in the NW quadrant. A number of elements: Li, K, Cs, Rb, with large ionic radius, or Ga, Sc, Ti, and Nb (and to a lesser extent Fe and P) having high field strength (charge/radius ratio) are associated in the NE quadrant and correspond to the Pegmatite suite deduced by correlation analysis; the PEG group also includes Mn, Co, Cu, Sn, Th and Zr. These elements are often associated with pegmatite lithology; ilmenite which contains Fe and Ti is also commonly found in high concentrations in pegmatite. The observations from metal processing areas and having Sn >LDL fall between element groupings corresponding to the BNM and pegmatite lithology suites. This is consistent with our interpretations, since some of the (now weathered to soil) ore material is suspected to be pegmatitic, with subsequent extraction and processing of metals in the BNM suite.

3.5 Spatial distribution of element indices

Whilst individual elements in a suite can be used to define an area of particular interest, examination of an elemental group (a composite index) can commonly provide better detail and definition of the phenomenon giving rise to the anomalous suite (Smith, Campbell et al. 1984, Mann, de Caritat et al. 2012). Our analysis of the St. Algar's Farm MMI data – correlation analysis, PCA and multi-element plots – leads logically to the use of such indices. The index points can be plotted and contoured to produce an Index plot. This has been done for two suites, BNM and PEG for the area sampled at St. Algar's Farm (Figure 5).

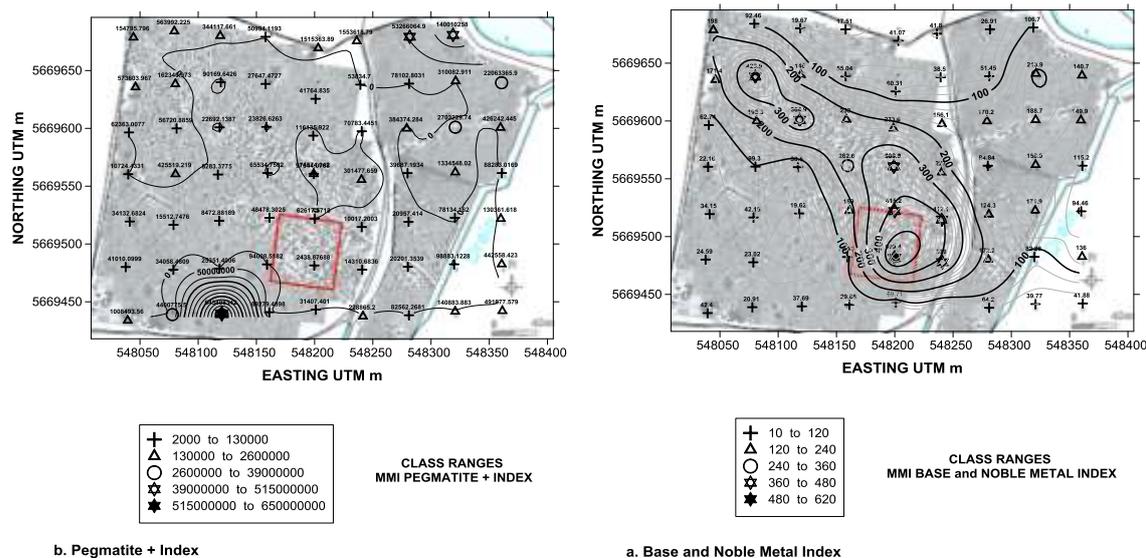


Figure 5. Plots (a) base and noble metal index (BNM) (b) pegmatite + index (PEG) at St Algar's Farm. The scheduled area which consists of the winged villa, cupellation zone and burnt area is shown as a square, whilst Building 1 lies to the north of it in the centre of the sampled area. The locations of these archaeological features are shown in Figure 2. Contours are superimposed on a grey magnetic gradiometry base.

The Noble and Base Metal suite have been compiled into the Base and Noble Metal Index (BNM) (Figure 5(a)). It is a simple additive index constructed by taking the normalized-to-the mean values for the elements Ba, Ag, Au, Cu, Pb_{calc}, Sn and Tl. Index units are ppb. The contoured CPM values of the BNM index are shown superimposed on the gradiometric magnetic base image (Lambdin, 2011) to show the relationship with the interpreted archaeology in Figure 5a. The BNM index defines two quite distinct zones. The area between the 100 and 300 ppb contours includes the settlement area and areas of known human activity. The 300 ppb contour encloses the known major areas of metal processing. The evidence suggests that roasting/smelting of primary ore was carried out in and around Building 1, whilst silver

cupellation of the smelted lead was undertaken in the winged villa area. The BNM Index is a very valuable tool for defining the distribution of previous human activity on the site.

The PEG + index is a multiplicative index constructed by multiplication of the normalized-to-the-mean values for the elements Nb, Zr, Rb, Th and Cs. The PEG + index (Figure 5b) highlights not only a sample (SAF15) at the south-western edge of the sampled area, but several samples on the eastern side, adjacent to the stream which drains the St Algar's site. The PEG + index plot is very different from that of the BNMI plot and may be indicative of the presence of pegmatite or Sn processing in the southern part of the area in the vicinity of sample SAF15.

3.6 The source of the lead processed at St. Algar's Farm

The Charterhouse lead mines, located about 40 km west northwest of St. Algar's Farm (see Figure 1) have been considered (Dunster and Dungworth 2012, Dungworth, Comeau et al. 2013) a possible source of the lead which was processed at the site. To investigate this possibility, five soil samples were collected from around the Charterhouse Lead mine and subjected to multi-element MMI analysis. The results were compared with those obtained from the St. Algar's site using the Degree of Geochemical Similarity (DOGS) statistical method described in (Mann, de Caritat et al. 2016). The log transformed mean elemental concentration for each element of the Charterhouse soils was used as the comparator against which all of the log transformed St. Algar's Farm samples were evaluated. The DOGS Correlation Coefficients reveal a pattern very similar to that shown by the plot of the Base and Noble Metal Index for the St. Algar's Farm MMI samples and is strongly indicative that the ore materials processed at St Algar's Farm were sourced from the Charterhouse lead mines. Correlation coefficient values range from 0.798 in the area of geochemical background to 0.898 near the northwest trackway, along which it is believed the ore was transported to the metal processing site. Values of greater than 0.880 were obtained for samples (13) from

northwest trackway area, the metal processing area and areas adjacent to it. A contoured plot of the DOGS Correlation Coefficient values is shown in Figure 6. This plot shows a strong similarity to that of the BNMI plot in Figure 5a. It is noteworthy that some of the samples with the highest values are those which are enriched in Ba, a trace element present as the accessory mineral barite in the Charterhouse ore and not commonly present in this type of Pb deposit in the U.K.

The very strong multi-element correlation between the St. Algar's Farm soils (especially those in the area associated with the transport and processing of the lead ore) and those from Charterhouse provide strong support for the hypothesis that the Charterhouse lead mines were the source of the lead processed at St. Algar's Farm.

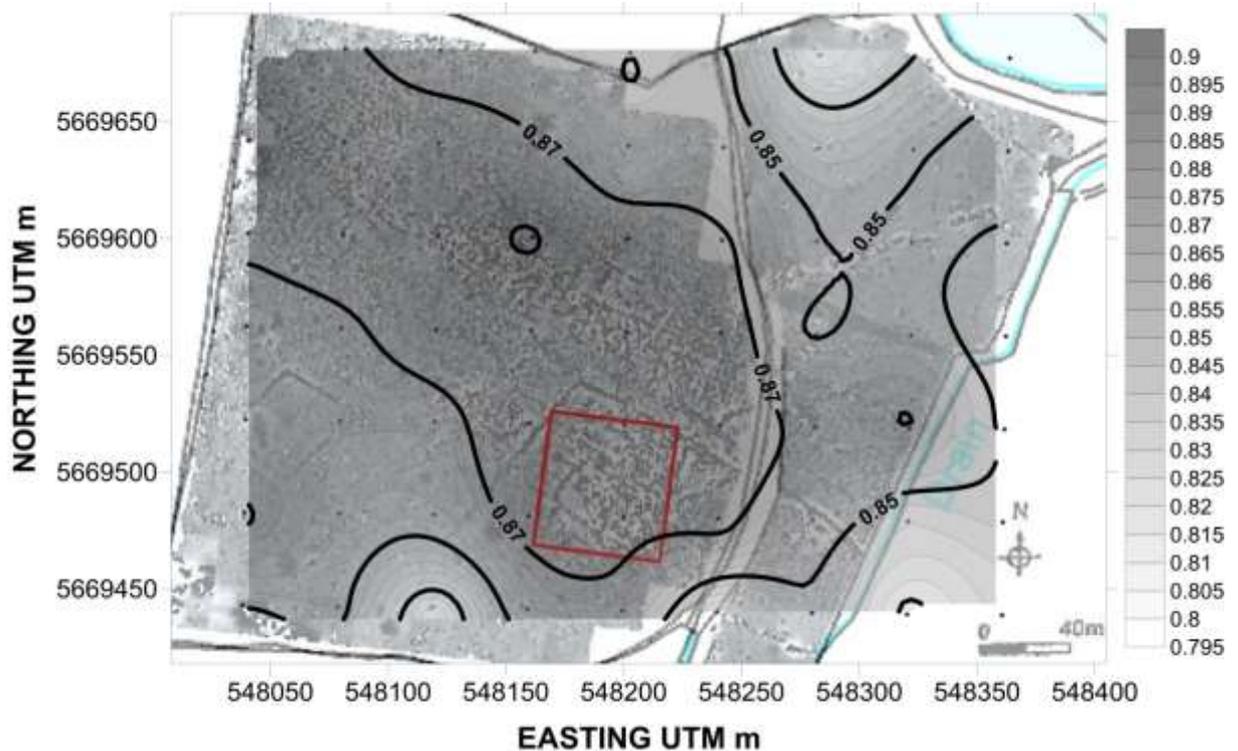


Figure 6. Contoured plot of DOGS Correlation Coefficients for log transformed St. Algar's Farm MMI multi-element soil data compared to the log transformed multi-element means for the Charter house soil.

3.7 Possible Sources for Tin at St Algar's Farm

The closest possible source of Sn ore available in the Roman period would have been from Dartmoor in Devon, a distance of about 130 km to the southwest, where tin was mined by the Romans at Erme Valley (Thorneycroft, Pirrie et al. 2004) which is located to the south of Dartmoor. It is also known that tin from Cornwall was used in the manufacture of Roman pewter as remnants of pewter moulds have been found at the tin mining site of Leswyn St. Just (Henig 2002).

In order to establish a possible provenance for the Sn observed in e.g. sample SAF15 (and four others with similar multi-element profiles, as indicated by DOGS r correlation coefficient values of > 0.95) at St Algar's Farm, a small number of additional MMI samples were taken at likely sites for Sn in Devon and Cornwall. Table 3 contains their locations, and in addition the DOGS correlation factor r (Mann et al, 2016) for these samples versus the SAF15 sample.

Table 3. DOGS r values for MMI samples from Devon & Cornwall versus sample SAF15.

SAMPLE	LOCATION	COUNTY	DOGS r VALUE
SAF15	St Algar's Farm	Somerset	1
GEMAS #3449	Penzance	Cornwall	0.784
DC04	R. Erme Dartmoor	Devon	0.784
DC05	R. Plym Dartmoor	Devon	0.820
DC06	Merrivale Dartmoor	Devon	0.241
DC07	Dartmeet	Devon	0.600
DC08	R. Dart Dartmoor	Devon	0.726
BO09	St Neot R. Bodmin	Cornwall	0.629
CO10	R.Fal Grampound	Cornwall	0.427
CO11	Wheal Jane Truro	Cornwall	0.378

Sample DC05 from the banks of the River Plym, immediately south of Dartmoor has the highest correlation with SAF15 ($r=0.820$), but samples DC04 from the banks of the River Erme, and the GEMAS sample #3449 from a field near Penzance in Cornwall also have high correlation (r values = 0.784). All of the samples in Table 3 had significant concentrations of MMI Sn (the highest Sn=160ppb being in the River Plym DC05 sample), and other elements diagnostic of pegmatites or s-type granites, e.g. Cs, Nb, Ti. These elements are included in the pegmatite index, and of course in the calculation of DOGS r values.

3.8 Comparison of St. Algar's Farm soil MMI and strong-acid digest results

To evaluate the comparative efficiency of MMI extraction with strong-acid digestion, ten of the MMI samples, selected to represent the range of geochemical environments (background to anomalous) were also subjected to strong-acid digestion (SAD) with concentrated aqua regia. Comparison of SAD results with the MMI results has been undertaken for a range of elements to evaluate the relative effectiveness of MMI to provide meaningful results in the documentation of the archaeological features of this site. The geochemical contrast was determined for a range of elements of interest for each technique. The contrast chosen was maximum/minimum rather than 4QM/1QM because only 10 samples were analysed by both techniques and quartile statistics were considered not to be meaningful. Comparative figures are shown in Table 4.

For all 13 elements the MMI extraction provided a greater geochemical contrast than did the strong-acid digestion, a direct consequence of the lower background concentrations achieved by MMI because it does not significantly dissolve soil matrix materials.

Table 4. Mean Geochemical contrast (maximum/minimum) for selected elements for MMI and SAD analyses from 10 selected soil samples from St. Algar's Farm.

ELEMENT	MMI CONTRAST	SAD CONTRAST	MMI/SAD CONTRAST
Ag	15.6	14.18	1.1
Zn	2.56	1.63	1.6
Cu	6.85	3.42	2.0
Ba	2.26	1.6	1.4
Tl	1.6	1.14	1.4
Sn	51.25	30.94	1.7
Sb	173	57.67	3.0
Ce	1.43	1.08	1.3
Th	1.43	1.07	1.3
Zr	1.29	1.03	1.3
Cs	2.05	1.02	2.0
Rb	2.15	1.13	1.9
Nb	1.64	1.1	1.5
Li	1.88	1	1.9

4.0 DISCUSSION

4.1 Geochemical context of St. Algar's Farm

To place background concentrations from St. Algar's Farm into a more regional context, the background values (1QM) were compared with the MMI 1QM values obtained from agricultural soil samples taken in south-east England as part of the Geochemical Mapping of Agricultural Soils (GEMAS) regional soil sampling programme (Reimann, Birke et al. 2014,

Reimann, Birke et al. 2014). Fifty four samples taken approximately 50 km apart comprise the GEMAS south-east England database used for this comparison.

The St. Algar's Farm 1QM values for elements of interest are shown in comparison with the GEMAS 1QM values in Table 5.

Table 5. Comparison of MMI SAF and MMI GEMAS 1QM values. Elemental values are in ppb. Student T-tests conducted on the 1QM values from both the SAF and GEMAS elemental suites demonstrated in all cases that the differences were significant at the 99.9% level.

	St. Algar's (SAF)	GEMAS S.E. England	SAF/GEMAS
Element	1QMean	1Q Mean	1QM/1QM
Ag	4.75	2.64	1.80
As	10	8.23	1.22
Au	0.05	0.5	0.10
Ba	693	237	2.92
Ca	590938	552140	1.07
Ce	153	12	12.75
Cu	413	750	0.55
Fe	23560	16000	1.47
Nb	0.25	0.25	1.00
P	460	1729	0.27
Pb	5829	150	38.86
Sb	0.94	2.59	0.36
Sn	0.5	0.26	1.92
Ti	25.44	12	2.12
Tl	1.13	0.25	4.52
Zn	200	461	0.43

Comparison of the 1QM MMI data for St Algar's farm and GEMAS shows that a large number of elements at SAF are anomalous compared to GEMAS SE England, even at background concentrations. Pb (38.9×) and Ce (12.8×) are strongly enriched at St. Algar's Farm; Tl (4.52×) is moderately enriched whilst Au (0.1×), P (0.27×), Sb (0.36×) and Zn

(0.43×) are depleted. It is probable that the relative enrichment of Pb and Tl represented by the 1QM is indicative of the widespread background pollution to soils on the St. Algar's Farm site from the Roman lead processing activities. That pollution probably resulted from the roasting and smelting of Pb ore, which produced considerable lead vapours and litharge (PbO), much of which was dumped or stored at various places, in or adjacent to the metal processing areas on the site (Dunster and Dungworth 2012). The fact that the 1QM concentrations of other elements associated with the Pb processing (Au, Ag, Cu, Sb and to a lesser extent Ba), are not very different from the GEMAS concentrations is indicative that these metals were not widespread across the site (thereby creating an elevated SAF 1QM had they been so), but are substantially contained within the metal processing areas and associated areas on human activity.

4.2 The effectiveness of MMI in defining multi-element anthropogenic soil geochemical anomalies.

The distribution plot of the Base and Noble Metal suite elements (Figure 2) clearly delineates an area of anomalously high elemental concentrations over the areas in which excavation has confirmed that lead processing was carried out and in the broader zone of human settlement (Lambdin and Holley 2011, Lambdin and Holley 2012). The wide range of elements, combined with the ability to detect anomalies at low concentrations and the high geochemical contrast for many elements demonstrates that MMI clearly defines the lead processing areas. The BNM Index plot graphically augments the distribution plots and provides greater definition of the elements which characterize the processing and also the spatial limits of those areas. The results also indicate that precious metals may have been extracted in areas other than just the predominant Pb processing site.

There is evidence from both the pegmatite (PEG) elemental suite and the comparison with s-type granite samples from Devon and Cornwall (Table 3) that processing of tin-bearing pegmatite has taken place on the St Algar's site. Tin, which has been found at concentrations (from strong-acid digest) of up to 164 ppm at St Algar's Farm (G. Sylvester unpublished data), is anomalous in the MMI analyses on this site in several samples (including the type samples of the two defined elemental suites) and its presence at these concentrations is unexpected, as the underlying geology precludes it being of *in situ* origin. It is almost certain that the tin used in the pewter manufacture at nearby (25km) Camerton was Cornish. Pewter from Camerton and other local sites in Somerset (e.g. Lansdown, 5 km north of Bath) was used extensively in Bath (about 25km away) for the production of vessels and Bath Curse Tablets (Flint 1999) and it is possible that the tin found at St. Algar's Farm was used to produce pewter, as fragments of pewter were recovered during field walking during the 1970's (Lambdin and Holley 2011).

The MMI multielement concentration plots for the metal processing area and pegmatite lithology samples have shown that each group displays enrichment in a characteristic elemental suite. However, there are some elements which are found to be present in elevated concentration in both the metal processing and pegmatite lithology groups. These elements include Sn, as noted above, Nb, Ti, and to a lesser extent Cs, Ga, Li and Tl. The overlap of these elements between groups may mean that there was also an overlap of Pb and Sn processing activities on the site (as indicated by the overlapping distribution of Sn between the BNM and PG elemental suites in Figure 4). It could also be showing that pollution from these individual activities was widespread on the site as has been stated for the Pb processing by Dunster and Dungworth (2012).

One of the results of this work has been the delineation of MMI geochemical anomalies which are located in areas that appear to be underlain by potentially interesting archaeology and

which have not, as yet, been investigated. These targets include a very strong multielement anomaly of (Pb, Au, Ag, Pb, Tl, Sb, Cu, Ba, Nb, Sn) over what appears, from the magnetic gradiometry, to be a building (Building 1), located about 100 m north of the winged villa within the metal processing area defined by the MMI geochemistry. There is a similar, but slightly weaker anomaly of the same elements (Area 1) located adjacent to the Building 1 anomaly and a number of spot high anomalies on, or adjacent to, the interpreted north-west trackway in the zone of human settlement. These anomalies all warrant follow up investigation as does the strong multielement anomaly (Nb, Ti, Sn, Fe, Cr, As, Sc, Al, Ga, Rb, K, Li, Zr, Th, P, Cr) presented by sample SAF15, located near the southern margin of the investigated area.

A further indication of the effectiveness of multi-element MMI soil geochemistry was provided by the comparative study of the soils at St. Algar's Farm with those in the vicinity of the Charterhouse lead mine and known tin mining sites in Devon and Cornwall. The results strongly support the contention that the Pb processed at St. Algar's Farm was sourced from the Charterhouse mines, and that Sn bearing material from Devon and/or Cornwall has been incorporated into metallurgical procedures at the St Algar's Farm site.

5.0 CONCLUSIONS

Soil analysis using MMI clearly defines and characterizes multi-elemental suites (Pb, Tl, Au, Ag, Sb, Cu, Ba, Nb, and Sn) which delineate the documented metal processing activities on this site. MMI also outlined new geochemical anomalies (of the same elements) within the area of metal processing and human settlement, which may indicate significant buried archaeological features and which require follow-up investigation. In addition, other elemental suites (Nb, Ti, Sn, Fe, Cr, As, Sc, Al, Ga, Rb, K, Li, Zr, Th, P, Cr) have defined geochemical targets which,

although not located in areas of former human settlement (as defined by the magnetic gradiometry), may be indicative of tin ore processing on the site and require follow-up work.

MMI soil geochemistry has been shown here to be an effective archaeological prospection and documentation tool. Sampling can be readily undertaken by field personnel and the analyses are relatively inexpensive given that high quality data for up to 53 elements can be obtained at low ppb concentration detection limits when linked with ICP-MS. Discrimination against dissolution of the soil matrix by the MMI extraction solution has allowed anthropogenic derived sources of anomalism to be enhanced. These features make MMI an ideal tool for archaeological application as it allows the identification and use of a wider range of elements that may have anthropogenic significance.

It is concluded that MMI soil geochemistry is a valuable tool for locating and defining areas of potential archaeological significance on this site and is made significantly more powerful when integrated with the results of geophysical investigations.

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