Sampling and Analyzing Metals in Soils for Archaeological Prospection: A Critique

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This paper presents a critique of current methods of sampling and analyzing soils for metals in archaeological prospection. Commonly used methodologies in soil science are shown to be suitable for archaeological investigations, with a concomitant improvement in their resolution. Understanding the soil-fraction location, concentration range, and spatial distribution of autochthonous (native) soil metals is shown to be a vital precursor to archaeological-site investigations, as this is the background upon which anthropogenic deposition takes place. Nested sampling is suggested as the most cost-effective method of investigating the spatial variability in the autochthonous metal concentrations. The use of the appropriate soil horizon (or sampling depth) and point sampling are critical in the preparation of a sampling regime. Simultaneous extraction is proposed as the most efficient method of identifying the location and eventual fate of autochthonous and anthropogenic metals, respectively. © 2004 Wiley Periodicals, Inc.

INTRODUCTION

The chemical analysis of soils to determine metal concentrations has become an accepted form of archaeological prospection and investigation. The basis for such investigations is that past anthropogenic activity has changed the relative concentrations of a range of metals found in the soils and sediments of areas associated with human use. Archaeologists often do not make the distinction between soil and sediment (Middleton and Price, 1996). Soils are pedogenically modified sediments, but unconsolidated, unweathered sediments are not soils, even if they are derived from soils (Stein, 1985, 1987; Mandel and Bettis, 2001). However, the terms have been used subjectively, depending on the focus of the research in question (Holliday, 1990). As both soils and sediments may have their metal concentrations changed by anthropogenic deposition, soil will be used as a generic term in this paper. Furthermore, for simplicity, metalloids and phosphorus are included in this paper, with behavioral differences explained where necessary.

The number of metals used in soil prospection has grown over time. For example, burials, food-waste disposal, and animal excretion were shown to increase P and

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Ca soil concentrations (Lutz, 1951; Parsons, 1962; Cook and Heizer, 1965), and burning firewood was shown to increase soil Mg concentrations (Heidenreich and Navratil, 1973). The production and use of coins, jewelry, and pigments caused elevated Cu and Pb concentrations (Davies et al., 1988). Some biophile elements (those essential to plant and animal growth), including B, Cu, Mg, Mn, Ni, P, Se, and Zn have been shown to accumulate in the soil due to human activity (Bethell and Carver, 1987; Ottaway and Matthews, 1988), and copper mining and smelting have been shown to increase Cu, Pb, and Mn concentrations (Pyatt et al., 1999; Pyatt et al., 2002). The number of metals used may also increase. For example, Snyder et al. (1975) listed 51 elements ingested/inhaled and secreted by humans on a daily basis (34 metals, 7 metalloids, and 10 nonmetals).

In effect, archaeological investigations of metals in soils are biogeochemical assays, biogeochemical, in this context, being the interaction of biotic and abiotic environmental cycles involving materials of biological (organic) and geological or mineral (inorganic) origin (Manahan, 1994:36). Biogeochemical assays have been used to identify settlement sites (Sjoberg, 1976), define site boundaries (Konrad et al., 1983; Haslam and Tibbett, 2001), investigate the impact of prehistoric agriculture on soils and landscapes (Sandor et al., 1986), and identify settlement features (Conway, 1983; Craddock et al., 1985; Bethell and Carver, 1987). Bintliff et al. (1992) expected biogeochemical assays to become increasingly important to the interpretation of field data, as only a small percentage of sites of interest would ever be excavated. This expectation would seem to be borne out by the number of investigations that have utilized biogeochemical assays since 1992 (e.g., Lewis et al., 1993; Linderholm and Lundberg, 1994; Middleton and Price, 1996; Entwistle et al., 1998, 2000; James, 1999; Wells et al., 2000; Parnell et al., 2002).

The spatial distribution of anthropogenically altered metal concentrations provides the information from which most archaeological inferences are drawn in biogeochemical assays (Conway, 1983; Aston et al., 1998; James, 1999; Wells et al., 2000). The determination of this distribution (as described in the published literature) generally follows the same strategy; soil samples are collected from the site and from location(s) presumed to be off-site, and, hence, unaffected. Metals are chemically extracted from the soil samples, and their concentrations measured. The metal concentrations of the on-site soils are then compared to off-site metal concentrations, commonly known as the "background" in the archeological literature. Differences in metal concentration are then ascribed some archaeological significance.

The above strategy requires a number of assumptions to be made by the investigators: (1) that the on-site samples are taken from locations that will provide the optimum archaeological information; (2) that representative off-site metal concentration values have been determined; (3) that these off-site metal concentrations (often described by a single arithmetic mean) are appropriate for resolving on-site values; (4) that if total or pseudototal extractions are used, the spatial distribution of the anthropologically deposited metal concentrations can still be determined and will not be masked as a fraction of native or autochthonous concentrations; and (5) that partial extraction methods extract the desired component, the anthropogenically deposited metals. These assumptions are unsafe unless the variation and chemistry of the soil medium being examined are understood, an issue given scant consideration in current practice.

Soil is known to be a heterogeneous medium (Petersen and Calvin, 1986; Nortcliff, 1988; Stark, 1994). The autochthonous metal concentrations within the soil have been shown to exhibit marked concentration variability and spatial dependence at a range of scales, both horizontally and vertically (Crepin and Johnson, 1993; Parkin, 1993; Saldana et al., 1998). Metals in the soil exhibit speciation; that is, they exist in a range of chemical forms, such as oxides, carbonates, and sulphides. Soil metals also exhibit fractionation; that is, they are bound in specific ways in the soil matrix, such as easily extractable, adsorbed, and organically bound (Stover et al., 1976; Sposito, 1982). These properties vary from soil to soil. The post-depositional behavior and eventual fate of anthropogenic metals depends upon the form in which they were deposited and the chemical, biological, and physical characteristics of the soil in which they were deposited (Korte et al., 1976; Lund and Fobian, 1989). This will vary from soil to soil.

The implications of the innate spatial, physical, and chemical variability of metals in soil are not new to archaeology. Concerns about practical ways to address suitable sampling regimes have been expressed by many workers (Cook and Heizer, 1965; Proudfoot, 1976; Hammond, 1983; Cradock et al., 1985; Gurney, 1985; Bethell and Mate, 1989). The importance of understanding the range and scale of autochthonous soil-metal concentrations was noted by others, including Conway (1983), Linderholm and Lundberg (1994), Middleton and Price (1996), and Crowther (1997). Aston et al. (1998) considered autochthonous variability to be a limiting factor in the archaeological use of biogeochemical assays, and the implications that soil-property variability has for sampling regimes was acknowledged by Entwistle et al. (2000). The methods used to extract metals from soils have also undergone examination in a number of published biogeochemical assays. Linderholm and Lundberg (1994) found strong acid extraction and total dissolution to give comparable results. Lewis et al. (1993), Middleton and Price (1996), and Scudder et al. (1996) considered that a dilute acid extraction differentiated anthropogenically deposited metals from autochthonous concentrations and would improve the interpretive capability of assays. Chelating agents were used by Bintliff et al. (1992), Wells et al. (2000), and Parnell et al. (2002), again in the belief that only metals of anthropogenic origin would be extracted.

UNDERSTANDING THE BACKGROUND

The first step to addressing these perceived weaknesses in biogeochemical surveying is to understand the “background,” which is the soil matrix in which the anthropogenic metals were deposited. In practice, this means effectively sampling an off-site location to determine the soil fraction, concentration range, and spatial distribution of the autochthonous metals. Although a complete understanding of the nature of the soil cannot be achieved without an unreasonable amount of sampling and analysis, a good estimation of the soil properties can be achieved. This can then be used to improve the resolution of the on-site assay by determining the most suitable sampling interval and extraction methodology for the on-site investigation.

The spatial variability and range of scales of soil properties contain both systematic and random components (Trangmar et al., 1985). The systematic variability is expressed in the field as gradual or distinct changes in soil properties, which can be explained in terms of soil-forming processes and factors, landforms, and geomorphic processes. The random variability is deemed to be a result of differential lithology, hydrology, weathering, and biological factors at a given scale of observation (Wilding and Drees, 1983), from the regional (Van Wambeke and Dudal, 1978) to the microscopic (Blevins et al., 1970; Miller et al., 1971).

The heterogeneity identified in soil-variability studies depends on the scale or frequency of observation (Hammond et al., 1958; Nortcliff, 1978; Burrough, 1993). Thus, the accuracy of statements made about any soil property is largely dependent on the amount of variation within the area sampled and the scale of the sampling regime (Trangmar et al., 1985). The scale-dependency of soil properties gives them a spatial continuity. Distribution is not entirely random, in that observed values close to each other on the ground are more likely to be similar than those further apart (Burrough, 1983; Parkin, 1993; Saldana et al., 1998). Attempts have been made to describe the variability of soil properties using classical parametric statistics (e.g., Beckett and Webster, 1971; Webster and Butler, 1976; Wilding and Drees, 1978, 1983). However, Trangmar et al. (1985) note that traditional methods of statistical analysis do not typically consider the spatial dependence soils exhibit. Traditional statistics assume that measured observations are independent of their distribution in space. That is, that soil variation is randomly distributed and the sampling unit mean is the expected value at any location within the unit, with error expressed as the within-unit variance (Hamlett et al., 1986; Cambardella et al., 1994; Rahman et al., 1996). The spatial dependence of soil properties means that, from a mathematical standpoint, the value of a property is a function of its position. Webster and Oliver (1990:213) note that, although the variation is so irregular that a complete mathematical description is not feasible, it is not wholly random. There is some structure, in that values at close proximity tend to be more similar than those that are widely separated. Thus, the property can be regarded as a random variable and its variation in space treated statistically. The variation of soil properties, or the natural background "noise," can be estimated using Geostatistics. This provides a set of descriptive tools for incorporating the spatial coordinates of soil properties in data processing (Goovaerts, 1998, 1999) and provides insight into the nature of variability in soil properties which conventional statistics do not (Rahman et al., 1996). Geostatistics allows the description and modeling of spatial patterns, the prediction of properties at unsampled locations, and the assessment of the uncertainty attached to these predictions (Burgess et al., 1981; Isaaks and Srivastava, 1989; Desbarats, 1996; Goovaerts 1998). Geostatistical methods were proposed for archaeological prospecting by Zubrow and Harbaugh (1978) and have been used in studies that have obvious archaeological applications, such as determining the distribution of metals from contamination sources in soils (Goovaerts and Webster, 1994; Webster et al., 1994; Bonifacio et al., 1996), mapping local variations in heavy metal concentration due partly to anthropogenic activity (Webster et al., 1994), and designing grid-cell layouts for sampling, thereby preserving the spatial heterogeneity of the original data (Brannan and Hamlett, 1998).

Spatial patterns in soils can be described by semivariograms, which use the dissimilarity between observations as a function of the separation distance (Isaacs and Srivastava, 1989; Webster and Oliver, 1990; Goovaerts, 1998). Semivariograms can describe the variation of single and multiple property values and characterize the spatial distribution of specific classes of values (Goovaerts, 1998, 1999). They can also be used to design optimal sampling regimes (Stein and Ettema, 2003). However, because geostatistical data are a function of separation, such analysis is scale-dependent (Srivastava, 1996). Conventional methods of estimating scale in geostatistical analyses rarely encompass more than one order of magnitude, yet soil-property variations have been shown to exceed this level (Youden and Mehlich, 1937; Oliver and Webster, 1986). Webster and Oliver (1990:222, 1993:155) noted that a satisfactory semivariogram requires data from a minimum of 100 sampled locations, probably too many for an archaeological-site director to sanction when considering the cost of collection and analysis.

According to Youden and Mehlich (1937), these problems can be overcome by using a nested-sampling regime, which describes the spatial scale of the variation. They used a nested-sampling regime in which the population of interest could be divided into distinct stages, with classes created by the initial division of the population being subdivided repeatedly in a hierarchical fashion. An individual observation thus embodied a contribution from each stage of division, including an unresolved variance in the smallest subdivision. Youden and Mehlich (1937) showed that, for a property distributed in space, the stages of the hierarchical system could be represented by different distances, provided that these were suitably nested in pairs. A comprehensive explanation of the statistical treatment of nested-sampling regimes is given by Snedecor and Cochran (1980).

Figure 1 illustrates part of a sample-collection strategy for a four-stage nested regime. A number of primary sampling stations are chosen at a predetermined distance from each other. At each primary station, two secondary stations are chosen, again at a predetermined distance. The process is repeated, and two tertiary stations are chosen for each secondary station. Finally, two sampling points are chosen for each tertiary station. Soil samples are only collected from the sampling points. The number of primary stations, separation distances, and subdivisions used in practice are subjective and would be dependent on the site under investigation.

Figure 2 illustrates the hierarchical nature of a four-stage nested-sampling regime with n primary stations. Eight samples would be collected for each primary station, and the total number of samples collected would be 8n. The regime is balanced, as at each stage of subdivision the classes are divided equally and the components of variance may be regarded as independent, thereby allowing confidence limits to be determined.

The variance associated with separation distance is estimated from the mean squares of the classes in each stage of the nested regime. For the first stage, the sum of the squares of deviation of the means of the primary stations from the general

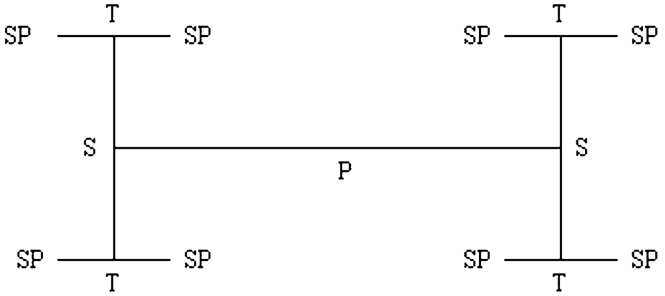

Figure 1. Part of a four-stage nested-sample collection strategy, showing secondary stations (S), tertiary stations (T), and sampling points (SP) at each primary station (P).

mean is calculated and multiplied by the number of values used to determine a primary station mean. For stage 2, the sum of squares of the deviation of the mean of each secondary station from the mean of the primary station to which it belongs is calculated and multiplied by the number of values used to determine a secondary station mean. This procedure is then repeated for the other stages. The total sum of squares is equal to the sums of squares of the individual stages. The mean squares are calculated by dividing the sums of squares at each stage by the appropriate degrees of freedom. In the example shown in Figures 1 and 2, there would be n – 1 degrees of freedom for the first stage. At the second stage, there would be 2n – 1 degrees of freedom. However, differences between primary stations already accounts for n – 1 degrees of freedom, so there are only (2n – 1) – (n – 1), or n degrees of freedom at stage 2. Each pair of secondary stations contributes 1 degree of freedom from which to estimate the variance due to differences between secondary stations within primary stations. Similarly, in the subsequent stages, each pair of values contributes 1 degree of freedom. Thus, in stage 3 there are 2n degrees of freedom, and in stage 4 there are 4n degrees of freedom. The mean square (ms) at each stage, apart from the last, contains a unique contribution to the variance of that stage plus contributions from each of the lower stages. The estimated components of variance at each stage are determined as shown below:

Stage 4	(ms stage 4)/x_4
Stage 3	(ms stage 3 – ms stage 4)/x_3
Stage 2	(ms stage 2 – ms square stage 3)/x_2
Stage 1	(ms stage 1 – ms square stage 2)/x_1

Here, x_1, x_2, and x_3 are the number of observations in an individual class at each stage, respectively. In a four-stage balanced regime, $x_1 = 8$, $x_2 = 4$, $x_3 = 2$, and $x_4 = 1$. The percentage contribution to the total variance can be calculated for each stage from these values.

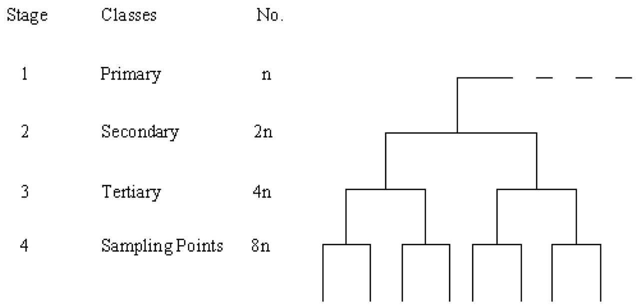

Figure 2. A model of a balanced, hierarchical, four-stage soil-sampling scheme with n primary stations. The figure shows the subdivisions at a primary station.

Oliver and Webster (1986) showed that further sampling economy could be achieved by using an unbalanced nested sampling regime, replicating at only a proportion of the sampling centers, at one or more of the divisional stages, once sufficient degrees of freedom had been reached. Figure 3 illustrates an unbalanced regime. Using this model, the total number of sampling points would be 6n. As before, the number of degrees of freedom at any stage is the number of classes at that stage less the number of classes in the stage above. The mean squares are calculated in the same way, as are the sums of squares. However, the number of observations at each stage is not the same. This unbalanced approach makes the statistical procedures for analysis slightly more complicated. However, Gates and Shiue (1962) and Gower (1962) developed statistical procedures for such calculations.

Balanced nested-sampling regimes have been used successfully to design efficient sampling strategies for investigating soil-property variation within individual fields (Hammond et al., 1958) and to measure the contribution of soil properties from different distances to the overall variation (Webster and Butler, 1976; Nortcliff, 1978). They provide a relatively simple, less expensive, and statistically valid method of estimating the variation in background metal concentrations, and would provide an excellent best-practice method for biogeochemical assays in archaeology. However, it must be emphasized that the results from such exercises may be skewed if the collected soil samples are of different sizes or from different depths or horizons.

SOIL SAMPLES

The three most significant pedogenic processes are the weathering and breakdown of inorganic and organic materials in the soil, the translocation of materials within the soil profile, and the accumulation of materials in the soil horizons. The rate

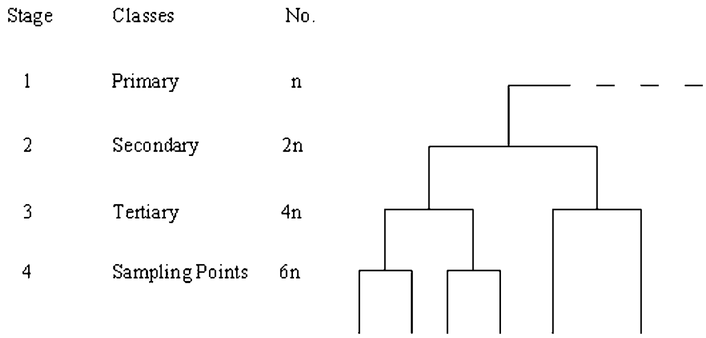

Figure 3. A model of an unbalanced, hierarchical, four-stage soil-sampling scheme with n primary stations. The figure shows the subdivisions at a primary station.

at which these processes operate is determined by climate, topography, vegetation, soil fauna, the nature of the parent material, and the time over which the processes have acted (Brady, 1990:54). The concentrations of metals, of both natural and archaeological origin, at any point within the soil horizons will depend upon the rate at which these processes have occurred and the amount of anthropogenic activity, both archaeological and modern, to which they have been subjected. Therefore, it is vital that soil samples for analysis and comparison are collected from the same soil horizon both on- and off-site. The depth at which a given soil horizon is found, and the thickness of that horizon, may vary spatially. This possible variation must be considered in a sampling program.

The size of soil samples used in biogeochemical prospection often seems arbitrary and appears to have been determined by convenience. However, the support size (i.e., the volume from which data is collected) is important (Stein and Etterna, 2003). A sample could be as large as a bulked sample from a test pit, which may weigh several kilograms, or as small as an augered core weighing only a few grams. In a large area, the number of samples may be regarded as infinite, which simplifies subsequent statistical treatment. However, the degree of variation observed between samples is likely to be size-dependent. The larger the sample on which measurements are made, the more variation is likely to be both encompassed within it and possibly hidden by it. The concentration of any metal within a 10 × 10 cm sample may have been much higher at one edge of the sampled area than another. However, the final subsample is likely to give a concentration value between the two extremes. Thus, in bulked samples, there could appear to be less variation between samples than actually exists. Literature on the assessment of potentially contaminated land recommends that spot samples be used in preference to bulked, composite samples for precisely this reason (ICRCL, 1987; Ferguson, 1992). A point-sampling strategy, using a corer to a known depth, would seem most appropriate for archaeological use, as noted by Entwistle et al. (2000).

METALS IN SOIL

Metals are naturally present in soils as a result of weathering from lithospheric parent material (Jones and Jarvis, 1981; Yong et al., 1992:25). Metal concentrations in soil vary enormously, and can be naturally high when the soil has developed over ultrabasic source rocks (e.g., Cr 1000–3400 ppm, Ni 270–3600 ppm, Cu 40–150 ppm) and typically lower when developed on calcareous rocks (e.g., Cr < 1 ppm, Ni < 1 ppm, Cu 7–28 ppm) (Alloway, 1995:155, 183). Aston et al. (1998) suggest there are at least five ways in which soil-metal concentrations may have been altered by human activities: habitation, stalled animals, fires/hearths, metalworking, and other activities, such as crop processing and leather working. All these activities produce waste, which, after deposition, alters the physical and chemical composition of the soil, including enrichment by elements present in the waste. The fate of metals added to the soil depends on the physiochemical form in which they are deposited (Davidson et al., 1986; Tack and Verloo, 1995; Chlopecka et al., 1996), as well as prevalent environmental and edaphic factors (Ross, 1994:63; Harter and Naidu, 2001). Chlopecka et al. (1996) demonstrated that anthropogenic metals are more mobile and potentially available when added to the soil than pedogenic or lithogenic forms. For the purposes of biogeochemical prospection, this means that key metals of anthropogenic origin may be found in specific soil fractions. These fractions may differ from those in which the same autochthonous metals are found.

Speciation has been defined as the determination of the precise chemical form in which a metal exists, such as its oxidation state. In soils, determining metal speciation requires the identification and quantification of the different species, forms, or phases in which elements occur (Tack and Verloo, 1995). It has been operationally defined by the extraction technique used to quantify it and functionally defined by the soil fraction in which the metal is held, such as soluble or extractable (Alloway, 1995:91). It has also been defined by the particle-size fraction to which metals in the soil are bound (Ducaroir and Lamy, 1995). The variety of definitions causes some confusion between the terms *speciation* and *fractionation*. Speciation should ideally be used to refer to the precise chemical form in which a metal exists in the soil (e.g., oxidation state).

Fractionation is the term used to describe the location of metals in the soil, or the specific soil components that retain metals. The processes that have the greatest effect on the retention of metals in soil are those that involve adsorption from the liquid to the solid phase. These include cation exchange (nonspecific adsorption), specific adsorption, coprecipitation, and organic complexation (McBride, 1989; Ross, 1994:63). Most metals exist as cations in the soil solution, with certain exceptions such as Mo, V, and metalloids, such as P, As, Sb, and Se, which form anions (Alloway, 1995:19). Adsorption by cation exchange is dependent on the number of negative charges (exchange sites) on the soil colloids (for the elements that form anions, it is dependent on the number of positive charges). To achieve electroneutrality (the most stable state), the negative charge on the colloid must be balanced by positive charge from the soil-solution cations. Ions are exchanged between the soil solution and colloids to achieve this state. The negative colloid charges are either permanent—that is, independent of pH and due to innate mineral charges and isomorphous substitution—or pH-dependent (Brady, 1990:195–199). Cation exchange is reversible, diffusion-controlled, stoichiometric, and usually subject to selectivity by the adsorbent material. The selectivity establishes a replacing order among cations that is determined by their valency and degree of hydration. Ions with a high valency have high replacing power, and ions with a high degree of hydration have low replacing power (Brummer, 1986).

Specific adsorption of metals is the exchange of ions with surface ligands, which are the coordinated neutral or anionic groups around a central metal ion in a complex molecule. Specific adsorption is particularly associated with amorphous oxides of Al, Fe, Mn, and soil organic matter. Partly covalent bonds are formed with lattice ions, which results in far greater adsorption of metal ions than would be expected from the cation-exchange capacity of a soil (Brummer, 1986). Specific adsorption is pH-dependent and strongly related to the hydrolysis of the metal ions, with those metals most able to form hydroxy complexes specifically adsorbed to the greatest extent. Specific adsorption can also occur by the diffusion of metal ions into minerals in the soil, such as goethite, illites, smectites, and Mn oxides (Plant and Raiswell, 1983; Brummer and Herms, 1983; Brummer, 1986; McBride, 1989).

Coprecipitation is the simultaneous precipitation of a chemical agent in conjunction with other elements. These mixed solids are commonly clay minerals, hydrous Fe and Mn oxides, and calcite (Alloway, 1995:20). In addition to cation exchange, humic substances can adsorb metals by forming coordination complexes with metallic ions and by chelation. Organic ligands, not necessarily humic in origin, can form soluble complexes with metals that prevent them from being adsorbed or precipitated (Sposito, 1983). Soil organic matter and the oxides of Fe and Mn, normally found as gels, surface coatings, and complex mixtures on particles and pore surfaces, are accepted as being mainly responsible for soil-metal retention (Miller et al., 1983, 1985).

Solid-phase humic substances adsorb metals by forming chelate complexes, in addition to being involved in cation-exchange reactions (Alloway, 1995:22). Humic acids are regarded as the metal-immobilizing fraction of soil organic matter, as their large molecular weight means they are generally less mobile than the lower-molecular-weight fulvic acids (Piccolo, 1989). Because of their low molecular weight, organic ligands can form soluble complexes with metals that prevents the metal from being adsorbed or precipitated. Metal ions may also form coordination complexes with humic compounds, which possess suitable reactive groups, such as hydroxyl, carboxyl, and phenoxyl radicals. Ross (1994:127) stated that there are at least nine soil fractions in which metals may be held and which are commonly used in the investigation of soil contamination by metals from anthropogenic sources: soluble, extractable, carbonate, adsorbed, organically bound, Mn oxide occluded, amorphous Fe occluded, crystalline Fe occluded, and residual.

The complexity of soil-metal chemistry outlined above casts some doubt on whether total or pseudo-total metal-extraction procedures commonly used in archaeological biogeochemical assays are necessarily the best methods in all cases. They may, in fact, disguise the anthropogenic enrichment of the soil under investigation when certain species of metals are incorporated into particular soil fractions. Consider three possible scenarios:

1. If a metal X is deposited anthropogenically in the form of two species, each of which is bound to a different soil fraction and there is no natural soil X, a total or pseudo-total extraction will provide the required resolution in the analytical data.
2. If metal X is naturally present in the soil and bound to the same two soil fractions, then only a careful determination of the off-site autochthonous concentrations, and their variation, will allow the archaeologically relevant information to be recovered.
3. If the naturally present X is bound to a number of different fractions, including one in which the anthropogenically deposited X is bound, as well as considering the off-site background concentration, the application of chemical-extraction methods that determine the concentration in the particular soil fraction of interest may greatly enhance the resolution of archaeologically relevant soil-mapping data.

It is likely that anthropogenic metal deposition will enrich only particular metal fractions of the soil. For example, Cu from metal-working may remain part of the soil inorganic pool, while Cu added from the stalling of animals will be incorporated into the organically bound fraction. Therefore, the best-practice scenario for archaeology would be to determine the soil fraction to which anthropogenic metals are bound, and analyze appropriately for these, removing much of the native metals from the soil-mapping data. This means that, for each site, some preliminary work would be necessary to determine the most suitable extraction method.

METAL EXTRACTION

The enormous body of literature on soil analysis can be broken down into three generalized protocols for the extraction of soil metals: total analysis, single extraction, and sequential extraction. Total analysis involves the use of hydrofluoric acid to break down the largely silicate matrix of soils and an oxidizing acid to attack soil organic matter and sulfides. Pseudo-total analysis can be achieved by using a mixture of mineral acids. These do not dissolve the silicate material in soils, but are vigorous enough to dissolve metals not bound to the silicate phases (Ure, 1995), thereby allowing a close approximation of the total metal content to be made. Single extractions use a chemical extractant, usually a weak or dilute acid (e.g., CH_3COOH) or a chelating agent (e.g., EDTA, DTPA), to remove metal(s) from a particular soil fraction. For instance, this method can be used to determine the "plant available" soil metals by extracting them from the soluble, extractable, and organically bound soil fractions (Davies et al., 1987; Rappaport et al., 1988). The most widely used approach to characterize the species of metals and the soil fractions to which they are bound is sequential extraction, often referred to as speciation (Quevauviller et al., 1994). This is the application of a series of increasingly strong extractants to the same soil sample, intended to isolate individual metal phases in the soil (Lake et al., 1984). A number of sequential extraction schemes have been developed empirically. Generally, the soluble and exchangeable fractions are extracted using dilute solutions of replacement cation salts (e.g., 0.1M $CaCl_2$, 1M NH_4NO_3, etc.). Oxidizing agents (e.g., HNO_3, H_2O_2) are used to extract organically bound fractions, while reducing agents (e.g., $NH_2OH.HCl$) release metals bound to Fe and Mn oxides. Finally, strong acids are used to extract the residual or occluded metals (Quevauviller et al., 1994).

Though a series of extractants of increasing strength should allow individual metal species in the soil to be more precisely isolated, in practice, there are overlaps between adjacent fractions (Hooda and Alloway, 1994). The identification of, and discrimination between, different metal species is more closely related to the extractants and procedures used than to the true species of the metal. The metal species extracted using sequential extraction are thus operational in nature, and do not necessarily accurately represent the true metal content of the individual soil fractions (Barbanti and Siginolfi, 1988; Tack and Verloo, 1995; Luo and Christie, 1998; Zemberyova et al., 1998; Ahumada et al., 1999). The number of reagents and different applications for which sequential extraction is used makes comparison between studies difficult. The extraction procedures only crudely differentiate between the metal fractions, and there is uncertainty about the way the extractants remove the metals. The labile metal phases may be transformed during sample preparation, readsorption or precipitation could occur during extraction (Barbanti and Siginolfi, 1988; Bunzl et al., 1999; Gomez-Ariza et al., 1999), and the amount of metal extracted may be dependent on the duration of the process and the ratio of soil to solution used (Sahuquillo et al., 1999). The need to define sequential extractions operationally was demonstrated by Usero et al. (1998), who conducted a comparative study on three commonly used sequential extraction techniques: those of Tessier et al. (1979), Kersten and Forstner (1986), and Ure et al. (1993). The comparison showed that, for the same soil samples, the metal distribution determined by the three procedures was significantly different.

Despite these problems, sequential extraction procedures have proved their potential in environmental analysis (Tessier and Campbell, 1991). They have been shown to be an efficient method of conducting comparative studies between natural and contaminated land, as well as areas characterized by different types of contamination (Scokart et al., 1987; Hirner, 1992; Hooda and Alloway, 1994; Tack and Verloo, 1995; Gauthreaux et al., 1998; Wada and Wada, 1999). Sequential extraction has been used to compare metal fractionation in natural soils (Shuman, 1979; Barona and Romero, 1996) and the change in metal distribution over time in soils treated with sewage sludges (Nyamangara and Mzezewa, 1999; Walter and Cuevas, 1999). However, Salomons (1993) and Luo and Christie (1998) cautioned that it is important to accept a common scheme so that results from different research projects can be compared and common data bases on the mode of occurrence of metals in soils and sediments can be developed.

An alternative to sequential extraction is simultaneous extraction. In this method, a number of single extractions, using a separate aliquot of soil for each phase under investigation, are carried out simultaneously. A number of comparisons have been made between the two methodologies. Gupta et al. (1990) compared a simultaneous extraction with the sequential extraction procedure used by Stover et al. (1976). Bendell-Young et al. (1992), Tack et al. (1996), and Tack and Verloo (1999) compared simultaneous extractions to the sequential extraction procedure developed by Tessier et al. (1979). The comparisons showed that simultaneous and sequential determinations of metal speciation were generally equivalent. Bendell-Young et al. (1992) and Tack and Verloo (1999) concluded that the use of simultaneous extraction—instead of sequential extraction—could be justified for practical purposes, the advantages being that there would be no risk of sample loss between consecutive phase separations and washing steps, and that results could be obtained more quickly. Simultaneous extraction would seem to be the ideal method for use in biogeochemical assays for archaeology. In time, known extractants may be recognized as the best way of targeting specific archaeological features. For example, Cu from metalworking may be best extracted by a mineral acid, whereas Cu from stalled animals may be best extracted by an oxidizing agent.

CONCLUSIONS

To derive the best-quality archaeological information from biogeochemical surveys, the resolution of the soil-metal assay must be optimized. This poses a number of considerations that should be addressed when planning such an exercise. The range and scale of the autochthonous spatially dependent variability of the soil metals in question must be determined. This information provides the background against which possible anthropogenic metal-concentration elevations are compared (Eidt, 1985; Lillios, 1992). If the range and scale of the naturally present metal concentrations are not known, the quality of the archaeological inferences drawn from comparisons to these values must be, at best, speculative, and, at worst, incorrect.

The sampling-regime interval must take into account the spatial scale of the natural variability of the soil metals under investigation, as any anthropogenic influence on soil-metal concentrations will be superimposed upon this scale. A regime with a sampling interval that is too large will miss a proportion, possibly a large proportion, of the information it should have been designed to collect. An interval that is smaller than necessary will add needlessly to the cost of the collection and analysis of soil samples. Though the majority of archaeological biogeochemical prospection is likely to take place at ground level, using surface horizons, it must be remembered that soil-metal concentrations may vary with depth. Sampling regimes and procedures must use the appropriate horizon in the soil profile, with the knowledge that the depth of a given horizon may vary over a given area.

The analysis of soil samples should take into account the speciation and fractionation of soil metals. Anthropogenically deposited metals may exist as different species from autochthonous forms, and may be bound to different fractions and/or different aggregate sizes. Extraction procedures targeted at specific metal species or soil fractions are more likely to yield information of archaeological relevance than total or pseudo-total extractions, which may mask the anthropogenic metal content of interest behind autochthonous concentrations.

The cost of archaeological excavations makes the use of biogeochemical surveys an increasingly important method of investigation. Though planning and analysis are expensive, using poor sampling regimes and ineffective analytical techniques to cut costs is counterproductive. Biogeochemical surveys that are unlikely to find the information they were designed to retrieve can potentially result in a loss of money and archaeological information. Although past biogeochemical surveys have produced interesting information, how much more may have been achieved with the application of the geostatistical and chemical analysis tools that are now common in environmental soil science? Archaeological science can no longer afford to ignore the technical but necessary avenues required to improve its survey practice. We encourage archaeologists to consider the wealth of knowledge in the scientific literature reviewed above that might greatly improve the resolution of biogeochemical prospection.

EXAMPLE

Figure 4 illustrates a hypothetical archaeological site. The remains of archaeological features are approximately 30 cm below surface level. The site is thought to have been a small Bronze Age metal production center. It is situated on soil of the Blacktoft series, which has a dark grey/brown, slightly calcareous, silty clay Ap horizon that extends to a depth of 35 cm. Underlying this is a Bw horizon, which is a brown, stoneless, silty clay loam to 55 cm, which overlies a Bg horizon of brown, mottled, stoneless, silty clay loam to 90 cm (Jarvis et al., 1984). The adjacent Quorndon series has a very dark grey/brown, slightly stony, sandy loam Ap horizon that extends down to 20 cm. The underlying Bg1 horizon is olive brown with ochreous mottles and overlies a greyish-brown, mottled, stony, sandy loam to 80 cm (Jarvis et al., 1984). Where no soil map is available, soil cores from the surrounding area would need to be taken and compared to those taken from the site. Characteristics such as horizon depth, soil texture, color, etc., should enable the archaeologist to locate off-site areas on the same soil type as the site under investigation.

In this example, the range and spatial scale of autochthonous concentrations of copper and tin were determined using a four-stage nested sampling regime. Five primary stations were chosen, in areas where there was no archaeological evidence. Each primary station was separated from its neighbor by the same distance. The separation distance would depend on the size of the site under investigation, in this hypothetical case, the distance was 40 m, approximately the same as the N–S length of the site. The secondary stations were 20 m apart, the tertiary stations 10 m apart, and the sampling points 5 m apart. The sampling regime gave 40 soil samples (material from 2 horizons in each), collected using a 2.5 cm diameter corer, to a depth of 50 cm.

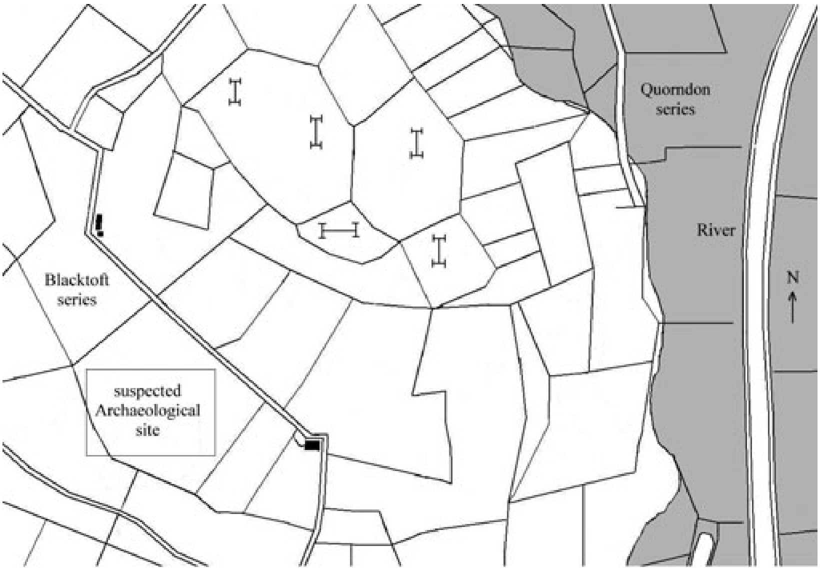

Figure 4. A sampling regime to determine the range and spatial scale of autochthonous metal concentrations for hypothetical archaeological site.

Random subsamples of both horizons (approximately 1 g) were subjected to simultaneous extraction, to determine the autochthonous metal concentrations in the exchangeable, carbonate, organic, and residual fractions of the soils. Magnesium chloride, sodium acetate, nitric acid, and hydrochloric acid with hydrofluoric acid, respectively, were used as extractants. Analysis revealed that the autochthonous metals in questions were adsorbed on the organic and carbonate fractions of the Ap horizon and the organic fraction of the Bw horizon. Subsamples from the remaining cored samples were subjected to simultaneous metal extraction, using sodium acetate and nitric acid to determine the metal concentrations in each. The results gave maximum and minimum values for the autochthonous concentrations of copper and tin for comparison to on-site values. Nested analysis of variance showed that, in the Ap horizon, 46% of the variance occurred over a distance of 40 m, 42% occurred over 20 m, 11% over 10 m, and the remaining 1% over 5 m. In the Bw horizon, 53% of the variance occurred over 40 m, 37% over 20 m, 8% over 10 m, and 2% over 5 m.

Consequently, the on-site sampling regime used was a standard grid pattern with an interval of 10 m, which would incorporate 98.5% of the concentration variation of the autochthonous metals. This maximum interval gave 35 samples for analysis. Subsequently, areas thought to be of further interest could be sampled more intensively.

REFERENCES

Ahumada, I., Mendoza, J., Navarrete, E., & Ascar, L. (1999). Sequential extraction of heavy metals in soils irrigated with waste water. Communications in Soil Science and Plant Analysis, 30, 1507–1519.

Alloway, B.J. (1995). Heavy metals in soils (2nd edition). Bury St. Edmunds, UK: Blackie Academic and Professional.

Aston, M.A., Martin, M.H., & Jackson, A.W. (1998). The potential for heavy metal soil analysis on low status archaeological sites at Shapwick, Somerset. Antiquity, 72, 836–847.

Barbanti, A., & Sighinolfi, G.P. (1988). Sequential extraction of phosphorus and heavy metals from sediments: Methodological considerations. Environmental Technology Letters, 9, 127–134.

Barona, A., & Romero, F. (1996). Distribution of metals in soils and relationships among fractions by principal component analysis. Soil Technology, 8, 303–319.

Beckett, P.H.T., & Webster, R. (1971). Soil variability: A review. Soil and Fertilizers, 34, 1–15.

Bendell Young, L., Dutton, M., & Pick, F.R. (1992). Contrasting methods for determining trace metal partitioning in oxidised lake sediments. Biogeochemistry, 17, 205–219.

Bethell, P.H., & Carver, M.O.H. (1987). Detection and enhancement of decayed inhumations at Sutton Hoo. In A. Boddington, N. Garland, & R.C. Janaway (Eds.), Death, decay and reconstruction (pp. 10–21). Manchester, UK: Manchester University Press.

Bethell, P.H., & Mate, I. (1989). The use of soil phosphate analysis in archaeology: A critique. In J. Henderson (Ed.), Scientific analysis in archaeology and its interpretation (pp. 1–29), Oxford University Commission for Archaeology Monograph 19. Oxford: Oxford University Press.

Bintliff, J.J., Davies, B., Gaffney, C., Snodgrass, A., & Water, A. (1992). Trace metal accumulations in soils on and around ancient settlements in Greece. In P. Spoerry (Ed.), Geoprospection in the archaeological landscape (pp. 9–24), Oxbow Monograph 18. Oxford: Oxbow Books.

Blevins, R.L., Holowaychuk, N., & Wilding, L.P. (1970). Microbiology of soil fabric at the tree-root-soil interface. Soil Science Society of America Proceedings, 34, 460–465.

Bonifacio, E., Melis, P., Senette, C., & Zanini, E. (1996). Spatial dependence of Pb and Cd in some Sardinia soils. Fresnius Environmental Bulletin, 5, 517–522.

Brady, N.C. (1990). The nature and properties of soils (10th edition). New York: Macmillan.

Brannan, K., & Hamlett, J.M. (1998). Using geostatistics to select grid-cell layouts for the AGNPS model. Transactions of the American Society of Agricultural Engineers, 41, 1011–1018.

Brummer, G.W. (1986). Heavy metal species, mobility and availability in soils. In M. Bernhard, F.E. Brinckman, & P.J. Sadler (Eds.), The importance of chemical speciation in environmental processes. Heidelberg: Springer-Verlag.

Brummer, G.W., & Herms, U. (1983). Influence of soil reaction and organic matter on solubility of heavy metals in soil. In B. Ulrich & J. Pankrath (Eds.), Effects of accumulation of air pollutants in forest ecosystems (pp. 233–243). Dordrecht: Reidel.

Bunzl, K., Trautmannsheimer, M., & Schramel, P. (1999). Heavy metals in the environment. Journal of Environmental Quality, 28, 1168–1173.

Burgess, T.M., Webster, R., & McBratney, A.B. (1981). Optimal interpolation and isarithmic mapping of soil properties VI: Sampling strategy. Journal of Soil Science, 31, 643–659.

Burrough, P.A. (1983). Multiscale sources of spatial variation in soil. I. The application of fractal concepts to nested levels of soil variation. Journal of Soil Science, 34, 577–597.

Burrough, P.A. (1993). Soil variability: A late 20th century view. Soils and Fertilizers, 56, 529–562.

Cambardella, C.A., Moorman, T.B., Novak, J.M., Parkin, T.B., Karlen, D.L., Turco, R.F., & Konopka, A.E. (1994). Field scale variability of soil properties in central Iowa soils. Soil Science Society of America Journal, 58, 1501–1511.

Chlopecka, A., Bacon, J.R., Wilson, M.J., & Kay, J. (1996). Forms of cadmium, lead and zinc in contaminated soils from southwest Poland. Journal of Environmental Quality, 25, 69–79.

Conway, J.S. (1983). An investigation of soil phosphorus distribution within occupation deposits from a Romano-British hut group. Journal of Archaeological Science, 10, 117–128.

Cook, S.F., & Heizer, R.F. (1965). Studies on the chemical analysis of archaeological soils. Los Angeles: University of California Press.

Cradock, P.T., Gurney, D., Pryor, F., & Hughes, M. (1985). The application of phosphate analysis in the location and interpretation of archaeological sites. Archaeological Journal, 142, 361–376.

Crepin, J., & Johnson, R.L. (1993). Soil sampling and environmental assessment. In M.R. Carter (Ed.), Soil sampling and methods of analysis (pp. 5–18). Boca Raton, FL: Lewis.

Crowther, J. (1997). Soil phosphate surveys: Critical approaches to sampling, analysis and interpretation. Archaeological Prospection, 4, 93–102.

Davies, B.E., Bintliff, J.L., Gaffney, C.F., & Water, A.T. (1988). Trace metal residues in soil as markers of ancient site occupation in Greece. In D.D. Hemphill (Ed.), Proceedings of the 22nd Trace Substances in Environmental Health Symposium (pp. 391–398). St. Louis, MO: University of Missouri.

Davies, B.E., Lear, J.M., & Lewis, N.J. (1987). Plant availability of heavy metals in soils. In P.J. Coughtrey, M.H. Martin, & M.H. Unsworth (Eds.), Pollutant transport and fate in ecosystems (pp. 267–275), British Ecological Society Special Publication 6. Oxford: Blackwell Scientific.

Davidson, D.A., Harkness, D.D., & Simpson, I.A. (1986). The formation of farm mounds on the Isle of Sanday, Orkney. Geoarchaeology, 1, 45–60.

Desbarats, A.J. (1996). Modeling spatial variability using geostatistical simulation. In S. Rouhani, R.M. Srivastava, A.J. Desbarats, M.V. Cromer, & A. Johnson (Eds.), Geostatistics for environmental and geotechnical applications (pp. 32–48), STP1283. Philadelphia: American Society for Testing and Materials.

Ducaroir, J., & Lamy, I. (1995). Evidence of trace metal association with soil organic matter using particle size fractionation after physical dispersion treatment. The Analyst, 120, 741–745.

Eidt, R.C. (1985). Theoretical and practical considerations in the analysis of anthrosols. In G. Rapp & J.A. Gifford (Eds.), Archaeological geology (pp. 155–190). New Haven, CT: Yale University Press.

Entwistle, J.A., Abrahams, P.W., & Dodgshon, R.A. (1998). Multi-element analysis of soils from Scottish historical sites. Interpreting land-use history through the physical and geochemical analysis of soil. Journal of Archaeological Science, 25, 53–68.

Entwistle, J.A., Abrahams, P.W., & Dodgshon, R.A. (2000). The geoarchaeological significance and spatial variability of a range of physical and chemical soil properties from a former habitation site, Isle of Skye. Journal of Archaeological Science, 27, 287–303.

Ferguson, C.C. (1992). The statistical basis for spatial sampling of contaminated land. Ground Engineer, 25, 34–38.

Gates, G.E., & Shiue, C.J. (1962). The analysis of variance of the S-stage hierarchical classification. Biometrics, 18, 529–536.

Gautheaux, K., Noble, C.O., Falgoust, T., Beck, M.J., Sneddon, J., & Beck, J.N. (1998). Reliability and reproducibility of a sequential extraction procedure for trace metal determination in marsh sediments in southwest Louisiana. Microchemical Journal, 60, 175–183.

Gomez-Ariza, J.L., Giraldez, I., Sanchez-Roda, D., & Morales, E. (1999). Metal readsorption and redistribution during the analytical fractionation of trace elements in oxic esturaine sediments. Analytica Chimica Acta, 399, 295–307.

Goovaerts, P. (1998). Geostatistical tools for characterizing the spatial variability of microbiological and physio-chemical soil properties. Biology and Fertility of Soils, 27, 315–334.

Goovaerts, P. (1999). Geostatistics in soil science: State of the art and perspectives. Geoderma, 89, 1–45.

Goovaerts, P., & Webster, R. (1994). Scale dependent correlations between topsoil copper and cobalt concentrations in Scotland. European Journal of Soil Science, 45, 79–95.

Gower, J.C. (1962). Variance component estimation for unbalanced hierarchical classification. Biometrics, 18, 537–542.

Gupta, S., Mehrotra, I., & Singh, O.V. (1990). Simultaneous extraction scheme: A method to characterise metal forms in sewage sludge. Environmental Technology, 11, 229–238.

Gurney, D.A. (1985). Phosphate analysis of soils: A guide for the field archaeologist, Technical Paper No. 3. Birmingham, AL: Institute of Field Archaeologists.

Hamlett, J.M., Horton, R., & Cressie, N.A.C. (1986). Resistant and exploratory techniques for use in semivariogram analysis. Soil Science Society of America Journal, 50, 868–875.

Hammond, L.C., Pritchett, W.L., & Chew, V. (1958). Soil sampling in relation to soil heterogeneity. Soil Science Society of America Proceedings, 22, 548–552.

Hamond, F.W. (1983). Phosphate analysis of archaeological sediments. In T. Reeves-Smyth & F.W. Hammond (Eds.), Landscape archaeology in Ireland, BAR Report 116 (pp. 47–80). Oxford: British Archaeological Reports.

Harter, R.D., & Naidu, R. (2001). An assessment of environmental and solution parameter impact on trace metal sorption by soils. Soil Science Society of America Journal, 65, 597–612.

Haslam, R.R., & Tibbett, M. (2001). The influence of aggregate size fraction on a soil metal assay at Merrivale. In G. Füleky (Ed.), Proceedings of the 1st International Conference on Soils and Archaeology, Százhalombatta, Hungary (pp. 48–50). Gödöllo: Környezetkímélo Agrokémiáért Alapítvány.

Heidenreich, C.E., & Navratil, S. (1973). Soil analysis at the Robitaille site. Part 1: Determining the perimeter of the village. Ontario Archaeology, 20, 25–32.

Hirner, A.V. (1992). Trace element speciation in soils and sediments using sequential chemical extraction techniques. International Journal of Environmental Analytical Chemistry, 46, 77–85.

Holliday, V.T. (1990). Pedology for archaeologists. In N.P. Lasca & J. Donahue (Eds.), Archaeological geology in North America, Centennial Special Volume 4 (pp. 525–540). Boulder, CO: Geological Society of America.

Hooda, P.S., & Alloway, B.J. (1994). Changes in operational fractions of trace metals in two soils during two years of reaction time following sewage sludge treatment. International Journal of Environmental Analytical Chemistry, 57, 289–311.

International Committee on the Redevelopment of Contaminated Land. (1987). Guidance on the assessment and redevelopment of contaminated land. ICRCL 59/83 (2nd edition). London: Department of the Environment.

Isaaks, E.H., & Srivastava, R.M. (1989). An introduction to applied geostatistics. New York: Oxford University Press.

James, P. (1999). Soil variability in the area of an archaeological site near Sparta, Greece. Journal of Archaeological Science, 26, 1273–1288.

Jarvis, R.A., Bendelow, V.C., Bradley, R.I., Carroll, D.M., Furness, R.R., Kilgour, I.N.L., & King, S.J. (1984). Soils and their use in northern England, Bulletin No. 10. Harpenden: Soil Survey of England and Wales.

Jones, L.H.P., & Jarvis, S.C. (1981). The fate of heavy metals. In D.J. Greenland & M.H.B. Hayes (Eds.), The chemistry of soil processes (pp. 593–620). London: Wiley.

Kersten, M., & Forstner, U. (1986). Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. Water Science Technology, 18, 121–130.

Konrad, V.A., Bonnichsen, R., & Clay, V. (1983). Soil chemical identification of ten thousand years of prehistoric human activity areas at the Munsungun Lake thoroughfare, Maine. Journal of Archaeological Science, 10, 13–28.

Korte, N.E., Skopp, J., Fuller, W.H., Niebla, E.E., & Alesii, B.A. (1976). Trace element movement in soils: Influence of soil physical and chemical properties. Soil Science, 122, 350–359.

Lake, D.L., Kirk, P.W., & Lester, J.N. (1984). Fractionation, characterisation and speciation of heavy metals in sewage sludge and sewage amended soils: A review. Journal of Environmental Technology, 13, 175–184.

Lewis, R.J., Foss, J.E., Morris, M.W., Timpson, M.E., & Stiles, C.A. (1993). Trace element analysis in pedoarchaeology studies. In J.E. Foss, M.E. Timpson, & M.W. Morris (Eds.), Proceedings of the First International Conference in Pedo-Archaeology (pp. 81–88), Special Publication 93-03. Knoxville, TN: University of Tennessee Agricultural Experiment Station.

Lillios, K.T. (1992). Phosphate fractionation of soils at Agroal, Potuga. American Antiquity, 57, 495–506.

Linderholm, J., & Lundberg, E. (1994). Chemical characterization of various archaeological soil samples using main and trace elements determined by inductively coupled plasma atomic emission spectrometry. Journal of Archaeological Science, 21, 303–314.

Lund, U., & Fobian, A. (1989). Pollution of two soils by arsenic, chromium and copper, Denmark. Geoderma, 49, 83–103.

Luo, Y.M., & Christie, P. (1998). Choice of extraction technique for soil reducible trace metals determines the subsequent oxidisable metal fraction in sequential extraction schemes. International Journal of Environmental Analytical Chemistry, 72, 59–75.

Lutz, H.J. (1951). The concentration of certain chemical elements in the soils of Alaskan archaeological sites. American Journal of Science, 249, 925–928.

Manahan, S.E. (1994). Environmental chemistry (6th edition). Boca Raton, FL: Lewis.

Mandel, R.D., & Bettis, E.A., III. (2001). Use and analysis of soils by archaeologists and geoscientists: A

North American perspective. In P. Goldberg, V.T. Holliday, & C.R. Ferring (Eds.), Earth sciences and archaeology (pp. 173–204). New York: Kluwer Academic/Plenum.

McBride, M.B. (1989). Reactions controlling heavy metal solubility in soils. Advances in Soil Science, 10, 1–56.

Middleton, W.D., & Price, T.D. (1996). Identification of activity areas by multi-element characterization of sediments from modern and archaeological house floors using inductively coupled plasma atomic emission spectroscopy. Journal of Archaeological Science, 23, 673–687.

Miller, F.P., Wilding, L.P., & Holowaychuk, N. (1971). Canfield silt loam, a Fragiudalf: II. Micromorphology, physical, and chemical properties. Soil Science Society of America Proceedings, 35, 324–331.

Miller, W.P., McFee, W.W., & Kelly, J.M. (1983). Mobility and retention of heavy metals in sandy soils. Journal of Environmental Quality, 12, 579–584.

Miller, W.P., Martens, D.C., & Zelany, L.W. (1985). Effect of sequence in extraction of trace metals from soils. Soil Science Society of America, 50, 598–601.

Nortcliff, S. (1978). Soil variability and reconnaissance soil mapping: A statistical study in Norfolk. Journal of Soil Science, 29, 403–417.

Nortcliff, S. (1988). Soil formation and characteristics of soil profiles. In A. Wild (Ed.), Russell's soil conditions and plant growth (pp. 168–212). Harlow, UK: Longman Scientific and Technical.

Nyamangara, J., & Mzezewa, J. (1999). The effect of long term sewage sludge application on Zn, Cu, Ni and Pb levels in a clay loam soil under pasture grass in Zimbabwe. Agriculture, Ecosystems and Environment, 73, 199–204.

Ottaway, J.H., & Matthews, M.R. (1988). Trace element analysis of soil samples from a stratified archaeological site. Environmental Geochemistry and Health, 10, 105–112.

Oliver, M.A., & Webster, R. (1986). Combining nested and linear sampling for determining the scale and form of spatial variation of regionalised variables. Geographical Analysis, 18, 227–242.

Parkin, T.B. (1993). Spatial variability of microbial process in soil—a review. Journal of Environmental Quality, 22, 409–417.

Parnell, J.J., Terry, R.E., & Nelson, Z. (2002). Soil chemical analysis applied as an integrative tool for ancient human activities in Piedras Negras, Guatemala. Journal of Archaeological Science, 29, 379–404.

Parsons, R.B. (1962). Indian mounds of northeast Iowa as soil genesis benchmarks. Journal of the Iowa Archaeological Society, 12, 1–70.

Petersen, R.G., & Calvin, L.D. (1986). Sampling. In A. Klute (Ed.), Methods of soil analysis, Part 1. Physical and mineralogical methods, Agronomy Monograph No. 9 (2nd edition, pp. 33–51). Madison, WI: American Society of Agronomy.

Piccolo, A. (1989). Reactivity of added humic substances towards plant available heavy metals. The Science of the Total Environment, 81/82, 607–614.

Plant, J.A., & Raiswell, R. (1983). Principles of environmental geochemistry. In I. Thornton (Ed.), Applied environmental geochemistry (pp. 1–39). London: Academic Press.

Proudfoot, V.B. (1976). The analysis and interpretation of soil phosphorus in archaeological contexts. In D.A. Davidson & M.J. Shakley (Eds.), Geoarchaeology (pp. 93–113). London: Duckworth.

Pyatt, F.B., Amos, D., Grattan, J.P., Pyatt, A.J., & Terrell-Nield, C.E. (2002). Invertebrates of ancient heavy metal spoil and smelting tip sites in southern Jordan: Their distribution and use as bioindicators of metalliferous pollution derived from ancient sources. Journal of Arid Environments, 52, 53–62.

Pyatt, F.B., Barker, G.W., Birch, P., Gilbertson, D.D., Grattan, J.P., & Mattingly, D.J. (1999). King Solomon's miners—starvation and bioaccumulation? An environmental archaeological investigation in southern Jordan. Ecotoxicology and Environmental Safety, 43, 305–308.

Quevauviller, P., Rauret, G., Muntau, H., Ure, A.M., Rubio, R., López-Sánchez, J.F., Fiedler, H.D., & Griepink, B. (1994). Evaluation of a sequential extraction procedure for the determination of extractable trace metal contents in sediments. Fresnius Journal of Analytical Chemistry, 349, 808–814.

Rahman, S., Munn, L.C., Zhang, R., & Vance, G.F. (1996). Rocky Mountain forest soils: Evaluating spatial variability using conventional statistics and geostatistics. Canadian Journal of Soil Science, 76, 501–507.

Rappaport, B.D., Martens, D.C., Reneau, R.B., & Simpson, T.W. (1988). Metal availability in sludge amended soils with elevated metal levels. Journal of Environmental Quality, 17, 42–47.

Ross, S.M. (1994). Toxic metals in soil-plant systems. Chichester, UK: Wiley.

Saldana, A., Stein, A., & Zinck, J.A. (1998). Spatial variability of soil properties at different scales within three terraces of the Henares river (Spain). Catena, 33, 139–153.

Salomons, W. (1993). Adoption of common schemes for single and sequential extraction of trace metals in soils and sediments. International Journal of Environmental Analytical Chemistry, 51, 3–4.

Sandor, J.A., Gersper, P.L., & Hawley, J.W. (1986). Soils at prehistoric agricultural terracing sites in New Mexico: III. Phosphorus, selected micronutrients and pH. Soil Science Society of America Journal, 50, 177–180.

Sahuquillo, A., López-Sánchez, J.F., Rubio, R., Rauret, G., Thomas, R.P., Davidson, C.M., & Ure, A.M. (1999). Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. Analytica Chimica Acta, 382, 317–327.

Scokart, P.O., Meeus-Verdinne, K., & De Borger, R. (1987). Speciation of heavy metals in polluted soils by sequential extraction and ICP spectrometry. International Journal of Environmental Analytical Chemistry, 29, 305–315.

Scudder, S.J., Foss, J.E., & Collins, M.E. (1996). Soil science and archaeology. In D.L. Sparks (Ed.), Advances in agronomy (Volume 57, pp. 1–76). London: Academic Press.

Shuman, L.M. (1979). Zinc, manganese and copper in soil fractions. Soil Science, 127, 10–17.

Sjoberg, A. (1976). Phosphate analysis of anthropic soils. Journal of Field Archaeology, 3, 447–454.

Snedecor, G.W., & Cochran, W.G. (1980). Statistical methods (7th edition). Ames, IA: Iowa State University Press.

Snyder, W.S., Cook, M.J., Nasset, E.S., Karhausen, L.R., Parry Howells, G., & Tipton, I.H. (1975). Report of the task group on reference man, International Commission on Radiological Protection No. 23. Oxford: Pergamon Press.

Sposito, G. (1982). On the use of the Langmuir equation in the interpretation of “adsorption” phenonema. II. The “two surface” Langmuir equation. Soil Science Society of America, 46, 1147–1152.

Sposito, G. (1983). The chemical form of trace metals in soils. In I. Thornton (Ed.), Applied environmental geochemistry (pp. 123–170), Geology Series. London: Academic Press.

Srivastava, R.M. (1996). Describing spatial variability using geostatistical analysis. In S. Rouhani, R.M. Srivastava, A.J. Desbarats, M.V. Cromer, & A.I. Johnson (Eds.), Geostatistics for environmental and geotechnical applications. West Conshohocken, PA: American Society for Testing and Materials.

Stark, J.M. (1994). Causes of soil nutrient heterogeneity at different scales. In M.M. Caldwell & R.W. Pearcy (Eds.), Exploitation of environmental heterogeneity by plants (pp. 255–284). London: Academic Press.

Stein, J.K. (1985). Interpreting sediments in cultural settings. In J.K. Stein & W.R. Farrand (Eds.), Archaeological sediments in context (pp. 5–19). Orono, ME: Center for the Study of Early Man.

Stein, J.K. (1987). Deposits for archaeologists. Advances in Archaeological Method and Theory, 11, 337–395.

Stein, A., & Ettema, C. (2003). An overview of spatial sampling procedures and experimental design studies for ecosystem comparisons. Agriculture, Ecosystems, and Environment, 94, 31–47.

Stover, R.C., Sommers, L.E., & Silviera, D.J. (1976). Evaluation of metals in waste water sludge. Journal of the Water Pollution Control Federation, 48, 2165–2175.

Tack, F.M.G., & Verloo, M.G. (1995). Chemical speciation and fractionation in soil and sediment heavy metal analysis: A review. International Journal of Environmental Analytical Chemistry, 59, 225–238.

Tack, F.M.G., & Verloo, M.G. (1999). Single extractions versus sequential extraction for the estimation of heavy metal fractions in reduced and oxidised dredged sediments. Chemical Speciation and Bioavailability, 1(2), 43–50.

Tack, F.M.G., Vossius, H.A.H., & Verloo, M.G. (1996). A comparison between sediment metal fractions, obtained from sequential extraction and estimated from single extractions. International Journal of Environmental Analytical Chemistry, 63, 61–66.

Tessier, A., & Campbell, P.G.C. (1991). Comment on “Pitfalls of sequential extraction.” Water Resources, 25, 115–117.

Tessier, A., Campbell, P.G.C., & Besson, M. (1979). Sequential extraction procedure for the speciation of trace metals. Analytical Chemistry, 51, 844–851.

Trangmar, B.B., Yost, R.S., & Uehara, G. (1985). Application of geostatistics to spatial studies of soil properties. Advances in Agronomy, 38, 45–94.

Ure, A.M. (1995). Methods of analysis for heavy metals in soils. In B.J. Alloway (Ed.), Heavy metals in soils (2nd edition). Glasgow: Blackie Academic and Professional.

Ure, A.M., Quevauviller, P., Muntau, H., & Griepink, B. (1993). Speciation of heavy metals in solids and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. International Journal of Environmental Analytical Chemistry, 51, 135–151.

Usero, J., Gamero, M., Morillo, J., & Gracia, I. (1998). Comparative study of three sequential extraction procedures for metals in marine sediments. Environmental International, 24, 487–496.

Van Wambeke, A., & Dudal, R. (1978). Diversity of soils in the tropics. American Society of Agronomy Special Publication, 34, 13–28.

Wada, D., & Wada, S. (1999). Kinetics of speciation of copper, lead and zinc loaded to soils that differ in cation exchanger composition at low moisture content. Communications in Soil Science and Plant Analysis, 30, 2363–2375.

Walter, I., & Cuevas, G. (1999). Chemical fractionation of heavy metals in a soil amended with repeated sewage sludge application. Science of the Total Environment, 226, 113–119.

Webster, R., & Butler, B.E. (1976). Soil survey and classification studies in Ginniderra. Australian Journal of Soil Research, 14, 1–24.

Webster, R., & Oliver, M.A. (1990). Statistical methods in soil and land resource survey. New York: Oxford University Press.

Webster, R., & Oliver, M.A. (1993). How large a sample is needed to estimate the regional variogram adequately? In A. Soares (Ed.), Geostatistics troia '92 (pp. 155–166). Dordrecht, the Netherlands: Kluwer Academic.

Webster, R., Atteia, O., & Dubois, J-P. (1994). Coregionalization of trace metals in the soil of the Swiss Jura. European Journal of Soil Science, 45, 205–218.

Wells, E.C., Terry, R.E., Parnell, J.J., Hardin, P.J., Jackson, M.W., & Houston, S.D. (2000). Chemical analyses of ancient anthrosols in residential areas at Pieda Negras, Guatemala. Journal of Archaeological Science, 27, 449–462.

Wilding, L.P., & Drees, L.R. (1978). Diversity of soils in the tropics. American Society of Agronomy Special Publication, 34, 1–12.

Wilding, L.P., & Drees, L.R. (1983). Spatial variability and pedology. In L.P. Wilding, N.E. Smeck, & G.F. Hall (Eds.), Pedogenesis and soil taxonomy. I: Concepts and interactions (pp. 83–116). Amsterdam: Elsevier.

Yong, R.N., Mohamed, A.M.O., & Warkentin, B.P. (1992). Principles of contaminant transport in soils. Amsterdam: Elsevier.

Youden, M.W., & Mehlich, A. (1937). Selection of efficient methods for soil sampling. Contributions of the Boyce Thompson Institute for Plant Research, 9, 59–70.

Zemberyova, M., Zwaik, A.A.H., & Farkasovska, I. (1998). Sequential extraction for the speciation of some heavy metals in soils. Journal of Radioanalytical and Nuclear Chemistry, 229, 67–71.

Zubrow, E.B.W., & Harbaugh, J.W. (1978). Archaeological prospecting: Kriging and simulation. In I. Hodder (Ed.), Simulation studies in archaeology (pp. 109–122). Cambridge, UK: Cambridge University Press.

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