Long Paper

Illuminating the Darkness

Using Geochemical Survey in Archaeological Reconnaissance and Evaluation for Major Infrastructure Developments

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Abstract: High resolution geochemical survey offers professional archaeology a new means to evaluate the presence and/or absence of archaeological deposits. Innovation in XRF technology has allowed the instrumentation to be miniaturised and powered by portable battery systems. This now allows for the *in-situ* analysis of archaeological soils and sediments and the rapid processing of data to better inform mitigations strategies as they happen. The method undertakes the mapping of chemical variability across a site or landscape and the detection and identification of chemical anomalies. Unlike geophysical prospection which tends to quantify a single property (i.e. magnetic flux or electrical resistance), geochemical prospection relies on the detection of up to 34 chemical elements, each of which is largely independent of geophysical properties and with many elements being, in part, the result of an anthropogenic contribution to soils. It is argued that geochemical spatial survey offers an independent method of detecting archaeology and can increase the confidence with which archaeological deposits are identified or areas declared as being devoid of archaeology otherwise known as “blank areas”. While geochemistry can offer a novel and independent means of prospection, it is best deployed in tandem with geophysics and/or other techniques such as field-walking, multispectral imaging, or LiDAR. The uptake of high resolution geochemical survey by the sector will allow archaeologist better target archaeological deposits in response to research priorities.

Keywords: *Prospection—Geochemistry—Infrastructure—Evaluation*

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Introduction

Geophysical prospection, especially using the fluxgate gradiometer, is a long established and respected method employed routinely by archaeologists to aid in the location, delimitation, and characterisation of archaeological sites (Clark, 1996, Gaffney, 2008, Gaffney and Gater, 2003). In contrast to geophysical techniques, *geochemical* prospection is used rarely despite being first used around a century ago (Arrhenius, 1929; 1931) and most likely at a slight earlier date than geophysics

(Hesse, 2000). The reasons for archaeologists failing to embrace geochemistry with the same appetite as that shown towards geophysics are manifold and complex, yet fundamentally there are simple practical reasons why geochemistry remains little used in routine archaeological investigations.

From its outset geophysics has been a field-based activity, with data gathered relatively rapidly (even initially) and processed soon after to provide an 'image' of buried archaeological deposits. In contrast, geochemical prospection is difficult. The technique requires a fieldwork phase where samples are collected, bagged and logged before being returned to a laboratory for drying and preparation by technicians prior to analysis using either instrumentation or originally wet assay or titrations. This has meant that even with the development of sensitive and rapid laboratory based analytical instrumentation, geochemistry has been expensive and slow. This high cost and lengthy preparation and analysis times associated with traditional lab-based soil analysis has meant that, if geochemistry is used at all, then it is only for very limited numbers of samples.

Low sample numbers have meant that the kinds of results that geochemical surveys have produced are often markedly different to geophysical surveys and demand a more in depth understanding of both the chemistry and quantitative results in comparison to geophysical survey where today even a first year undergraduate could be expected to have some degree of literacy with 'reading' a geophysical survey plot. A typical gradiometer survey is today typically undertaken at high resolution (4+readings/meter) often with multiple probe arrays on a cart-based system pulled by a vehicle, meaning that entire landscapes can be covered rapidly and in detail. The final survey plot normally shows these surveys as greyscale images where features such as ditches, pits and hearths can be clearly seen. While specialist geophysicists are notably fluent in the detailed *reading* of such plots, even novice archaeologists can quickly gain some insight into a site by quickly reviewing gradiometer plots without worrying too much about the absolute magnetic flux levels. The continuous ground coverage offered by gradiometry survey means that recognisable features stand out in contrast to areas where no archaeological deposits are thought to exist. Over the decades of its routine usage archaeologists have developed a familiarity with *geophysical anomalies* and now know how certain types of archaeological features manifest geophysically.

Geochemical survey has normally taken samples at a much coarser resolution (cf. Arrhenius, 1929 – at 1km resolution) meaning that rather than discrete features being discernible, areas that show higher levels of human "activity" have been delineated. On a site-based investigation where contexts such as floor surfaces or spreads have been characterised by only a few samples the significance of absolute elemental concentrations are highlighted in contrast to background levels (however background is determined) (Haslam and Tibbett, 2004) to demonstrate the presence of human activity. Put simply, the results of geochemical survey have not been able to be *read* with a similar ease to geophysical survey quite simply because sample numbers, that is resolution, has been vastly lower due to the time and expense of analyses.

This has led to geochemical survey operating to quite different methods and standards than geophysical survey. While geophysical surveys are usually judged to be "successful" based on the clarity with which the archaeology is revealed, geochemical surveys have tended to be judged based on the accuracy and precision of the results and "fitness" of the analytical protocols used and only then by any apparent differences or structured variation shown. This has led to a rather conservative

treatment of geochemical survey as a technique which has in turn stifled innovation and development of a method that should, by rights, be being used alongside geophysics as an independent and complementary survey technique. After all, geophysics and especially gradiometer surveys may well be good at revealing some kinds of archaeology but they do not reveal all archaeology across all geologies and for all periods. This is most clearly showing within the context of UK developer-led archaeology where gradiometer surveys are routinely used, but often fail to identify features earlier than Iron Age/Romano-British (Chadwick, 2009, p. 35).

Developments in portable analytical equipment, particularly HH-pXRF (Frahm and Doonan, 2012), now allow for rapid and affordable *in-situ* analyses making higher resolution geochemical survey a technique that can be used routinely by archaeologists and in new and innovative ways (Figure 1). The increased speed and reduced costs per analysis mean that thousands of analyses can be conducted across a site or landscape allowing for the detailed spatial mapping of chemical variation. The rapidity with which data is returned means that the results of geochemical survey are now available almost instantaneously and can be conveniently used to inform evaluation and excavation strategies in real time. While *in-situ* soil analyses have been deployed in a number of research-based projects (Save et al*., 2*020) the technique has, up to now, made little impact in professional or development-led archaeology (Carver et al., 2021).



Fig. 1. A geochemical analysis being undertaken in the field using a portable XRF instrument (© Fusion JV).

The approach

Geochemical survey involves mapping the chemical variability across a site or landscape at a resolution commensurate with the archaeological features and/or activity areas that are being investigated. Areas of elevated chemical enhancement manifest as 'structured anomalies' against a background of lower level presence or even absence when specific elements are below the limit of detection. The term "structured anomaly" is used to describe a spatially discrete cluster of elevated readings that show a gradual rise and fall across space. The term is used in the interpretation of geochemical survey results as it avoids the distraction of single point high readings (hotspots) which should in some instances be understood as noise.

Geochemical survey is a sensitive technique that can detect subtle variability in soil chemistry brought about by a range of human activities. Anthropogenic enhancement of soils arises when communities undertake a range of activities such as burning, middening, habitation, burial, manuring, food and animal processing, and craft activities. Such activities may enhance the levels of trace elements in the soil sometimes by many orders of magnitude (e. g. copper (Cu) in the case of mining or metal working see Oonk et al., 2009). The total amount of any trace element in the soil will, in the case of an anthropogenically enhanced soil, relate to anthropogenic processes and in addition local geology/lithology (Wilson and Davidson, 2009). Table 1 below sets out some of the most common trace elements used by archaeologists as indicators for potential activities.

Table 1. Origins of key trace elements in geochemical analysis

Origin	Elements	Comments	References
Geology/Lithology	Na, Al, Ti, Sc, Zr, Nb, Cd, Cs, Hg	Na, K-soil mobility	Khan et al., 2013 Wilson and Davidson, 2009
Anthropogenic	P, Mg, Ca, Cu, Zn, Ni, Mn, Sr, Pb, Sn, K, S, Ba	P, Ca-middens, burials, livestock, food processing1. P, Mg-Wood burning2. Cu, Pb, Zn (Main anthropogenic indicators) + Cr, Mg, Mn, Ni, P, Se, Sn, Sr and Zn3 (Cu, Pb, Mn-at elevated levels ~>200ppm craft working i.e. metallurgy4)	Lutz, 1951; Cook and Heizer, 1965; Heidenreich and Navratil, 1973; Bethell and Maté, 1989; Holliday and Gartner, 2007; Ottaway, 1984; Pyatt, 1999; Pyatt et al., 2002, Davies et al., 1988; Wilson and Davidson, 2009, Bintliff and Degryse, 2022
Uncertain	V, Rb, Al, Cl, As	Local geological system dependency	Wilson and Davidson, 2009

Unlike geophysical prospection which tends to quantify a single property at any single location (i.e. magnetic flux or electrical resistance), geochemical prospection relies on the detection of up to 34 chemical elements, each of which is independent of geophysical properties. This means that geochemistry offers a method of prospection that is completely independent of geophysics yet has the potential to detect a number of elements that may be used to indicate a wide-range of human activities. This is not to suggest that the presence or absence of a single element is simply indicative of human activity. Rather, the levels at which an element occurs can indicate the type of activity that once occurred at a location, for instance, copper (Cu) may be enhanced by a range of activities including normal domestic activities, copper craft working and mining/ore preparation. Domestic activities might result in copper (Cu) concentrations up to ~50ppm, craft working i.e. bronze casting

may result in copper (Cu) levels of ~200ppm while mining and ore preparation may result in a soil copper (Cu) level of several thousand ppm. At present, the relationship between trace element signatures in soil and past activities is not fully understood and, with some notable exceptions, inhibits interpretation beyond the simple correlation between “human activity” and the elevation of key indicator elements i.e. P, Cu, Zn, Pb and K and Ca. There remains much potential to better explore the relationships between elemental combinations and past activities and to more fully understand the soil dynamics that both allow such signatures of past practices to endure and manifest as observed by geochemical survey.

One key concern of soil chemists and archaeologists alike has been the issue of sampling when undertaking geochemical survey. While it may appear favourable to undertake analyses on soils cored directly from an archaeological deposit, several studies have highlighted the potential for topsoil analyses to provide a good representation of buried archaeological deposits. Studies undertaken by Dungworth (2014) and Aston et al. (1998) have addressed the relationship between elemental variation and depth on archaeological sites concluding that there are strong correlations between surface and sub-surface analyses. This was something also noted in the works reported here as part of the Blank Area Testing investigations which were initially trialled on known sites (see Figure 2).

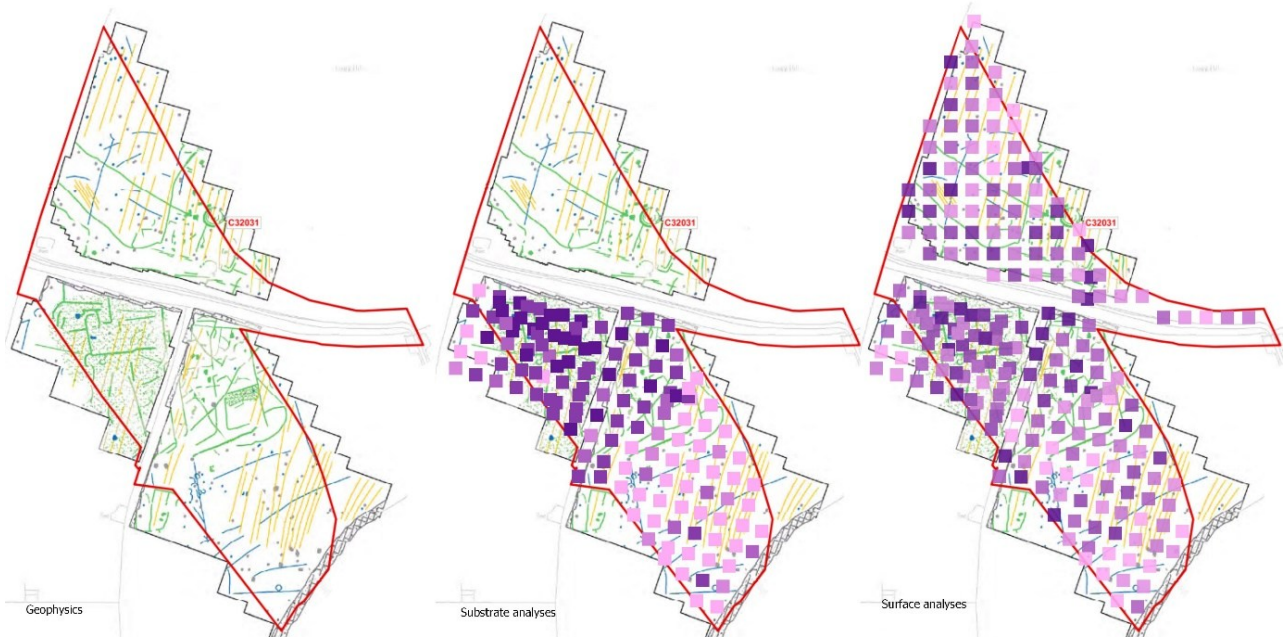


Fig. 2. A geophysics interpretation plot (left) with archaeological anomalies highlighted in green with the results for phosphorous (P) overlain in purple showing the measurements for samples taken from the surface as well as from the top of the substrate. (© Archaeological Research Services Ltd).

The mechanisms by which trace elements and nutrients are held and released from soil are complex. Elements such as potassium (K) and calcium (Ca) are leached away as water moves through soil yet other nutrients are retained by the hummus and clay fractions. Biotic cycling is the process whereby plants take up nutrients from the soil and transport them to be incorporated in vegetation. As seasonal growth diminishes, nutrients are returned to the soil as the plant decays and differentially enhances the soil surface with a range of trace elements (Eash et al., 2008). The surface enhancement produced by biotic cycling allows, in some cases, rapid geochemical survey of the

cleaned soil surface and avoids the need to analyse cored samples. With time-consuming coring not always necessary a greater number of samples can be taken in a set period of time meaning that surveys can be either more extensive or undertaken at higher resolution. It is good practice to assess the validity of surface analyses before embarking on the survey proper by undertaking an initial comparative study of cored and surface samples in the locality (Carver et al., 2021 see Figure 2 above, Dungworth, 2014). As mentioned earlier, it should be noted that not all elements are incorporated in metabolic process with equal affinity and hence biotic cycling may result in differential responses being observed for different indicator elements, for example, lead (Pb) is often found to have lower surface enhancement than other more metabolically active elements such as copper (Cu) or zinc (Zn).

The high sensitivity of pXRF instrumentation and its ability to detect trace elements at very low levels (ppm) means that chemical signatures across a site can be established from non-invasive surface analyses. This now provides the potential, albeit rarely realised, for rapid and cost-effective surveys on developer-led projects where efficient and rapid results are required and where complementary datasets to topographic (LiDAR) and geophysical survey are to be welcomed.

Since geochemical data is not coupled to corresponding geophysical data, geochemistry acts as a complementary yet independent dataset to geophysics, cropmark data or LiDAR data. While geochemical anomalies can enhance the interpretation of geophysical ones, geochemistry can also act as an independent test of “blank areas” as defined by geophysical, aerial and LiDAR surveys. This can be particularly useful in mitigating risk to cost and programme while providing developers and managers with new and independent data about the potential for encountering otherwise undetected archaeological remains during construction works. While geochemistry can offer a novel and independent means of prospection, it is best deployed in tandem with geophysics and/or other techniques such as fieldwalking, multi-spectral imaging or DSMs generated, more recently, from drone-based LiDAR (see Goodchild et al., this volume).

Blank Area Testing

High resolution spatial geochemical survey is still underused in the characterisation of archaeological landscapes and even more so in a commercial archaeological context. Although still limited there are now an increasing number of publications that document the successful deployment of *in-situ* geochemistry in both research and potentially professional/commercial contexts (Derham et al., 2013, Hayes, 2013, Coronel et al., 2014, Frahm et al., 2016, Doonan et al., 2016, Booth et al., 2017, Williams et al., 2020). The results that have been forthcoming from a number of projects are compelling, showing a clear correspondence between certain key elements including phosphorous, zinc (Zn), copper (Cu), lead (Pb) and potassium (K) and the areas of archaeology as identified by geophysics and cropmarks, and similarly low counts where such surveys identified little or no archaeology (see example above Figure 2).

While such studies have concentrated on demonstrating the correlation between the presence of archaeology and geochemistry, especially that visible through geophysics or excavation, few studies have focussed on the application of the technique to verify areas deemed “blank areas” by the absence of archaeology as determined by geophysical survey and/or cropmarks/LiDAR. This is an

application that may not attract much attention within research-driven projects as few archaeologists wish to prospect for the absence of archaeology or nothingness. However, within developer-funded archaeology there is a critical desire to establish and verify the absence of archaeological deposits. Providing certainty regarding the absence of significant deposits may seem, superficially, easy to establish. However, the variable response offered by geophysics across a range of geologies (Schmidt et al., 2016) means that even when geophysics points to the absence of archaeology few planning archaeologists are prepared to accept the results at face value and still stipulate the requirement for evaluation trenching to 'confirm' the absence of archaeology. The use of evaluation trenching may on occasion be a suitable method to establish the presence/absence of archaeology but it has been widely acknowledged that while evaluation trenches may be sufficient to detect Late Iron Age and Roman archaeology, at least within the context of UK archaeology, it is less successful for detecting archaeology from earlier prehistory or indeed from the early medieval period (Hey and Lacey, 2001).

The HS2 rail development is among the largest infrastructure projects currently underway in the world and in terms of mitigating its impact on archaeology is most likely one of the most extensive programmes currently active. While archaeology has largely been managed through a complex landscape modelling programme coupled with the results of aerial survey and geophysical survey, there remains a challenging problem of how to verify "blank areas".

In most instances, areas deemed 'blank' have been subjected to extensive campaigns of test-pitting which has been deployed in an adaptive strategy that effectively begins with a grid and then deploys further test pits in light of any finds that may be indicative of significant archaeological deposits. The difficulty with the use of test pits is that they only offer a small window on sediments and it is notoriously difficult to characterise or identify archaeology within a one metre square pit (Nance and Ball, 1986, CIfA, 2014). It is with these issues in mind that an extensive programme of geochemical survey was designed with the intention of independently verifying 'blank areas' while testing the ability of geochemical survey to identify the presence of "hard to find archaeology"; that is early prehistoric and early medieval archaeology.

An extensive geochemical survey approach to target a test-pit location was tested as part of the HS2 Blank Area Testing programme. Its selection was made because of the apparent success of emerging studies (see above), the willingness of HS2 to embrace innovative methods and ultimately because of the potential of method that could offer rapid, sensitive, non-invasive, and a cost-effective approach to the survey of a wide area. Being introduced and honed in an environment open to innovation and eager to address long-standing archaeological issues relating to testing blank areas and identifying 'hard to find' archaeology was a critical consideration that allowed the method to be developed not least as such environments are rarely encountered in commercial practice while the research community has resistance to addressing such topics.

The potential for portable XRF analysis to provide data that indicates a range of practices including burning (Mg, K, P), burial and disposal of animal remains (Ca, P), craft-working, especially metalworking (Cu, Sn, As, Pb), and a broad range of domestic activities (P, Cu, Zn, Pb) makes it ideal for determining absence or detecting hard to find archaeology especially when used in tandem with magnetic susceptibility survey (Bartlett, 1988). In this way the geochemical approach provided an appropriate method for rapidly and accurately assessing large land parcels in advance of a national

infrastructure development that required a high level of information to inform the mitigation strategy. Another benefit of using this technique was that it minimised impact on the surviving buried archaeology which meant key relationships remained intact until the mitigation phase.

While it is novel deployment of *in-situ* geochemical analysis and the technique is still very much at the testing phase, it has provided the ability to identify geochemical anomalies and to target these with test pit survey, fieldwalking and ultimately targeted strip, map and sample excavation supported by geoarchaeological trenching. The early results of test pitting have shown a varied correlation between geochemical anomalies and Early Prehistoric flint scatters (Upper Palaeolithic and Mesolithic) which are otherwise very hard to prospect for using traditional remote sensing techniques. While the precise conditions that underpin these correlations remain to be fully explored and tested, early results have highlighted the presence of at least four areas associated with Palaeolithic and Mesolithic flint scatters that have otherwise gone undetected. The full implications of this are currently being more fully explored.

As part of the method development, the technique has, in a similar vein to the emerging studies (see above) also shown utility in helping to delimit the extent of buried archaeological remains at known sites (i.e. LIA/Roman Ladbroke see Figure 2) and revealed evidence for spatial signatures that indicate zoning and the differential use of space across a site.

Conclusions

Given the speed, accuracy, spatial precision, and cost-effectiveness offered by rapid *in-situ* geochemistry, it is clear that it shows considerable promise for wider use in pre-determination evaluation works where it could be ideally applied alongside geophysics and/or fieldwalking in advance of highly targeted evaluation trenching.

As geochemical results are independent of parameters measured by geophysical surveys they offer an independent dataset that can add confidence to areas being deemed ‘blank areas’. *In-situ* geochemistry by pXRF has the ability to produce results across a range of geologies adds an important technique to the arsenal of the archaeologist’s methods. Similarly, its ability to function across a range of soil types and environments supports its use globally in addressing matters ranging from developer-led archaeology to designations of World Heritage sites.

Beyond prospection, the use of geochemistry during open area excavation or strip, map and sample excavations, provides a further context of use at the site-based scale where greater detail can be produced and questions addressed in relation to the specific use of key structures, buildings, and spaces across a given site. The utility of geochemical survey in archaeology is only just beginning to be tapped and its potential and roll out in a commercial archaeological context is an exciting prospect that will bring benefits to clients, archaeologists and the public.

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