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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Scientific editing by Robert Speakman

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 analyzed 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, Ti, 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 that 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. Multielement 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 multielement capacity allows a more detailed archaeological interpretation.

1 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 medieval villages (Arrhenius, 1931). The advent of inductively coupled plasma mass spectrometry (ICP-MS) presented the opportunity to analyze 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. Applications include distinguishing past domestic and agricultural activities (Davidson, Dercon, Stewart, & Watson, 2006), archaeological prospection (Aston, Martin, & Jackson, 1998; Bintliff, Davies, Gaffney, Snodgrass, & Waters, 1992; Entwistle, Abrahams, & Dodgshon, 2000; Schlezing & Howes, 2000), interpretation of space use (Cook et al., 2010; Cook, Clarke, & Fulford, 2005; Cook, Kovacevich, Beach, & Bishop, 2006), locating middens (Beck, 2007), inhumations and differentiated burial sites (Bethell & Carver, 1987; Sampietro & Vattuone, 2005), and identifying metal accumulation derived locally from ancient mining or mineral processing operations (Dunster & Dungworth, 2012; Dunster, Dungworth, & Lowerre, 2012; Grattan, Gilbertson, & Kent, 2013; Maskall, Whitehead, Gee, & Thornton, 1996; Maskall, Whitehead, & Thornton, 1995; Mighall, Grattan, Lees, Timberlake, & Forsyth, 2002).

The formation of anthropogenic geochemical anomalies in soils is complex. Oonk, Slomp, and Huisman (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 depend 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 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 nonacid digest (Mann, 2010; Stanley & Noble, 2008). 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 nonacid 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 favor 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 deposits in Ireland. Here, it was found that weak nonacid 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 (SAD) does, and which increase background (and thereby its detectability) by lowering the peak/noise ratio.

The MMI technique is based on a neutral alkaline solution containing both organic and inorganic ligands (Mann, 2010). The ligands provide complexing ability, while 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 X-ray fluorescence spectrometry (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, Demetriades, Filizmoser, & O’Connor, 2014a,b) analyzed agricultural soils from a widely spaced sampling grid by XRF and ICP-MS after both SAD 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, & de Caritat, 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 SAD investigations were included to determine whether the elemental species targeted by MMI provide more sensitive detection of archaeological anomalies than total analyses.

## 2 | MATERIALS AND METHODS

### 2.1 | Site description and sampling

An MMI geochemical soil sampling program was undertaken on and around the area of the Scheduled Monument centered 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 (Fig. 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 plowing 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 toward an irrigation channel that 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 that drain into the local stream network (Cranfield University, 2015).

Archaeological investigation of the site (excavated trenches based upon geophysical results) recovered evidence of three periods of Romano-British occupation (Lambdin, 2011; Lambdin & Holley, 2011b, 2012a, 2012b). These are (1) an early villa with internal room divisions and set within a square ditched area of first to second century CE age, (2) a winged corridor villa of likely second to third century age, and (3) a fourth 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 that has been interpreted as a yard (Lambdin & Holley, 2011b, 2012a,b). Recovered artifacts
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 fourth 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 portable XRF surface readings may be indicative of cupellation sites (Dungworth, Comeau, & Lowerre, 2013). While 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 \(^{14}C\) date of CE 131–155 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.

The St. Algar’s soils sampled were gray in color, appeared uniform in grain size and texture, and showed little visual variation. The site had been plowed 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 gray 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 (Fig. 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 cm² 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 spade to prevent sample contamination with metals. The sampling was thus designed to capture soil from the 10- to 25-cm 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 MMI 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 & Itard, 2003). The resultant leachate is allowed to settle and is sampled after 24 hours. A subsample of the clear leachate is withdrawn and presented to an 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 analyzed 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, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, U, W, Y, Yb, Zn, and Zr. Quality control and assessment (Caritat & 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 × LDL (Reimann, Filzmoser, Garrett, & Dutter, 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 that would normally be removed from the database (Reimann, Filzmoser, & Garrett, 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 analyses

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-transformed prior to correlation and analyses. Numerous lead (Pb) values were above the upper detection limit (UDL; 20,000 ppb); however, based on the strong linear relationship between Pb and thallium (Tl) and because Tl commonly displays geochemical behavior similar to Pb (geochemical coherency), Pb values ≥20,000 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 ($\text{Pb}_{\text{calc}}$) were used to overcome the distortion caused by the large number of samples containing Pb at levels > UDL.

Principal components analysis (PCA) was performed in R using correlation matrix of scaled, centered log ratio 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 centered log ratio transformation removes any dependencies between variables due to compositional closure (Reimann 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 & 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 intersample distance, as recommended by Reimann et al. (2008).

3 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 I. 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 fourth quartile (4QM) to the mean of the first quartile (1QM).

Elements of interest include those which at St. Algar’s Farm show strong (>10x) and moderately strong (5–10x) 4QM/1QM geochemical contrast. Table I shows that Ag (19.0), Pb_{calc} (15.8), Ti (13.2), Au
TABLE I  Statistical summary for St. Algar’s Farm MMI samples; elemental values are in ppb

| Element | Max. | Median | Max/1QM | Mean | SD  | 4QMean | 1QMean | 4QM/1QM |
|---------|------|--------|---------|------|-----|--------|--------|---------|
| Ag      | 398  | 10     | 83.8    | 29.9 | 57.5| 90.0   | 4.8    | 18.9    |
| As      | 20   | 5      | 2.0     | 16.7 | 5.2 | 10.0   | 10.0   | 1.0     |
| Au      | 2.2  | 0.2    | 44.0    | 0.4  | 0.4 | 0.6    | 0.1    | 12.4    |
| Ba      | 3470 | 920    | 5.0     | 1090 | 506 | 1781   | 693    | 2.6     |
| Ca      | 1,190,000 | 725,000 | 2.0   | 732,060 | 126 | 894,330 | 590,938 | 1.5     |
| Cd      | 65   | 38     | 3.0     | 38.4 | 13.0| 55     | 22     | 2.5     |
| Ce      | 907  | 315    | 5.9     | 351  | 188 | 153    | 153    | 3.9     |
| Co      | 439  | 38     | 27.3    | 66.6 | 78.1| 164    | 16.1   | 10.2    |
| Cu      | 2770 | 690    | 6.7     | 901  | 557 | 1584   | 412.5  | 3.8     |
| Fe      | 202,000 | 39,000 | 8.6   | 46,490 | 31  | 82,690 | 23,560 | 3.5     |
| Nb      | 6.4  | 0.7    | 25.6    | 1.4  | 1.3 | 2.6    | 0.3    | 10.2    |
| Ni      | 2420 | 1110   | 3.5     | 1150 | 423 | 1773   | 700    | 2.5     |
| P       | 1.3  | 0.6    | 2.8     | 0.7  | 0.2 | 1.0    | 0.5    | 2.1     |
| Pb      | 20,000 | 20,000 | 3.4    | 15,878 | 6229 | 20,000 | 5829   | 3.4     |
| Pb<sub>calc</sub> | 117,157 | 43,622 | 19.5  | 47,515 | 35,765 | 95,112 | 6013   | 15.8    |
| Sb      | 12   | 2      | 12.8    | 3.3  | 2.5 | 7.9    | 0.9    | 8.4     |
| Sn      | 17   | 0.5    | 34.0    | 1.1  | 2.2 | 2.9    | 0.5    | 5.8     |
| Ti      | 1100 | 16     | 43.2    | 127  | 196 | 336    | 25.4   | 13.2    |
| Tl      | 9.4  | 3.5    | 8.3     | 4.1  | 2.6 | 7.6    | 1.1    | 6.8     |
| Zn      | 2910 | 590    | 14.6    | 676  | 484 | 1305   | 200    | 6.5     |

(12.4), Nb (10.2), and Co (10.2) show strong enrichment, while Sb (8.4), Ti (6.8), Zn (6.5), and Sn (5.8) are moderately enriched. The enrichment of Pb<sub>calc</sub>, Ag, and Au is indicative of the Roman lead smelting operations at this site.

3.2  Single element spatial distributions

To examine the patterns of areal distribution of the elements of interest and to visualize 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<sup>®</sup> 12 software.

The single element diagrams (Fig. 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 & Holley 2011b, 2012b). Tin is most anomalous southeast 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 II. It includes the correlations for the 25 elements that provide the most useful information. Strong relationships (Pearson’s correlation coefficients > 0.8) exist between Pb and Tl, Ti and P, Fe and Zr, Zr and La and between all REEs. Moderately strong (Pearson’s 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, Tl 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 composed of the elements Pb, Tl, Ba, Ag, Au, Cu, and Sb, which is most likely indicative of the lead ore and possibly other material processed on site. The second is a suite composed 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 & Kontak, 2012) and could be reflective of the treatment of Sn-bearing pegmatite on this site.

3.4  Principal component analysis

Principal component analysis (PCA) confirmed the elemental associations deduced from the correlation analysis, and demonstrated a credible relationship between the spatial location of samples and their elemental suites (Fig. 4). While the complete set of principal components explains all of the variance in the multivariate data, the lower order components capture most of this variance and are most useful for discriminating observations. Four components collectively explaining nearly 80% of the multivariate variance were obtained (PC1 32.1%; PC2 23.1%; PC3 14.2%; PC4 8.4%). The PC1–PC2 space provided clear discrimination of element suites and observations, and higher order components did not separate observations adequately.
FIGURE 3  Spatial distributions of MMI Ag, Au, Pb, Sn, and Tl in soil at St. Algar’s Farm, using universal kriging (linear trend in \( \log_{10}(\text{MMI Zn}) \)) with exponential variogram models with fitted nugget implemented in geoR (Ribeiro & Diggle, 2015). Lower right panel shows estimated distribution of kriging variance using the example of Tl, on a \( \log_{10}(\text{MMI Tl}) \) scale. [Color figure can be viewed at wileyonlinelibrary.com]

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 characterized in PC1–PC2 space by an association of REE (including Y), refractory elements (Th, Zr), elements that can be associated with carbonates (Ca, Mg, Sr, Cd, U, Zn), and elements commonly cooccurring with Mn (Mn, Co, Ni). The presence of Ca, Mg, and Sr in the local lithology suite and relatively high Ca values (Table II) confirm the underlying bedrock has a high component of limestone. The elements Pb, Ba, Ti, 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 that 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 pegmatic, with subsequent extraction and processing of metals in the BNM suite.

3.5 | Spatial distribution of element indices

While 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 (Mann, de Caritat, & Prince, 2012; Smith, Campbell, & Litchfield, 1984). 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 (Fig. 5).

The Noble and Base Metal suite have been compiled into the BNM index (Fig. 5a). It is a simple additive index constructed by taking the normalized to the mean values for the elements Ba, Ag, Au, Cu, Pb\text{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, while 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 (Fig. 5b) highlights not only a sample (SAF15) at the southwestern edge of the sampled area, but several samples on the eastern side, adjacent to the stream that drains the St. Algar’s site. The PEG + index plot is very different from that of the BNM 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 Fig. 1) have been considered (Dungworth,
Possible Sources for Tin at St. Algar’s Farm  

The very strong multielement 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.

### 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 (Thordnyckyri Pirrie, & Brown, 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 molds 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, for example, 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 III contains their locations, and in addition the DOGS correlation factor r (Mann et al., 2016) for these samples versus the SAF15 sample.

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 correlations with SAF15.
FIGURE 4  Biplots for principal components analysis (PCA) of MMI compositional data for soil samples from St. Algar’s Farm, Somerset, UK. Plot (a) shows observations and component loadings in PC1-PC2 space; plot (b) shows the equivalent for PC3-PC4 space.

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

FIGURE 6  Contoured plot of DOGS correlation coefficients for log-transformed St. Algar’s Farm MMI multielement soil data compared with the log-transformed multielement means for the Charter house soil.

correlation ($r$ values = 0.784). All of the samples in Table III had significant concentrations of MMI Sn (the highest Sn = 160 ppb being in the River Plym DC05 sample), and other elements diagnostic of pegmatites or s-type granites, for example, Cs, Nb, and 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 SAD, 10 of the MMI samples selected to represent the range of geochemical environments (background to anomalous) were also subjected to 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 analyzed by both techniques and quartile statistics were considered not to be meaningful. Comparative figures are shown in Table IV.
TABLE III  DOGS r values for MMI samples from Devon and 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   | Two Bridges 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 |

TABLE IV  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              |
| Ti      | 1.6          | 1.14         | 1.4              |
| Sn      | 51.25        | 30.94        | 1.7              |
| Sb      | 1.73         | 57.67        | 0.3              |
| 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              |

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

4 | 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 southeast England as part of the Geochemical Mapping of Agricultural Soils (GEMAS) regional soil sampling program (Reimann et al., 2014a, 2014b). Fifty-four samples taken approximately 50 km apart comprise the GEMAS southeast 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 V.

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 vapors 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 & 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 multielement anthropogenic soil geochemical anomalies

The distribution plot of the BNM suite elements (Fig. 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 & Holley, 2011b, 2012). The wide range of elements, combined with the ability to detect anomalies at low concentrations and the high geochemical contrast for many elements demonstrate that MMI clearly defines the lead processing areas. The BNM index plot graphically augments the distribution plots and provides greater definition of the elements that 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 III) 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 (25 km) 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 25 km away) for the production of vessels and Bath Curse Tablets (Flint and Gordon 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 1970s (Lambdin & Holley, 2011b).

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 that 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 Ti. 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 Fig. 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, Ti, 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 (Fig. 2) anomaly and a number of spot high anomalies on, or adjacent to, the interpreted northwest 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 multielement 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 CONCLUSIONS

Soil analysis using MMI clearly defines and characterizes multielemental suites (Pb, Ti, 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 investigations. 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.

## ACKNOWLEDGMENTS

The contribution from SGS minerals in providing analysis results for the soil samples is gratefully acknowledged. The archaeological advice and assistance with the sampling provided by Dr. David Dungworth is also gratefully acknowledged. Statistical advice was supplied courtesy of Martin Firth, University of Western Australia. The authors would also like to thank the anonymous reviewers for their valuable comments and suggestions that have considerably improved this paper.

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How to cite this article: Sylvester GC, Mann AW, Rate AW, Wilson CA. Application of high resolution Mobile Metal Ion (MMI) soil geochemistry to archaeological investigations: An example from a Roman metal working site, Somerset, United Kingdom. Geoarchaeology. 2017;32:563–574. https://doi.org/10.1002/gea.21618