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Geochemical Analysis of Ancient Activities at Two Plazas in Cobá, Mexico

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A thesis submitted to the faculty of
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Master of Science

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ABSTRACT

Geochemical Analysis of Ancient Activities at Two Plazas in Cobá, Mexico

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Two plazas at Cobá, Mexico, may have been the place of market activity during the classic Maya period. The intense decomposition in the warm, moist soils of the Yucatan Peninsula precludes the identification of organic artifacts in archaeological contexts, but phosphorus and trace elements accumulation in soils may provide evidence of marketing activities. The spatial patterns of P and trace element concentrations were used to elucidate the types of ancient Maya activities that took place in those plazas. Phosphorus concentrations are highly correlated (p-value <0.01) with Fe, Mn, and Zn levels in both Plaza B and D. Although the soil geochemistry of Plaza B does not show a marketplace pattern in comparison with previous studies, the elemental concentrations and distributions within Plaza D join other lines of evidence to support the premise that marketplace activities took place at that location. Soil samples were analyzed using DTPA extraction, Mehlich II, Olsen, and Portable X-Ray Fluorescence (PXRF). Experiments were performed to study the suitability of PXRF for field studies. Aspects that were studied include granule size, soil moisture content, protective plastic films that could interfere with the X-Ray signal when placing the samples on top of the analyzer, and a comparison of certified soil standards to the PXRF elemental concentration readings. The results suggest that a field laboratory could be set up to air-dry and sieve soil samples to a minimum mesh size of #10 (> 2 mm).

Keywords: geochemistry, phosphorus, Archaeometry, trace metals, marketplace, Maya economy

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Chapter 1

GEOCHEMICAL ANALYSIS OF ANCIENT ACTIVITIES AT TWO PLAZAS IN COBÁ, MEXICO

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Abstract

Lines of evidence for ancient exchange plazas may include trade routes, open space, public structures, and rock alignments, but regular patterns in soil chemical concentrations also point to marketplace use. We applied geochemical and geospatial analysis of the floors of Plazas B and D at Cobá, to discover the chemical residues of P and metals associated with the exchange of foodstuffs and workshop items that may have been marketed there. The patterns of chemical residues in the floor of Plaza B suggest ritual activities while the linear, parallel patterns of P and trace element concentrations in Plaza D support the hypothesis of market exchange at that location.

Keywords: Cobá, DTPA, activity areas, marketplace, phosphorus

Introduction

Ancient Maya markets left few identifiable archaeological traces. As a result, sites of ancient activities are difficult to identify with certainty. Many items that were likely traded in markets were perishable, especially in the warm, humid conditions of Mesoamerica, and are almost certainly absent in the archaeological record (Cavanagh et al., 1988; Dahlin et al., 2009; Middleton et al., 2010; Wells, 2004). Other common goods were also taken by the inhabitants in events such as abandonment or moving (Manzanilla, 1996). Items made of organic materials may represent up to 90 percent of the total quantity of Maya's artifact record (Dahlin, 2007; Dahlin et al., 2007). Temporary structures in contemporary markets, such as market stalls, posts, and canopies leave only some traces at the end of the market day. Ancient markets, likewise, left few traces in the archaeological record, unlike the patterns of non-degradable items. Moreover, durable prestige goods such as obsidian, jade, and shells are found mostly in elite contexts and do not say much of utilitarian artifacts that might have been part of market economies (Dahlin et al., 2009).

Often-quoted letters by Cortes (1962) and Diaz del Castillo (1956) depict with great details what the marketplaces of the pre-Hispanic era looked like. Both Cortes and Castillo are astonished by the order and control of the markets, as well as with the quantity and variety of items sold (Hirth, 2009). An additional account by the Conquistadors shares his amazement at the size of the marketplace, daring to estimate that it could hold one hundred thousand people (López de Gómara, 1966), while Torquemada (1943) records peculiar marketplace transactions customs and manners.

Historically, the role of marketplaces in ancient Mesoamerica has been downplayed by a superficial treatment of the pre-Hispanic economies (Carrasco, 1978, 2001; Sanders et al., 1979), and many authors state that little attention has been given to market economies (Blanton, 1983; Braswell, 2010; Feinman and Nicholas, 2004, 2010; Garraty, 2009; Hirth 1998, 2009; Smith, 2010; Stark and Ossa 2010).

Since marketplaces are hard to identify, archaeologists have attempted to recognize market activities with a variety of approaches, such as the identification of physical remains or the manner that the marketplace affected the distribution of goods at the site and at the regional level (Dahlin et al., 2007; Garraty, 2009; Hirth, 1998; Hirth 2009; Minc, 2006). Another way to examine marketplaces is by studying the configuration of the site, focusing on the physical remains of market activity (Hirth, 1998), and it is the approach that this present study undertakes.

The configuration approach tries to determine the location of the marketplace by leveraging on three lines of evidence: large-scale architectural remains that characterize the general location of the marketplace, small-scale architecture that could help to identify the internal arrangement, and any soil geochemical signatures imprinted by marketplace activities (Dahlin et al., 2007; Dahlin et al., 2009; Hirth, 2009; Wurtzburg, 1991). In regards to large-scale architecture, marketplaces are believed to have occurred in large plazas, situated in central locations that were easily accessible, and linked by main roads and causeways. Some studies that relied on architecture remains, among other lines of evidence, to recognize marketplaces include Teotihuacan (Millon, 1973), Xochicalco (Hirth, 2000), Chichen Itza (Ruppert, 1943), Caracol (Chase, 1998), Chunchucmil (Dahlin, 2003) and Cobá (Folan et al, 1983). The small-scale architecture includes features such as aisles, stalls, and corridors, where vendors displayed their goods and through which buyers walked (Beals, 1975; Feldman, 1978; Warner, 1976; Wolf, 1959). Another characteristic to identify marketplaces is the immediacy to public structures (e.g.

ball courts or palaces) and water wells (Bair, 2010; Dahlin et al., 2007; Dahlin et al., 2009; Wurtzburg, 1991).

The third line of evidence is developed by analyzing the geochemical signatures in surface soils. It is understood that marketplaces generated a great deal of organic waste that would be assimilated into the plaza floors, thus increasing the chemical concentration of certain elements. Chemical compounds and their associated human activity that produces them have been reported in earlier studies, including: phosphorus (P) with food preparation, consumption and disposal (Terry et al., 2000), sodium (Na) and potassium (K) with the generation of ash in cooking hearths (Middleton and Price, 1996), along with iron (Fe) and mercury (Hg) compounds with the utilization of pigments in rituals (Wells et al., 2000). The elements that are being reported in this study are P, Fe, manganese (Mn), zinc (Zn), and copper (Cu), since evidence has linked these respective elements to middens (garbage disposal sites), burials, household contexts, and activities of ceremonies and feasting (Bair, 2010; Barba et al., 1996; Coronel et al., 2011; Dahlin et al., 2007; Dahlin et al., 2009; Fernández et al., 2002; Manzanilla and Barba 1990; Parnell et al., 2001; Parnell et al., 2002a; Parnell et al., 2002b; Terry et al., 2000; Terry et al., 2004;; Wells, 2004).

The recent development of geochemical methods to use as one line of evidence to identify marketplaces in the Maya area will aid in the discovery of ancient systems of economic exchange. The study and analyses of geochemical traces of phosphate and trace elements persisting in soils and floors have proven to be reliable in the identification of ancient activity areas that have been related to marketplaces. As organic materials were processed, consumed and disposed of, the phosphate and trace element constituents released from the organic matter became fixed in the surface soil (Barba, 1986; Barba and Ortiz 1992; Middleton, 1998;

Middleton and Price, 1996; Parnell et al. 2001; Terry et al. 2000). Fixed forms of P are very insoluble and resist oxidation, reduction and leaching (Holliday and Gartner, 2007; Wells, 2004). As for the nature of P, it is a fundamental constituent of living tissues (in the form of nucleic acids, phospholipids, nucleotides, etc.) (Sanchez, 2007), is present in products that households use (wood, plants, bones, meat, etc.) (Middleton, 2010) and its concentration in soils can be increased as organic materials such as plant and animal products are consumed and disposed of. Metallic residues from the crafting of stone and mineral pigments for painting are also fixed in soil surfaces (Holliday and Gartner, 2007; Parnell et al., 2002a; Parnell et al., 2002b; Wells et al., 2000).

When P and trace metals are present in higher concentrations compared to the natural background levels of the soil, this could indicate areas where activities centered on food stuffs or mineral materials handling took place. Pathways and plazas that were likely swept clean of organic materials or other types of waste have shown low phosphorus and metallic concentrations (Bair, 2010; Parnell et al., 2002a; Terry et al., 2004; Wells, 2004).

The presence of P in soils and floors at elevated concentrations has been adopted as a proxy for ancient food preparation, consumption, and disposal areas. Other minerals, such as Zn, are often correlated with P concentrations at these activity areas (Dahlin et al. 2007). Several studies of chemical analysis of Maya stucco floors have provided evidence of the effectiveness of stucco floors in fixing chemical residues that are byproducts originated from repeated activities that took place in that area (Barba, 1986; Barba et al., 1987; Barba and Manzanilla 1987; Manzanilla, 1996; Ortiz and Barba 1993; Wells, 2004). Plastered, artificial stucco floors provided a clean slate to imprint a geochemical signature by the inhabitants of the sites, since stucco floors are fairly homogenous and naturally low in P concentration (Bair, 2010; Barba et al., 1987; Holliday and Gartner, 2007; Manzanilla, 1996; Middleton et al., 2010). Furthermore, P compounds bind easily with a calcium (Ca) matrix, creating insoluble P compounds (Bair, 2010; Barba et al., 1996; Holliday and Gartner, 2007).

Objectives

As part of the field season 2010, two plazas in Cobá were sampled to identify areas of high phosphate and trace elements concentration. Patterns of high P and trace elements were analyzed to compare with previous patterns of marketplaces found in other Maya sites. A better understanding of the type of activities that could have taken place in these ancient Maya sites was acquired. The identification of market economy at Maya sites could allow us to gain more knowledge about the complex system of ancient Maya social organization, economy and trade.

In synthesis, the objectives of this study were to geochemically analyze gridded soil samples, to plot chemical concentrations geospatially and perform statistical analysis that could better elucidate patterns of P and trace elements within Plazas B and D of Cobá. A key aspect was also to map and take into account large and small-scale architecture in the configuration of the suspected marketplace area to relate the data to other lines of evidence.

Study Area

The site is located in the northeastern area of the Yucatan Peninsula, under the municipality of Cozumel (Figure 1). A portion of the ruins are within the boundaries of the present-day community of Cobá, in the state of Quintana Roo. The Cobá area is distinguished by limestone karst topography, with a landscape spotted with outcrop bedrock projections, large lakes, as well as small, linear depressions (Folan et al., 1983; Wilson, 1980). The average elevation is 20 m above sea level.

Cobá has been designated as one of the most important ancient cities of the pre-Hispanic Maya world (Benavides, 1981; Navarrete et al., 1979; Robles Castellano, 1990), because of the following attributes (Morley, 1968; Navarrete et al., 1979): proximity to five fresh-water lakes, prolonged Maya occupation (600-900-1200 AD), presence of 32 *estelas* (monuments sculpted in standing stone shafts), as well as raised causeways known as *sacbeob* (plural of *sacbe*: ancient plastered causeways; sac: white; be: road); at least 20 of them form a true web of roads that connect the central section of the site with external groups (Figure 2).

It was a city formed by a conglomerate of large-scale architecture (terminal sites) linked by a web of roads between each other (Robles Castellano, 1990). These roads vary in length between a few meters and more than 100 km (Thompson et al., 1932; Villa Rojas, 1934; Benavides, 1976a; Robles, 1976). Cobá was a major regional capital during the Late Classic and Early Post Classic period (600-900-1200 AD), with an estimated 20,000 structures which housed 55,000 inhabitants. One of the first explorers of this area, Thompson et al. (1932), suggests that Cobá, along with sites such as Zaclahtum, Chichen-Itzá, Uxmal, and Kabah, was abandoned or destroyed 300 years before the arrival of the foreigners (the Conquistadors), dating around 1212 AD (Navarrete et al., 1979).

Figure 3 shows Plaza B, which is located in the Group B of the archaeological site, according to the most common nomenclature. It consists of a Main Plaza (Thompson et al., 1932) delimited to the east by a sizeable structure called El Castillo (the castle) by Thompson et al. (1932) and also La Iglesia (the church) in Folan et al. (1983); this structure was restored in 1975. To the south, structure VII runs in an east-west direction. It is nearly 100 m long by 25 m wide, and up to 10 m tall. Structure XI is a large mound that forms the southwestern corner of the Main Plaza. To the north, structure XIII is 66 m long, running east-west, 25 m wide and close to 10 m tall. This plaza is approximately 10,000 m^2 in size. Archaeologists suggest that the main purpose of the area within Plaza B was strictly ritualistic or ceremonial (Folan et al., 1983; Thompson et al., 1932).

Plaza D (Figure 4) is delimited by the following structures: to the north, the structures III and VIII; to the west, the structures IX, X, and the end of the very important Sacbe I; to the east, structures IV, V, VI, and VII; and to the south the structures of greater altitude XI and XIV to the south. This plaza includes a very peculiar edifice called El Xaibe (also referred as the Cone) that presents round corners. Restored in the year 1975 (Folan et al., 1983), its focal location also originated another name for El Xaibe: the Crossroads Structure (Benavides, 1976b). Sacbe I is the longest of all the *sacbeob*: leaving from Plaza D it arrives at Yaxuna, an archaeological site a little over 100 km away (Navarrete et al., 1979). Sacbe I reaches a maximum height of 7 m and a width of 10 m. It is important to note that while Sacbe I starts right next to the boundaries of Plaza D, Sacbe 4, 6, and 8 also start very close to the borders of the plaza (Thompson et al., 1932). This suggests that Plaza D was a much transited location. The function of El Xaibe is still a mystery. However, Folan et al. (1983) suggested that rituals were offered at The Cone by merchants coming in and out of the plaza.

Soils encountered in the Plazas at Cobá are formed from highly weathered stucco and plaza fill. Outside the plazas, most soils are Leptosols (Bautista et al., 2005): a very shallow, gravelly type of soil. In the Yucatan peninsula, the soils formed when calcareous parent material weathered in the semi humid climate. For the most part, the soils in the Yucatan Peninsula are well-drained through the permeable limestone.

Methodology

Soil P is found in different forms (soluble and labile inorganic P, organic P, inorganic P fixed to Al, Ca, or Fe compounds, etc.), and not all analytical methods are able to measure these different forms at the same time. Thus, several methods exist to analyze for the different fraction of soil P (Terry et al., 2000). In general, four types of analysis have been performed in archaeology studies: chemical digestion of soil for total P concentrations, P fractionation, the spot test or ring test, and the extraction of soluble P by weak-acid or basic solutions (Holliday and Gartner, 2007; Terry et al., 2000). Often, extractable P does not correlate to total P. This lack of correlation could be attributed to several variables; for instance, while the extractable P method will not dissolve mineral and humus compounds that fix P, the total digestion will (generally by means of strong acids such as nitric and perchloric acid). However, the absolute concentration of soil P is not critical to know for archaeological studies, just the spatial variability of P levels in the soil. In regards to weak-acid and basic solution extractions, Terry et al. (2000) reported that the relationship between the weak-acid extraction (Mehlich II) and the basic solution extraction (Olsen) is strong ($r = 0.91$) and significant ($p < 0.05$). It must be mentioned that calcareous soil samples analyzed by the Mehlich II method tend to yield higher extractable P concentrations than the Olsen method, but these methods are correlated among each other nonetheless (Terry et al., 2000).

Phosphorus Analysis

A field laboratory was set up in the city of Cobá to analyze samples taken from Plaza B during the day. Timely and rapid soil P analysis allowed us to inspect more closely areas with high P concentrations before returning to the United States. All the samples from Plaza B were analyzed for P in Cobá using the Olsen method. In Plaza B, the following procedure was used to extract and analyze soil phosphorus: 2 g of air-dried and sieved (< 2 mm) soil was mixed with 20 ml of Olsen bicarbonate extraction solution (0.5 M $NaHCO_3$ buffered at pH 8.5), using 50 ml jars attached to a board allow analyze of six samples at a time. The samples were shaken for 30 minutes, after which they were filtered through a 15-cm diameter filter paper, collecting the filtrate in a similar group of six 50 ml jars. Then, 1 ml of the solution was dispensed into a colorimeter vial and diluted to 10 ml with deionized water, for a total dilution factor of 100. A packet of PhosVer 3 Reagent (HACH reagents, Ames, IA) was added to each sample, shaken for 60 seconds, and allowed to settle for four minutes for color development. Finally, the samples were measured with a HACH DR/850 Colorimeter, using the % Transmittance function at a wavelength of 690 nm. Phosphorus was calculated in mg kg^{-1} by means of a standard curve developed with known P levels.

Samples collected in Plaza D were delivered to the Brigham Young University Soil and Plant Analysis Laboratory (Provo, Utah, USA). In the formal laboratory setting, the Mehlich II extraction solution was used instead of the Olsen solution primarily because Mehlich II extraction time is 5 minutes instead of 30 minutes for the Olsen method. All other steps remained the same as described in the paragraph above. The relative standard deviation for the standard soil sample analyzed by the Mehlich II method was 4.4% (n=12), and for the Olsen method was 13.5% (n=10). The samples from Plaza D (n=376) were collected on a 10 m grid. However, from these 376 samples, only 354 samples had enough soil weight to perform DTPA analysis. Consequently, the results from the analysis of these 354 samples were reported in this study. Detailed information about the modifications in the Mehlich II method can be found in Terry et al. (2000). Plaza D covered a much bigger area than Plaza B. Structures, paths, rock alignments, and other features were recorded using Magellan MobileMapper™ units. Except for the contemporary paths built to accommodate tourist transit, the entire area was covered with thick vegetation. Transects were cut through the vegetation in a north-south, east-west direction.

Grids of 10 m and 5 m intervals were established by mean of flags and measuring tapes. Compasses and GPS units were also used to aid in the sampling and architecture mapping. Soil surface samples of 0-10 cm were collected using a plastic trowel following the removal of leaf litter layer and placed in a sterile plastic bag.

DTPA Analysis

At the Brigham Young University laboratory, samples for both Plaza B and D were analyzed for extractable trace metal concentrations using the DTPA (diethylenetriaminepentaacetic acid) chelate extraction procedure developed by Lindsay and Norvell (1978). Ten grams of air dried, sieved (<2 mm) soil were extracted with 20 ml of 0.005 M DTPA solution buffered at pH 7.3. The samples were shaken for two hours, after which the extracting solution was separated from the soil by centrifugation and filtration. The concentrations of Cu, Fe, Mn, and Zn were determined simultaneously on a Thermo ICPAES (Inductively Coupled Plasma Atomic Emission Spectrometer). DTPA solution was used as a blank and one quality control soil sample was analyzed with each run. The relative standard deviations for the extractable DTPA elements of the standard soil (n=10) were 3.8% for Cu, 3.1% for Fe, 9.4% for Mn, and 5.5% for Zn. The repeated analysis of the standard soil sample shows the high reproducibility of the obtained results.

Extractable element concentrations of study site soils were plotted with Surfer Software (Golden, CO) using a variogram analysis to determine spatial variability between different samples. The kriging model and variogram analysis were used to map the concentration isopleths. Correlation matrices of concentrations were produced to determine similarities among chemical concentrations of different elements within each plaza.

The samples collected in this study were from anthropogenic plaza fill and weathered stucco. There is no appropriate control for these soil samples. Background samples are usually a reason of concern among archaeologists (King, 2008; Wells, 2004). To address this issue, previous geochemical studies have determined background concentrations by averaging the 10% of the lowest concentrations in the samples (Bair, 2010; Dahlin et al., 2007; Fernández et al., 2002; Hutson and Terry, 2006; King, 2008; Parnell et al., 2001; Terry et al., 2004; Wells et al., 2000). The plaza samples lowest in P and trace elements may represent areas of lowest chemical enrichment by ancient human activities. All the statistical analyses were performed using the software JMP (SAS Institute Inc., Cary, NC).

Results and discussion

Plaza B

In total, 299 surface samples were collected in Plaza B. The maximum, minimum, averages, and background values of DTPA extractable elements in Plaza B are shown in Table 1. The site workers regularly use machetes and rakes to maintain the eastern third of Plaza B free of understory vegetation to accommodate tourists close to the structure called La Iglesia. The first six rows of samples were taken in the area clear of understory vegetation. The debris line that separated the vegetated from the non-vegetated area is all the organic material from trees nearby that has been raked into a pile approximately 0.5-1 m high, and appears to have accumulated for a long time. Through walking and scouting, we spotted, followed, and recorded rock alignments and structures (Figure 3).

The P concentration isopleths in Plaza B is shown in Figure 5. The areas of elevated P were on the north side of the plaza, with a highest P concentration of 109 mg kg^{-1}. Sample P concentrations were very low (4-6 mg kg^{-1}) close to La Iglesia and other structures that delimit the plaza. The P levels were also high along the contemporary line of debris, which was expected and most likely not related to ancient Maya activities. Background level of Olsen extractable P was approximately 7.5 mg kg^{-1}.

DTPA extractable Fe was highest in the non-vegetated area, relatively close to La Iglesia on the east side of the plaza (Figure 6). The highest Fe concentration was 24 mg kg^{-1}. Iron was found in concentrations of 10 to18 mg kg^{-1} close to the west side of the plaza. Clearly, some Fe concentrations were high also next to the debris line. Iron background level was of 2.8 mg kg^{-1}. It is possible that contemporary, long-term activities with Fe-based machetes and rakes contributed to these elevated Fe levels. Terry et al. (2004) reported high Fe levels in the earthen floor of the contemporary guard’s house at Aguateca, Guatemala; the high Fe concentrations were aligned with the benches where the guards sharpened their machetes.

Among the trace elements, Cu concentrations were very low, with the highest sample concentration around 1.6 mg kg^{-1} (Figure 7). The only noticeable pattern of Cu was located in the southwestern corner of the Plaza, close to structure VII and XI. Other spots with concentrations just above the limits of detectability of the ICPAES (~ 0.5 mg kg^{-1}) were distributed around the plaza without a clear pattern.

The Mn concentration isopleths is shown in Figure 8. The highest concentrations were around the southwestern corner of the plaza, ranging from 22 to 29 mg kg^{-1}. Manganese concentrations of 17-22 mg kg^{-1} were also distributed mostly in the west side of the plaza. Background level of Mn was of 5.9 mg kg^{-1}. Manganese is a common element associated with pigments (Bair, 2010; Wells, 2000), and elevated concentrations of Mn could be attributed to its presence in pigments used in ritual, workshop, and painting activities.

Zinc also was identified in high concentrations next to the southwestern corner of the plaza, around 7-11 mg kg^{-1} (Figure 9). The highest concentration (18 mg kg^{-1}) was identified in the southeast corner of the plaza at the foot of the Structure VII staircase. Background Zn level was of 0.9 mg kg^{-1}.

In the correlation matrix of extractable elements created for Plaza B, P was significantly correlated to Zn (r = 0.36) but negatively correlated to Fe (r = -0.40), meaning that when P was found, Fe was absent, and vice versa (Table 2). This negative correlation could show that activities involving these elements took place at different locations within the plaza.

Plaza D

The maximum, minimum, average, and background values of extractable elements in Plaza D are listed in Table 1. Phosphorus concentrations in the stucco floor of the plaza were not as high as reported in previous studies of plaza soils, such as those in Ceibal Group A (maximum P level: 533 mg kg^{-1}; average 81 mg kg^{-1}) (Bair, 2010), and Area D at Chunchucmil (maximum P level: 272 mg kg^{-1}; average 57 mg kg^{-1}) (Dahlin et al., 2010), but there was a pattern in the distribution of P in Plaza D (Figure 10). The linear, parallel patterns of elevated P concentration were located in the northwest corner of Plaza D. Background P level was of 7.4 mg kg^{-1}. In general, Plaza D has a pattern more closely related to other suspected marketplaces, such as the ones mentioned above. The patterns of P appeared to form three parallel lines, in a NE direction, and perpendicular to both the SW-oriented structures and the course of Sacbe I. These lines also appeared to be confined to the NW area within the plaza. The spatial distribution of these lines suggests that market aisles were erected and foodstuff were prepared, sold, and/or disposed of in this area. A similar pattern where high P levels were cornered against the delimiting structures is seen in Central Plaza Group A (Bair, 2010). The P distribution within Plaza D differed greatly from the P distribution seen in the current study of Plaza B, where elevated P appeared at the foot of structure XIII and along the contemporary debris line (Figure 5).

DTPA extractable Fe was found in high concentrations in several locations (Figure 11). First, a group of samples with high levels (36-46 mg kg^{-1}) were seen next to the start of Sacbe I, in the west side of the plaza. Then, elevated concentrations were in samples slightly outside the plaza, around the northeast area (41-46 mg kg^{-1}). A very interesting pattern was located around El Xaibe, in the east corner of the grid. High Fe concentrations of 26-31 mg kg^{-1} surrounded the Cone. It could be possible that the stucco of El Xaibe was painted with iron oxide pigments, and with time the stucco eroded down to form part of the soil. Another possible source of elevated Fe was the modern implements used to maintain the tourist paths, to rake loose plant material, or to cut vegetation. The highest Fe concentration was about 50.8 mg kg^{-1} and background levels were close to 2.9 mg kg^{-1}.

Copper was very low throughout the entire grid area (Figure 12). Concentrations did not exceed 2.5 mg kg^{-1}. A group of samples presented the highest levels of Cu (1.8-2.2 mg kg^{-1}) close to the middle of the plaza. Another area of elevated concentrations was seen in the northwest corner. However, the concentrations were so low that it is not possible to determine how the Cu soil concentrations came to be.

The element Mn showed a very interesting pattern in this plaza (Figure 13). The pattern of Mn closely resembled the one produced by the Fe concentration. Its highest levels of 41-50 mg kg^{-1} appeared in the southwest corner, close to the start of Sacbe I. Background Mn level was of approximately 5.7 mg kg^{-1}.

Zinc also showed a resemblance of the patterns created by the other trace elements (Figure 14). The group of samples with the highest concentrations was mostly located in the southwest corner of the plaza (4-7 mg kg^{-1}), close to the start of Sacbe I. Then, the pattern moved north and east of that area. Moreover, samples also exhibited high levels next to El Xaibe (4-7 mg kg^{-1}). In general, the concentrations of Zn were not elevated, but the samples clearly showed a pattern. Background levels were close to 0.8 mg kg^{-1}. The distribution of the Zn concentrations at this location had a resemblance of the pattern exhibited by the P levels, being the P concentrations shifted slightly northward in the grid. Phosphorus and Zn are generally known to be associated with each other in plant uptake studies.

From the correlation matrix of extractable elements from Plaza D, P had a highly significant negative correlation between Fe (r = -0.394), and Mn (r = -0.148), and a positive correlation with Zn (r = 0.263) (Table 3). The negative correlation of P with Mn and Fe suggests that specific activities were performed in different areas of the plaza, as it was suggested for the East Palace Court (Group E) location in Ceibal, Guatemala (Bair, 2010). Except for the correlation between Fe and Mn (r = 0.070), all the correlations between the trace elements were highly significant (p-value <.01). The highly significant correlation between P and Zn is important to notice, since it has been seen in other studies that P and Zn usually correlate with each other (Bair and Terry, 2009; Dahlin et al., 2007). For example, the correlation for P and Zn was also high in the following studies (correlations with * denote p-value significance at the 0.05

level and ** at the 0.01 level): Antigua, Guatemala, Open-Air Contemporary Market (r = 0.407*) (Dahlin et al., 2007); Group P-114 at Mayapan, Mexico (r = 0.366**), Group Y-45 (r = 0.412**), Square K (r = 0.720**), Central Plaza in Group A of Seibal (r = 0.187**), Group C in Seibal (r = 0.294**) (Bair, 2010); and Platform 341, Structures 351 and 383 at Xtobo, Mexico (r = 0.570**), Xtáabay Feature (r = 0.585**) (Anderson et al., 2011). This correlation between P and Zn may have an explanation when looking at the concentration of these elements in crops. For example, corn leaves have reported P concentrations of 220,000 mg kg^{-1} and Zn concentrations of 22 mg kg^{-1} (Mills and Jones Jr., 1997). Furthermore, a ratio of 200:1 in plant tissue between P and Zn is considered critical for growth in major crops (Jones Jr. et al., 1991). It is possible that plant matter was the major source of P and Zn enrichment in the soil, but though Fe and Cu are also micronutrients present in plant matter, mineral pigments constitute an additional source of Fe and Cu likely used by the ancient Maya (Wells, 2000).

Sacbe samples

In total, 28 *sacbe* samples were collected. The *sacbe* soil samples were taken on both sides of the path, as well as on top of the causeway, about 20 m west of the start of the *sacbe* close to the boundaries of Plaza D. The maximum, minimum, and average concentrations of the soil extractable elements are shown in Table 4.

Compared to the samples inside Plaza D, the elemental concentrations in the *sacbe* samples were low. Phosphorus averages were 12.3 mg kg^{-1} on top of the *sacbe*, and 5.8 mg kg^{-1} on the edges. The concentrations for the element Mn were similar, i.e. 23.1 mg kg^{-1} on top of the *sacbe* and 23.6 mg kg^{-1} on the edges. Copper concentrations were below 1 mg kg^{-1}, while Fe averages were 8.2 mg kg^{-1} on top and 14 mg kg^{-1} on the edges of the *sacbe*. Zinc levels on the edges were also low (2 mg kg^{-1}) and on top were higher (8.4 mg kg^{-1}). These low values suggest that activity related to foodstuff and craft production was probably nonexistent at this specific location of Sacbe I. High traffic areas have usually shown low elemental concentrations, since it is believed that any debris and organic matter would have been swept to the roadside (Bair, 2010; Barba and Ortiz, 1992; Dahlin et al., 2007; Fernández et al., 2002; Parnell et al., 2001; Parnell et al., 2002a; Terry et al., 2004; Wells, 2004).

Conclusions

Cobá was one of the most important cities of its time, and its influence extended through the network of *sacbeob* that converge at the site. The two plazas studied in this project, Plaza B and D, are not the only plazas where ancient marketplace activities may have occurred at this site. However, we believe that Plaza D does exhibit a marketplace pattern, such as having clusters of extractable elements away from major causeways, being a central location where many s*acbeob* converge, being close to public structures, and having amenities such as a water reservoir north of Plaza D (Dahlin et al., 2007; Dahlin et al., 2009; Wurtzburg, 1991). Moreover, the fact that there are two fresh-water lakes in the vicinity of the site cannot be overlooked, considering that surface water is almost absent from the Yucatan Peninsula. These characteristics, plus the geochemical distribution of extractable elements in association with large and small-scale architecture, suggest that marketplace activities occurred at this plaza. A pattern of elevated P, Mn, and Zn in the NW portion of the plaza suggests that activities of medium intensity occurred in that area. Moreover, the NW corner is close to the very important Sacbe I and could have been a place where vendors exhibited their items for people coming and leaving the site through Sacbe I.

In contrast, our data obtained in the study does not suggest any evidence that Plaza B was a place where marketplace activities occurred. There are few *sacbeob* that converge at this plaza or near it. As stated by archaeologists, this plaza was most likely used for ceremonial services (Folan et al., 1983; Thompson et al., 1932). Phosphorus distributions within Plaza B do not show a pattern of linear, parallel elemental concentrations that may represent ancient anthropogenic activities, but rather modern activities of sweeping and cleaning organic material in the area, related to the tourism at the site. We also believe that the Fe concentrations are more related to modern anthropogenic activities of raking organic debris and cutting vegetation using machetes than to ancient activities by the Maya. The distribution of Mn levels, by themselves, cannot hint that activities occurred at the south portion of the plaza, and Cu levels are too low to make any assumptions. The present study provides further evidence that human activities leave identifiable traces imprinted in the soil chemistry, and these signatures can aid in the interpretation of archaeological sites (Middleton et al., 2010).

References

Anderson, D. S., Bair, D.A., Terry, R.E., 2011. Soil geochemical analyses at the Preclassic site of Xtobo, Yucatan, Mexico. Ancient Mesoamerica. In Press.

Bair, D.A., 2010. The Dirt on the Ancient Maya: Soil Chemical Investigations of Ancient Maya Marketplaces. M.S. Thesis. Department of Plant and Wildlife Sciences. Brigham Young University, Provo. http://contentdm.lib.byu.edu/ETD/image/etd3789.pdf (accessed 08/09/2011).

Bair, D.A., Terry, R.E., 2009. Estudios geoquímicos de suelo en Mayapán, temporada 2008, in: Masson, M.A., C. Peraza Lope, C., Hare, T.S. (Eds.), Proyecto los fundamentos del poder económico de Mayapán, temporada 2008, University at Albany-SUNY, Albany, NY, pp. 377-384.

Barba, L. A., 1986. La química en el estudio de aéreas de actividad. Unidades habitacionales mesoamericanas y sus áreas de actividad, in: Manzanilla, L (Eds.). Arqueología, Serie Antropológica 76. Instituto de Investigaciones Antropológicas, Universidad Nacional Autónoma de México, Mexico City, pp. 21-39.

Barba L., Ludlow B., Manzanilla L., Valdez R., 1987. La vida doméstica en Teotihuacán: Un estudio interdisciplinario. Ciencia y Desarrollo 77, 21-32.

Barba, L., Manzanilla L., 1987. Superficie/excavación. Un ensayo de predicción de rasgos arqueológicos desde la superficie en Oztoyahualco. Antropológicas 1: 19-46.

Barba, L., Ortiz, A., 1992. Análisis químico de pisos de ocupación: un caso etnográfico en Tlaxcala, Mexico. Latin American Antiquity 3:63-82.

Barba L., Ortiz A., Link K., Lopez Lujan L., Lazos L., 1996. Chemical analysis of residues in floors and the reconstruction of ritual activities at the Templo Mayor, Mexico, in: Orna,

M. V. (Ed.). Archaeological chemistry: Organic, inorganic, and biochemical analysis, American Chemical Society, Washington, DC, pp. 139-156.

Bautista, F., Díaz-Garrido, S., Castillo-González, M., Zinck, J.A., 2005. Spatial Heterogeneity of the Soil Cover in the Yucatán Karst: Comparison of Mayan, WRB, and Numerical Classifications. Eurasian Soil Science 38, pp. S81-S88.

Beals, R., 1975. The Peasant Marketing System of Oaxaca, Mexico. University of California Press, Berkeley.

Benavides Castillo, A., 1976a. El sistema prehispánico de comunicaciones terrestres en la región de Cobá, Quintana Roo, y sus implicaciones sociales. Tesis Profesional, ENAH, México.

Benavides Castillo, A., 1976b. Coba, Quintana Roo. Reporte de actividades en Coba: un sitio maya en Quintana Roo. Cuadernos de los Centros (Mexico) No. 26:1-103.

Benavides Castillo, A., 1981. Los Caminos de Cobá y sus Implicaciones Sociales (proyecto Cobá). México: Instituto Nacional de Antropología e Historia.

Blanton, R. E., 1983. Factors underlying the origin and evolution of market systems, in: Ortiz, S. (Ed), Economic anthropology, University Press of America and Society for Economic Anthropology, Lanham, pp. 51–66.

Braswell, G.E., 2010. The rise and fall of market exchange: a dynamic approach to ancient Maya economy, in: Garraty, C.P, Stark B.L. (Eds). Archaeological Approaches to Market Exchange in Pre-Capitalist Societies, University of Utah Press.

Carrasco, P., 1978. La economía del México prehispánico, in: Carrasco, P., Broda, J. (Eds) Economía, Política e Ideología, México City: Instituto Nacional de Antropología e Historia, pp. 15–74.

Carrasco, P., 2001. Economic organization and development, in: Carrasco, D (Ed), The Oxford

Encyclopedia of Mesoamerican Cultures: The Civilizations of Mexico and Central America, Oxford: Oxford University Press, 1:363–66.

Cavanagh,W.G., Hirst S., Litton, C.D., 1988. Soil Phosphate, Site Boundaries, and Change Point Analysis. Journal of Field Archaeology 15: 67–83.

Chase, A., 1998. Planeación cívica e integración de sitio en Caracol, Belize: definiendo una economía administrada del período clásico Maya. Investigaciones de la Cultura Maya 6:26–44.

Coronel, E.G, Terry, R. E., Ramos, C. E., 2011. Prospección de fósforo en búsqueda de basureros antiguos en Tikal, Guatemala. Lentz, D. L., Ramos, C.E., Dunning, N.P., Scarborough, V.L., Grazioso Sierra, L. Proyecto de silvicultura y manejo de aguas de los antiguos Mayas de Tikal. Informe entregado a la Dirección de Patrimonio Cultural y Natural de Guatemala, Guatemala. 387 p.

Cortés H., 1962. Five letters of Cortes to the emperor. Norton and Company, New York.

Dahlin, B.H., 2003. Chunchucmil: A Complex Economy in NW Yucatan. Mexicon 25:129–138.

Dahlin, B.H., 2007. Phantom Artifacts at Chunchucmil (and elsewhere), Paper delivered at the Annual Meeting of the Society for American Archaeology, San Juan, Puerto Rico.

Dahlin, B.H., Jensen, C., Terry, R., Wright, D., Beach, T., 2007. In Search of an Ancient Maya Market. Latin American Antiquity 18:363–384.

Dahlin B.H., 2009. Ahead of Its Time? The Remarkable Early Classic Maya Economy of

Chunchucmil. Journal of Social Archaeology 9:341-367.

Dahlin B.H., Bair D., Beach T., Moriarty M., Terry R., 2010. The dirt on food: ancient feasts and markets among the Lowland Maya, in: Staller J. E., Carrasco M. (Eds.), Pre-Columbian Foodways: Interdisciplinary Approaches to Food, Culture, and Markets in Ancient

Mesoamerica, Springer, New York. pp. 191-232.

Diaz del Castillo, B., 1956. The Discovery and Conquest of Mexico, 1517-1521. Farrar, Strauss and Cudahy, New York.

Feinman, G.M., Nicholas, L.M., 2004. Unraveling prehispanic highland Mesoamerican economy: production, exchange, and consumption in the Classic period Valley of Oaxaca, in:

Feinman, G.M., Nicholas, L.M. (Eds.), Archaeological Perspectives on Political Economy, Salt Lake City: Univ. Utah Press, pp. 167–88.

Feinman, G.M., Nicholas, L.M., 2010. A multiscalar perspective on market exchange in the Classic period Valley of Oaxaca, in: Garraty, C.P., Stark, B.L. (Eds.), Archaeological Approaches to Market Exchange in Ancient Societies. Boulder, Univ. Colo. Press, pp. 85-98.

Feldman, L., 1978. Inside a Mexican Market, in: Lee, T., Navarrete, C. (Eds.), Mesoamerican Communication Routes and Culture Contacts, Papers of the New World Archaeological Foundation No. 40. Brigham Young University, Provo, pp. 219–222.

Fernández, F.G., Terry, R.E., Inomata, T., Eberl, M., 2002. An ethnoarchaeological study of chemical residues in the floors and soil of Q'eqchi' Maya houses at Las Pozas, Guatemala. Geoarchaeology: An International Journal 17:487-519.

Folan, W.J., Kintz, E.R., Fletcher, L.A., 1983. Coba: a classic Maya metropolis. New-York: Academic press.

Garraty, C.P., 2009. Evaluating the distributional approach to inferring market exchange: a test case from the Mexican Gulf lowlands. Lat. Am. Antiq. 20:157–74.

Hirth, K.G., 1998. The distributional approach: a new way to identify marketplace exchange in the archaeological record. Curr. Anthropol. 39:451–76.

Hirth, K.G., 2000. Ancient Urbanism at Xochicalco. The Evolution and Organization of a Prehispanic Society. Archaeological Research at Xochicalco Vol. 1. The University of Utah Press, Salt Lake City.

Hirth, K.G., 2009. Craft production in a central Mexican marketplace. Ancient Mesoam. 20:89–102.

Holliday, V.T., Gartner, W.G., 2007. Methods of soil P analysis in archaeology. Journal of Archaeological Science 34:301-333.

Hutson, S.R., Terry, R.E., 2006. Recovering social and cultural dynamics from plaster floors: chemical analyses at ancient Chunchucmil, Yucatan, Mexico. Journal of Archaeological Science 33:391-404.

JMP, Version 9. SAS Institute Inc., Cary, NC, 1989-2011.

Jones Jr., J.B., Wolf, B., Mills, H.A., 1991. Plant Analysis Handbook: A practical sampling, preparation, analysis and interpretation guide. Athens, Georgia: Micro-Macro Publishing Inc., pp. 7-8.

King, S.M., 2008. The Spatial Organization of Food Sharing in Early Postclassic Households: an Application of Soil Chemistry in Ancient Oaxaca, Mexico. Journal of Archaeological Science 35:1224-1239.

Lindsay, W.L. and Norvell, W.A., 1978. Development of a DTPA Soil Test for Zinc, Iron, Manganese, and Copper. Soil Sci. Soc. Am. J. 42: 421-428.

López de Gómara, F., 1966. Cortés: The Life of the Conqueror by his Secretary. Berkeley: Univ. Calif. Press.

Manzanilla, L., 1996. Corporate groups and domestic activities at Teotihuacan, Latin American

Antiquity 7:228-246.

Manzanilla, L., Barba, L., 1990. The study of activities in Classic households: two case studies from Cobá and Teotihuacan. Ancient Mesoamerica 1:41-49.

Middleton, W.D., 1998. Craft specialization at Ejutla, Oaxaca, Mexico: An archaeometric study of the organization of household craft production. Ph.D. dissertation. Madison: University of Wisconsin.

Middleton, W. D., Price, T. D., 1996. Identification of activity areas by multi-elemental characterization of sediments from modern and archaeological house floors using inductively coupled plasma – atomic emission spectroscopy, Journal of Archaeological Science, 23, 673–87.

Middleton, W.D., Barba, L., Pecci, A., Burton, J.H., Ortiz, A., Salvini, L., Rodriguez S.R., 2010. The Study of Archaeological Floors: Methodological Proposal for the Analysis of Anthropogenic Residues by Spot Tests, ICP-OES, and GC-MS. Journal of Archaeological Method and Theory 17(3):183-208.

Millon, R., 1973. Urbanization at Teotihuacan, Mexico. The Teotihuacan Map Vol. 1, Part 1. University of Texas Press, Austin.

Mills, H.A., Jones, B.J., 1997. Plant analysis handbook II: a practical sampling, preparation, analysis, and interpretation guide. Ball Publishing, Batavia, IL, USA.

Minc, L., 2006. Monitoring Regional Market Systems in Prehistory: Models, Methods, and Metrics. Journal of Anthropological Archaeology 25:82–116.

Morley, S.G., 1968. The Ancient Maya, Stanford University Press.

Navarrete, C., Con, M.J., Martínez Muriel, A., 1979. Observaciones arqueológicas en Cobá, Quintana Roo, Instituto de Investigaciones Filológicas, UNAM.

Ortiz Butron, A., Barba, L., 1993. La química en los estudios de aéreas de actividad, in: Manzanilla, L. (Ed.), Anatomía de un conjunto residencial teotihuacano en Oztoyahualco, vol. 2. Universidad Nacional Autónoma de México, Mexico City, pp. 617-660.

Parnell, J.J., Terry, R.E., Golden, C., 2001. The use of in-field phosphate testing for the rapid identification of middens at Piedras Negras, Guatemala. Geoarchaeology: An International Journal 16:855-873.

Parnell, J.J., Terry, R.E., Nelson, Z., 2002a. Soil chemical analysis applied as an interpretive tool for ancient human activities at Piedras Negras, Guatemala. Journal of Archaeological Science 29:379-404.

Parnell, J.J., Terry, R.E., Sheets, P.D., 2002b. Soil Chemical analysis of ancient activities in Cerén, El Salvador: A case study of a rapidly abandoned site. Latin American Antiquity 13:331-342.

Robles Castellano, F., 1976. Ixil. Cobá: Un sitio Maya en Quintana Roo, in: Benavides, A.C. (Ed.). Cuaderno de los Centros, no. 26, INAH, México, pp. 174-206.

Robles Castellanos, F., 1990. La Secuencia Cerámica de la Región de Cobá, Quintana Roo. Instituto Nacional de Antropología e Historia, Mexico, DF.

Ruppert, K., 1943. The Mercado, Chichen Itza, Yucatan. Contributions to American Anthropology History No. 43. Carnegie Institution of Washington D.C, pp. 223–260.

Sanchez, C.A., 2007. Phosphorus, in: Barker, A.V., Pilbeam, D.J. (Eds.), Handbook of Plant Nutrition. CRC Press, Boca Raton pp. 51-90.

Sanders, W.T., Parsons, J.R., Santley, R.S., 1979. The Basin of Mexico: Ecological Processes in the Evolution of a Civilization. New York: Academic.

Smith, M.E., 2010. Regional and local market systems in Aztec period Morelos, in: Garraty, C.P., Stark, B.L. (Eds.), Archaeological Approaches to Market Exchange in Ancient Societies. Boulder: Univ. Colo. Press pp. 161–82.

Stark, B.L., Ossa, A., 2010. Origins and development of Mesoamerican marketplaces: evidence from south-central Veracruz, in: Garraty, C.P., Stark, B.L. (Eds.), Archaeological Approaches to Market Exchange in Ancient Societies. Boulder: Univ. Colo. Press pp. 99–126.

Terry, R.E., Fernández, F.G., Parnell, J.J., Inomata, T., 2004. The story in the floors: chemical signatures of ancient and modern Maya activities at Aguateca, Guatemala. Journal of Archaeological Science 31:1237-1250.

Terry, R.E., Hardin, P.J., Houston, S.D., Jackson, M.W., Nelson, S.D., Carr, J., Parnell, J., 2000. Quantitative phosphorus measurement: A field test procedure for archaeological site analysis at Piedras Negras, Guatemala. Geoarchaeology: An International Journal 15:151-166.

Thompson, J.E., Pollock, H.E.D., Charlot, J., 1932. A preliminary study of the ruins of Cobá, Quintana Roo, Mexico. Carnegie institution of Washington Pub. No. 424, Washington, D.C.

Torquemada, J., 1943. Monarquía Indiana. Mexico City: S. Chávez Hayhoe.

Villa Rojas, A., 1934. The Yaxuna-Cobá Causeway. Contributions to American Archaeology 2(9):187-208. Carnegie Institution of Washington. Washington, D.C.

Warner, J., 1976. Survey of the Market System in the Nochixtlan Valley and the Mixteca Alta, in: Cook, S., Disken, M. (Eds.), Markets in Oaxaca. University of Texas Press, Austin, pp. 107–131.

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 Piedras Negras, Guatemala. Journal of Archaeological Science 27:449-462.

Wells, C., 2004. Investigating activity patterning in Prehispanic plazas: Acid-extraction ICP/AES analysis of anthrosols at Classic period El Coyote, northwest Honduras. Archaeometry 46:67-84.

Wilson, E.M., 1980. The physical geography of the Yucatan Peninsula, in: Moseley, E.H., Terry, E.D. (Eds.), Yucatan, a world apart. University of Alabama Press, Alabama.

Wolf, E., 1959. Sons of the Shaking Earth. The University of Chicago Press, Chicago.

Wurtzburg, S.J., 1991. Sayil: Investigations of urbanism and economic organization at an ancient Maya city. Statue University of New York, Albany.

Tables

Table 1. Maximum, minimum, and average concentrations (mg kg^{-1}) of P, Cu, Fe, Mn, and Zn in soils from Plaza B and D. The background concentrations are calculated by averaging the 10 percent of samples lowest in concentration.

	P	**Cu**	**Fe**	**Mn**	**Zn**
Plaza D, n= 354					
Maximum	14.7	2.6	50.8	50.2	7.9
Minimum	6.5	<0.1	<0.1	<0.1	<0.1
Average	9.2	0.4	12.6	17.8	2.2
Background	7.4	0.1	2.9	5.6	0.8
Plaza B, n= 299					
Maximum	109.4	1.6	24.1	29.1	18.2
Minimum	6.3	0.1	0.7	3.7	0.6
Average	15	0.3	10.8	14.7	2.9
Background	7.5	0.2	2.8	5.9	0.9

Table 2. Pearson’s correlation matrix of DTPA extractable P, Cu, Fe, Mn, and Zn for soil samples collected within Plaza B.

Multivariate Correlations (Pair-Wise)

	Cu	**Fe**	**Mn**	**Zn**
P	**0.2695**	**-0.4025**	**0.2115**	**0.3601**
Cu		**-0.1783**	**0.729**	**0.5275**
Fe			-0.0602	**-0.1849**
Mn				**0.3006**

Highly significant (<.01)

Table 3. Pearson's correlation matrix of DTPA extractable P, Cu, Fe, Mn, and Zn for soil samples collected within Plaza D.

Multivariate Correlations (Pair-Wise)

	Cu	**Fe**	**Mn**	**Zn**
P	0.042	**-0.394**	**-0.148**	**0.263**
Cu		**0.140**	**0.534**	**0.341**
Fe			**0.359**	0.070
Mn				**0.397**

Highly significant (<.01)

Table 4. Maximum, minimum, and average concentrations (mg kg^{-1}) of P, Cu, Fe, Mn, and Zn in soils collected on top and on the edges of Sacbe I.

		P	**Cu**	**Fe**	**Mn**	**Zn**
Sacbe Top	**n= 6**					
Maximum		17.9	0.5	11.4	27.2	16
Minimum		9.5	0.4	4.9	20.2	4.8
Average		12.3	0.4	8.2	23.1	8.4
Sacbe Edges	**n= 22**					
Maximum		6.5	0.5	18.9	29.2	3
Minimum		5.3	0.3	11.1	18.5	1.2
Average		5.8	0.4	14	23.6	2

Figures

Figure 1. The archaeological site of Cobá is located in the northwestern corner of the Yucatan Peninsula, Mexico.

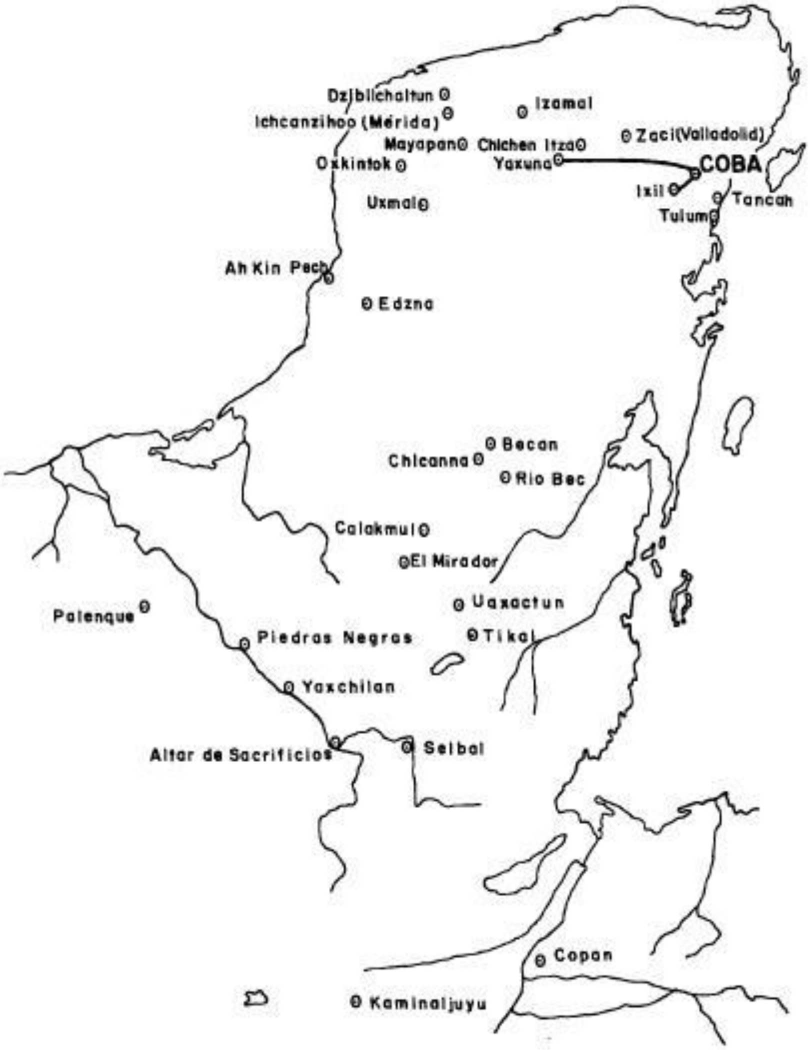


Figure 2. The direction of the s*acbeob* (ancient roads) at the archaeological site of Cobá.

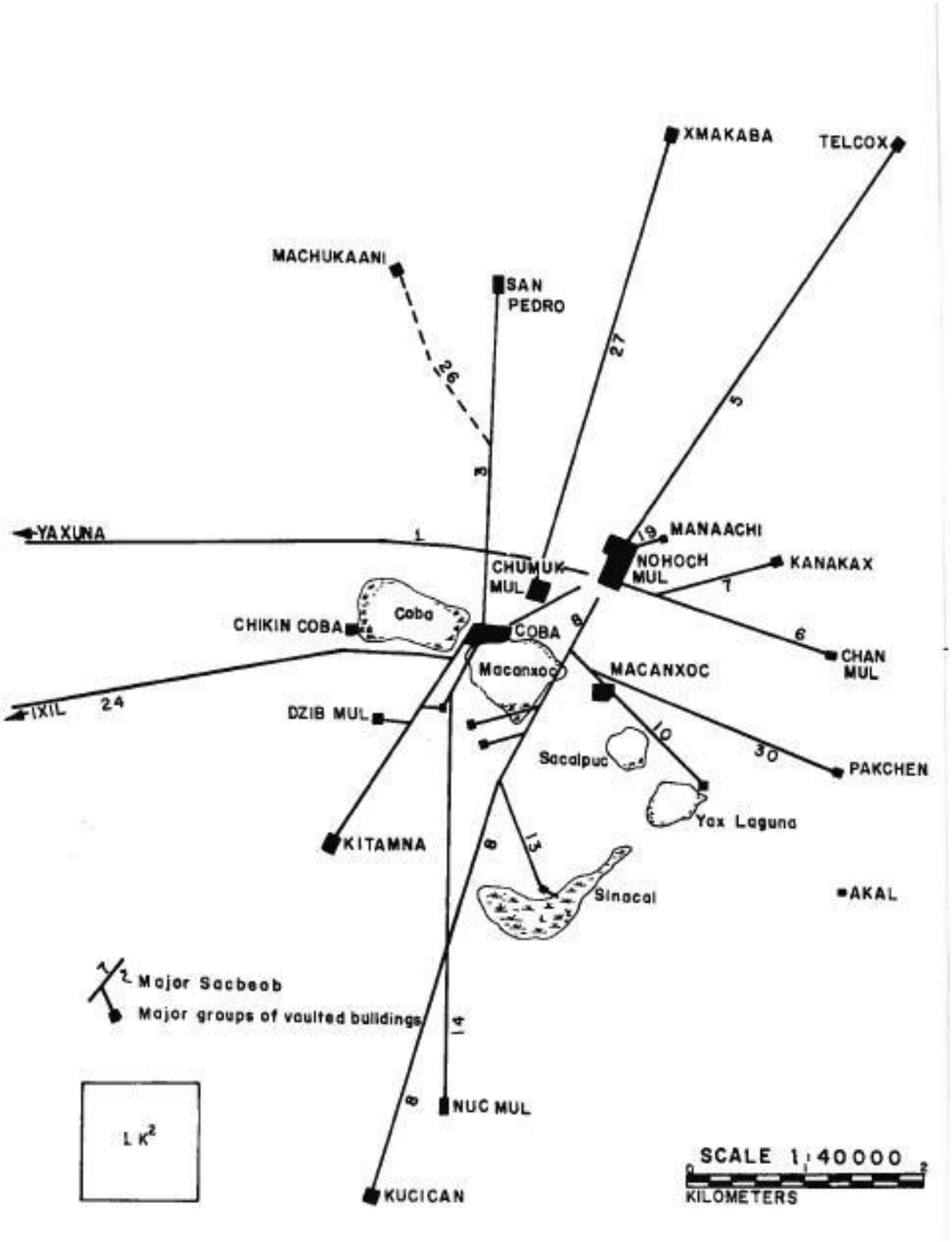


Figure 3. Structures and other features in Plaza B, Cobá.

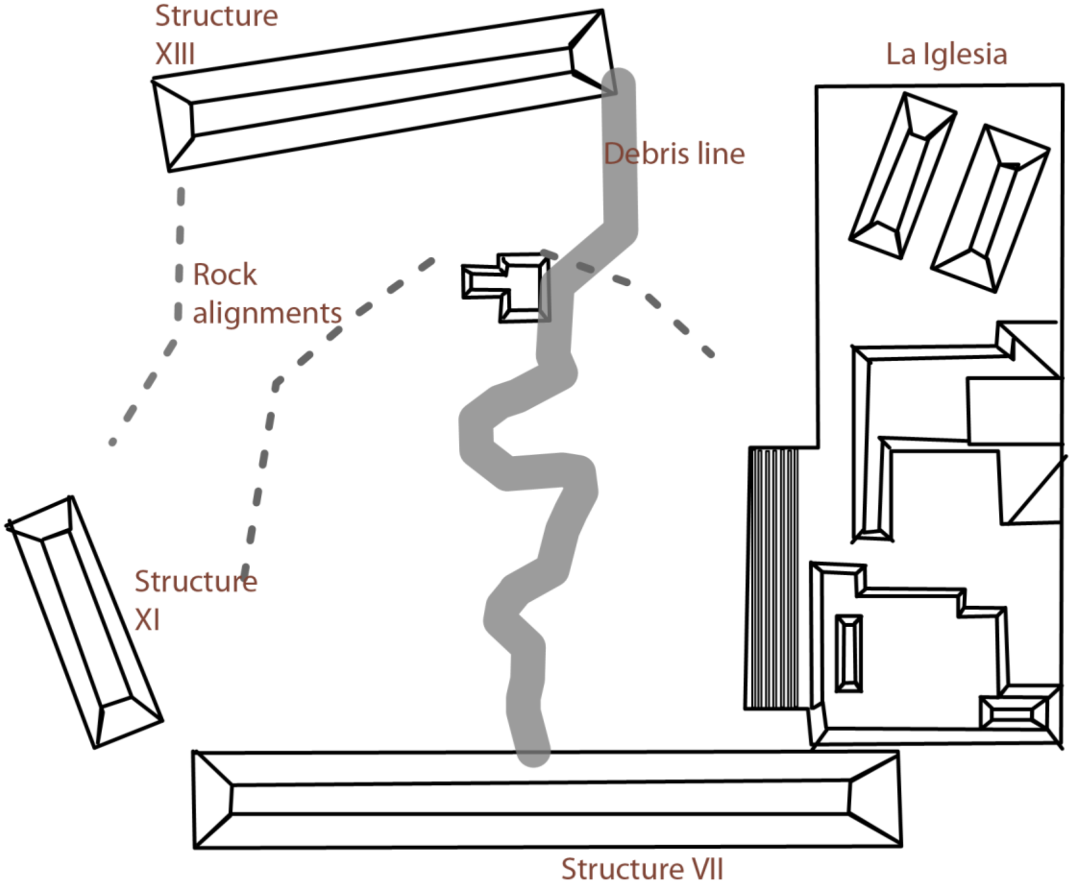


Figure 4. Structures, location of soil samples collected on top and on the edges of Sacbe I, and other features in Plaza D, Cobá. Image generated from GPS data taken in the field.

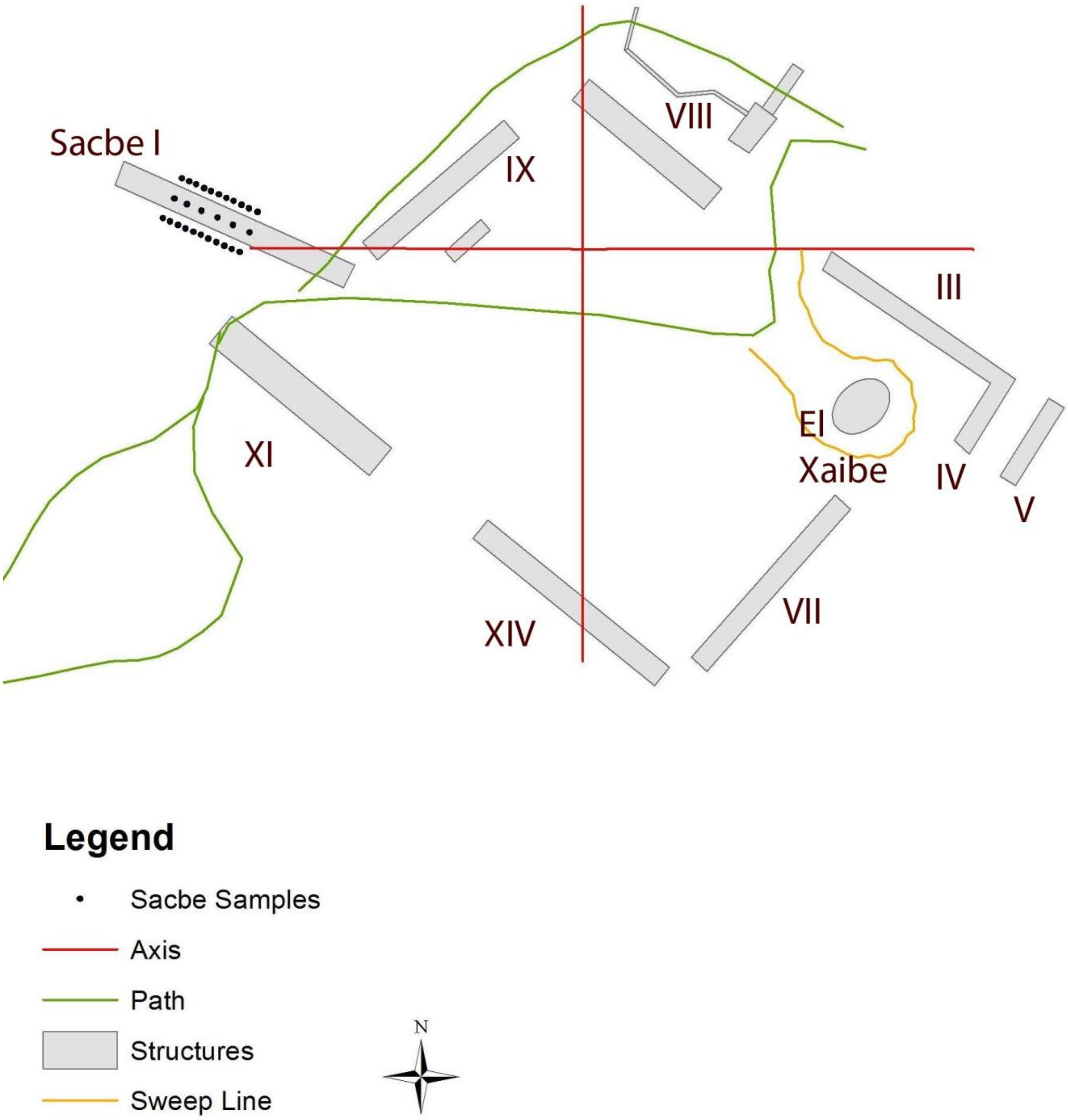


Figure 5. Plaza B samples associated with structures and other features, along with modeling of P concentrations (mg kg^{-1}).

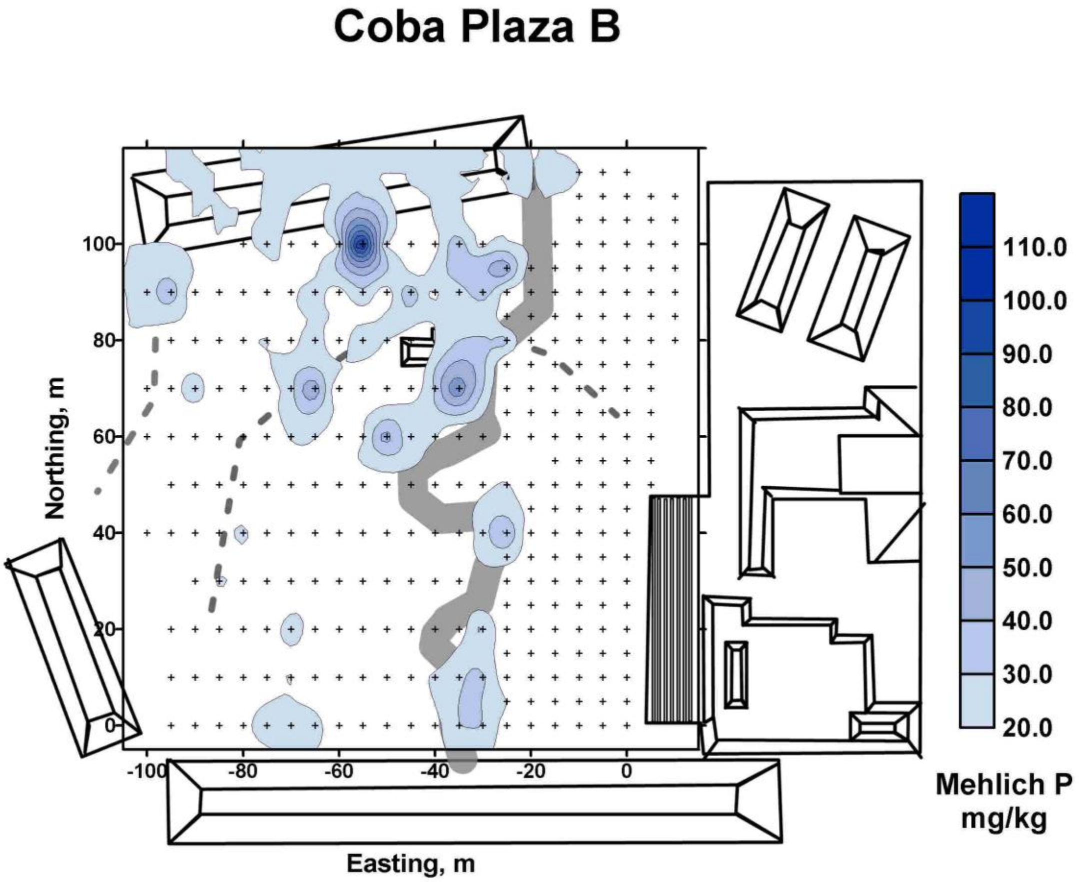


Figure 6. Plaza B samples associated with structures and other features, along with modeling of Fe concentrations (mg kg^{-1}).

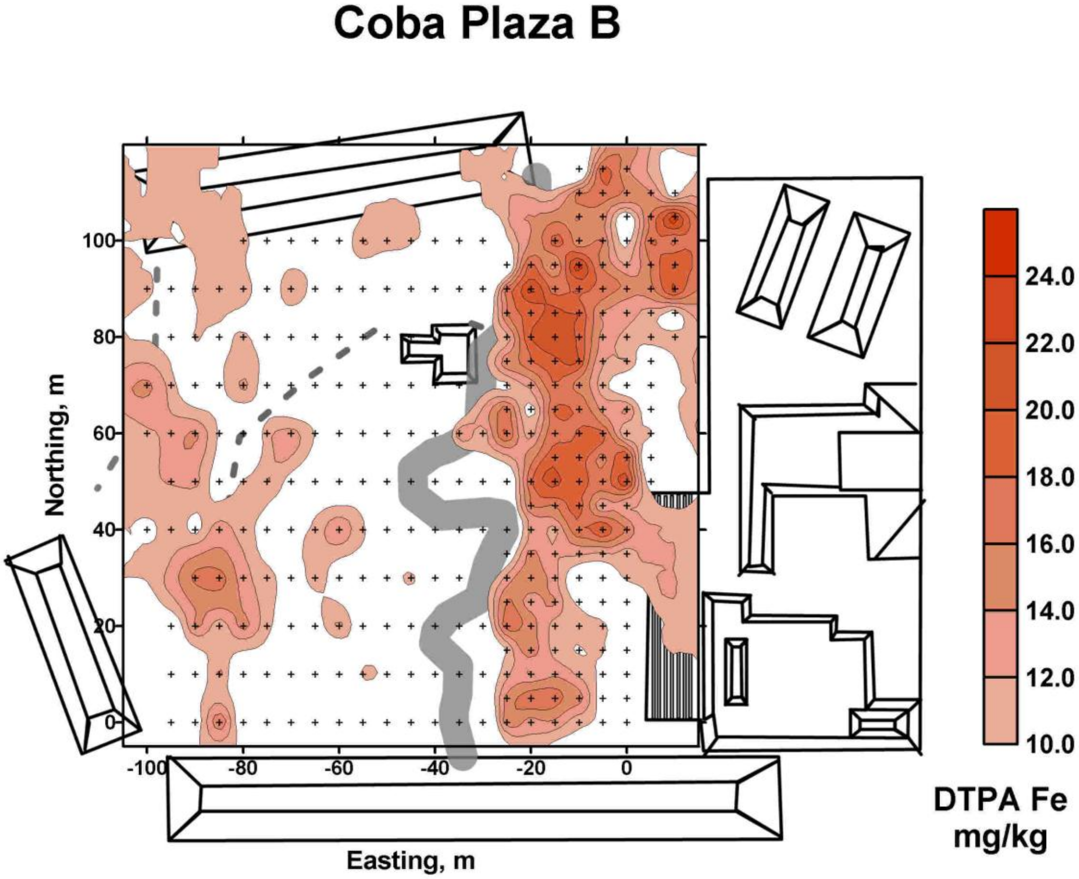


Figure 7. Plaza B samples associated with structures and other features, along with modeling of Cu concentrations (mg kg^{-1}).

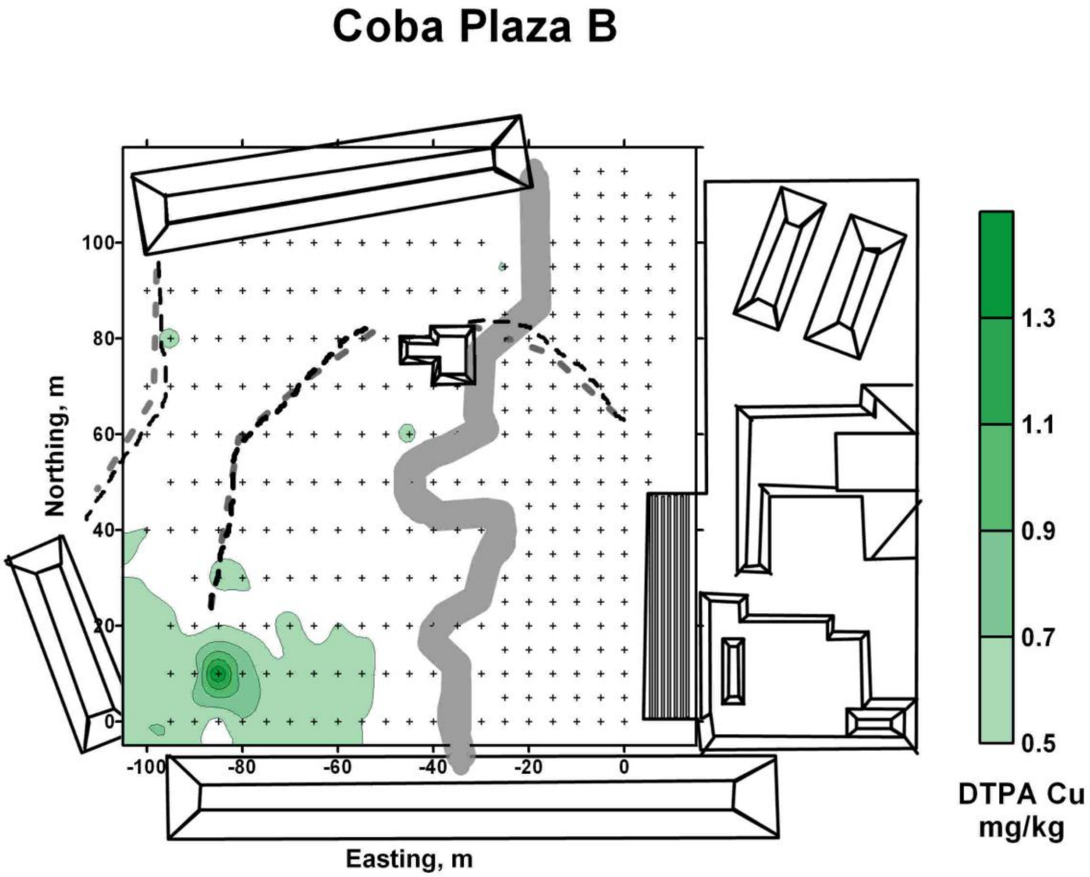


Figure 8. Plaza B samples associated with structures and other features, along with modeling of Mn concentrations (mg kg^{-1}).

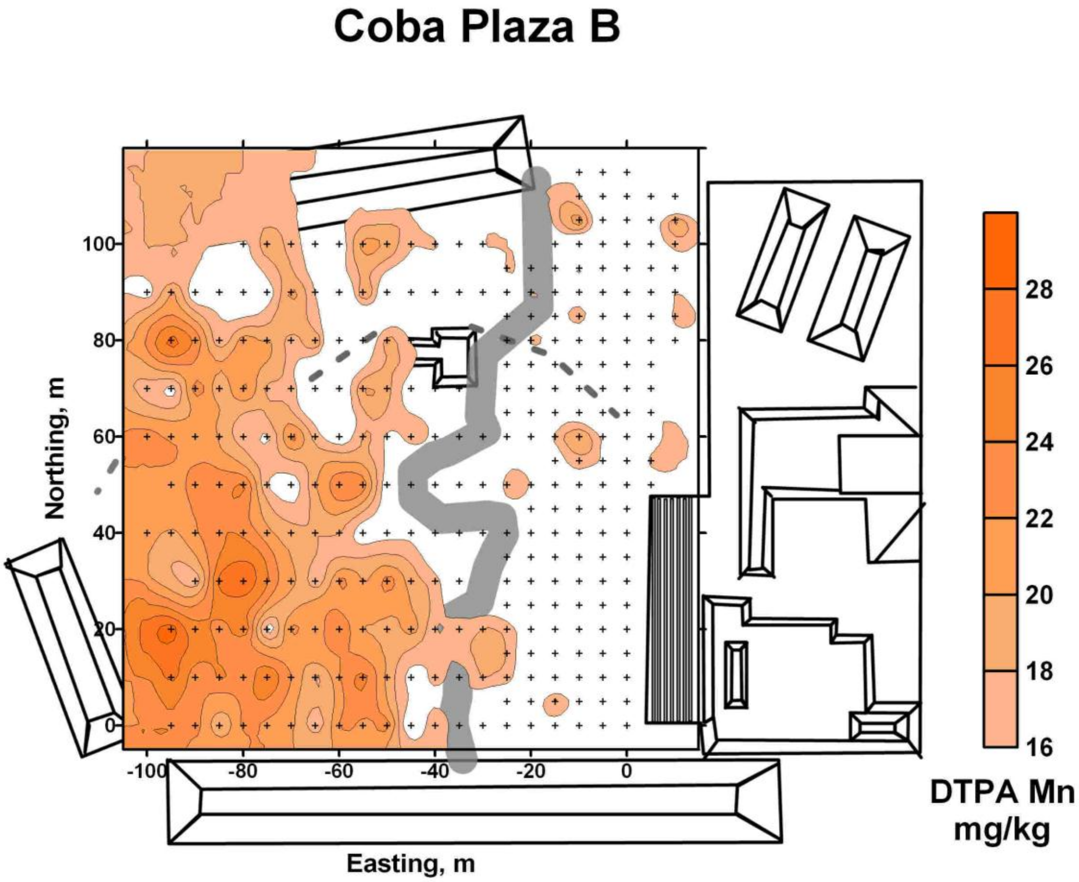


Figure 9. Plaza B samples associated with structures and other features, along with modeling of Zn concentrations (mg kg^{-1}).

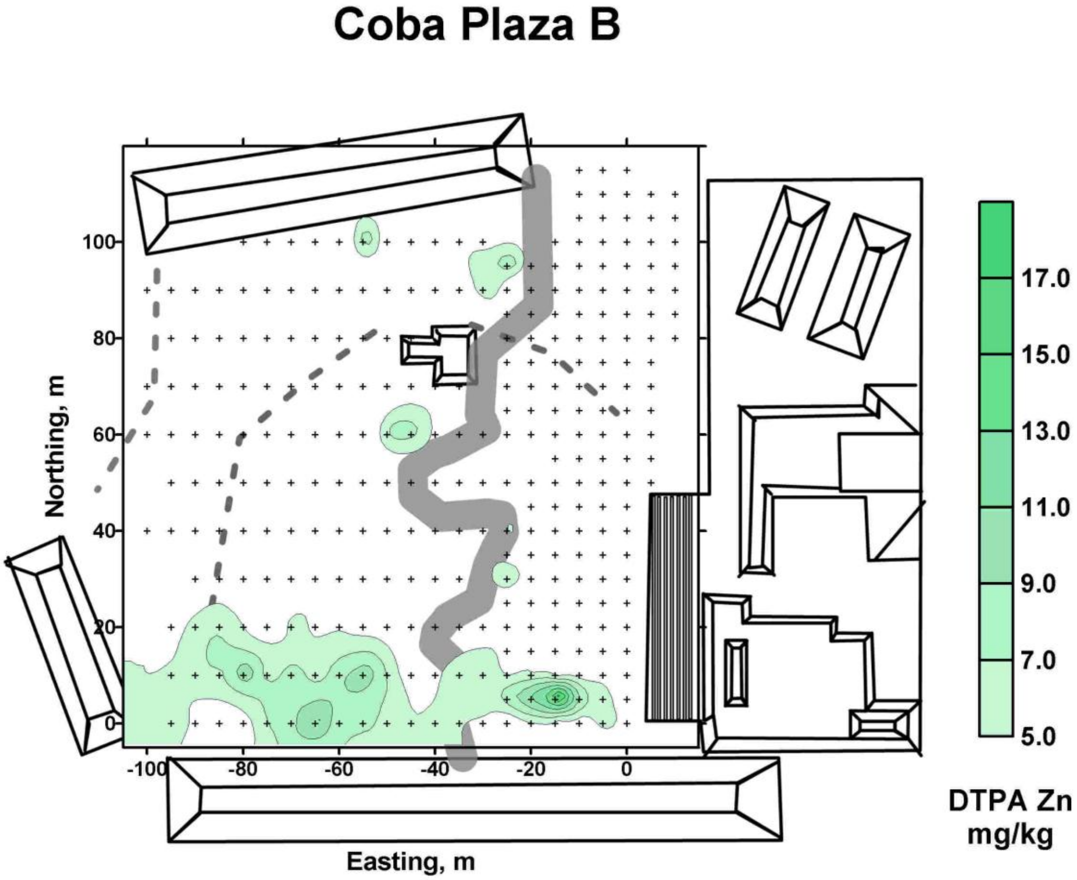


Figure 10. Plaza D samples associated with structures and other features, along with modeling of P concentrations (mg kg^{-1}).

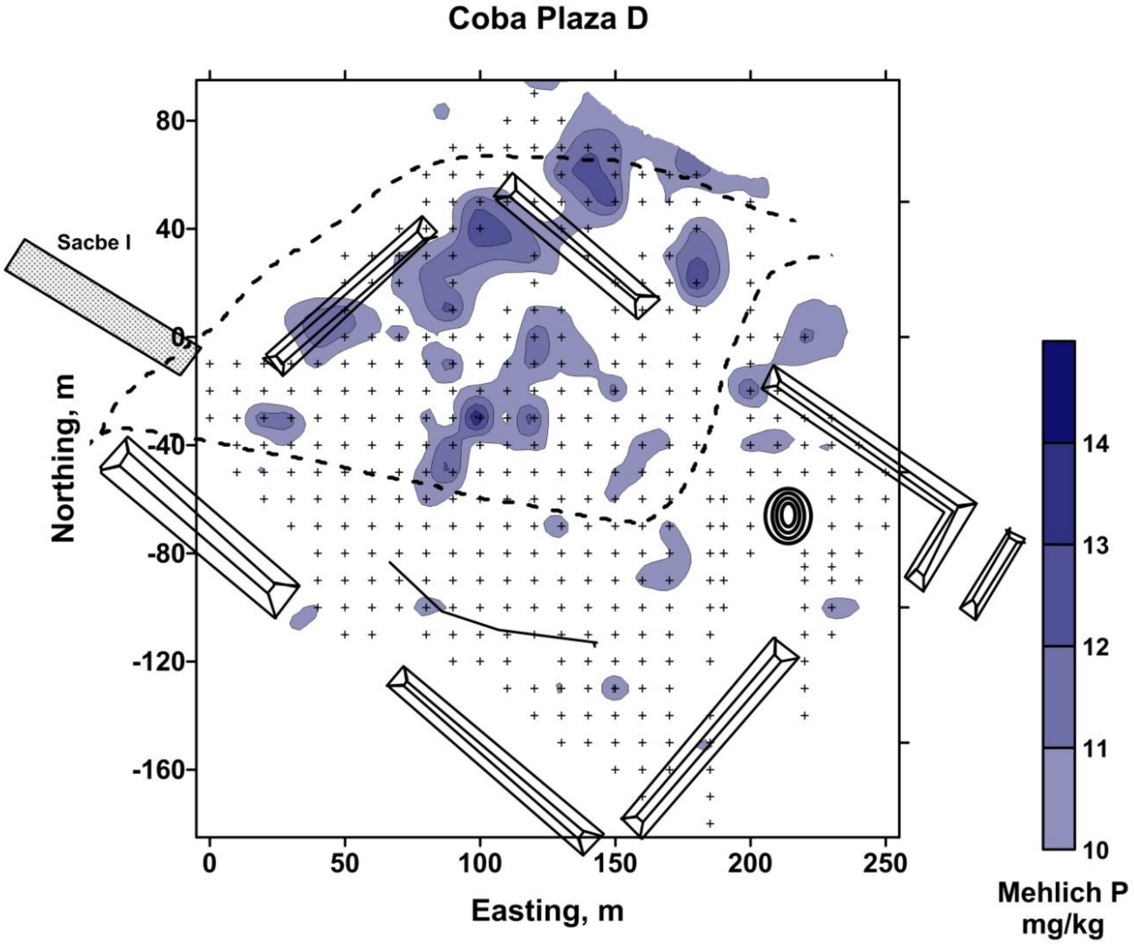


Figure 11. Plaza D samples associated with structures and other features, along with modeling of Fe concentrations (mg kg^{-1}).

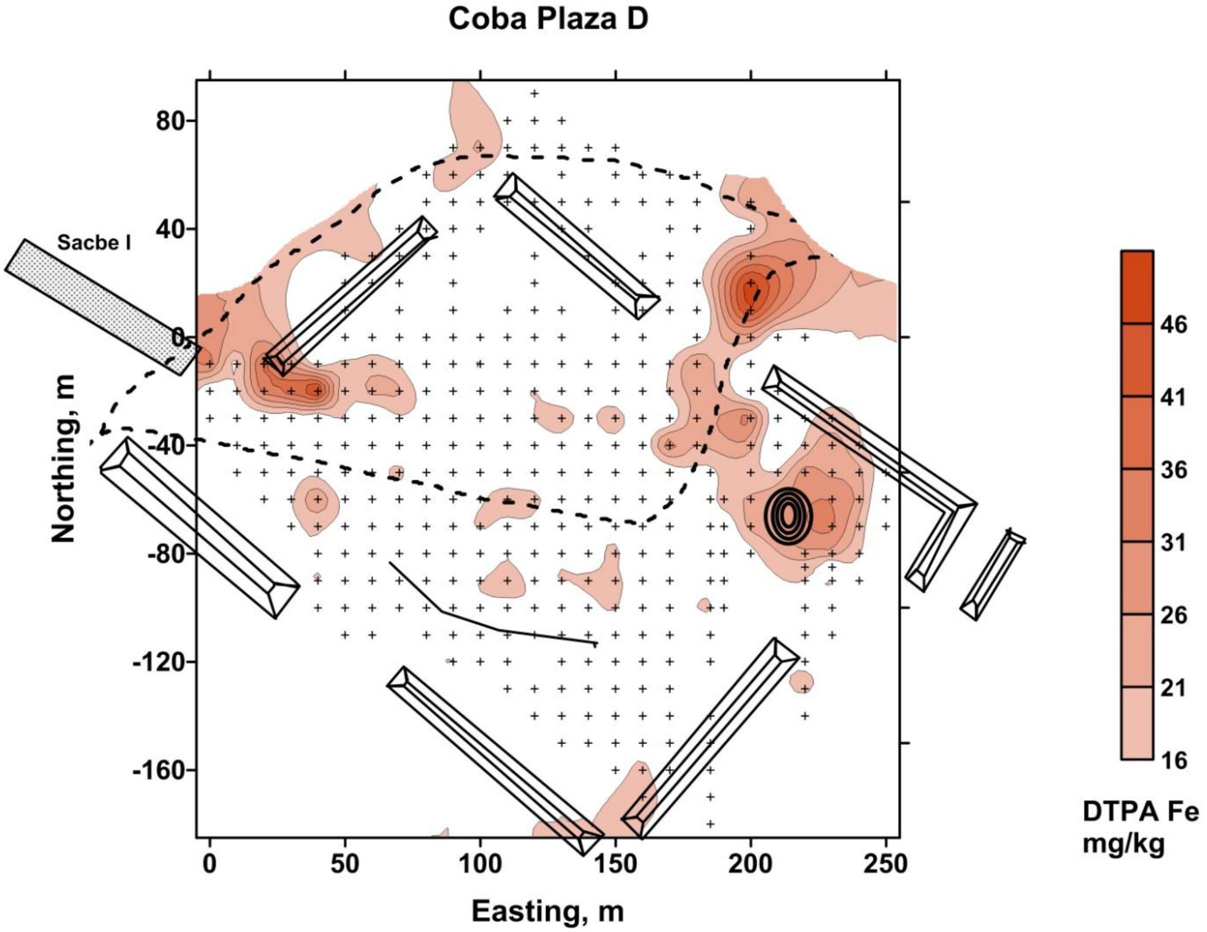


Figure 12. Plaza D samples associated with structures and other features, along with modeling of Cu concentrations (mg kg^{-1}).

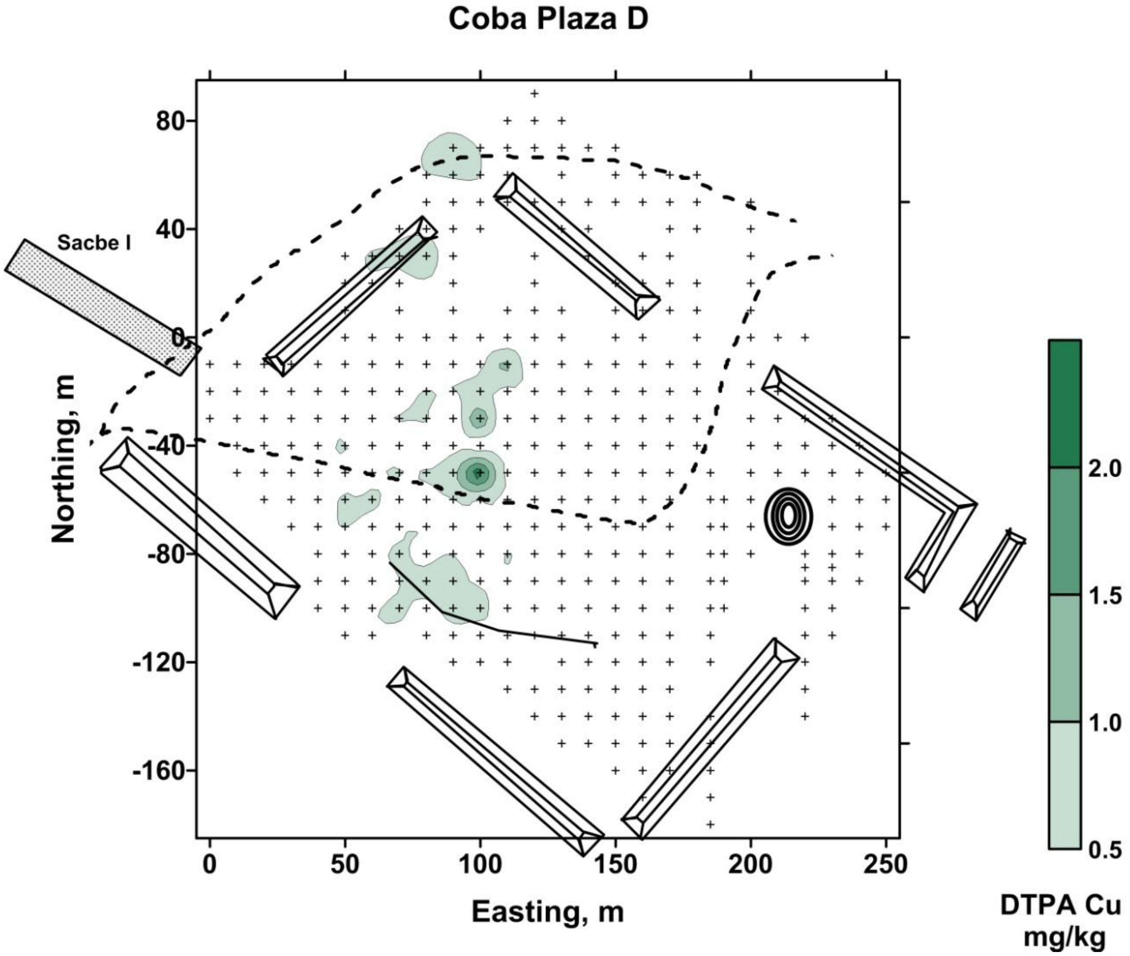


Figure 13. Plaza D samples associated with structures and other features, along with modeling of Mn concentrations (mg kg^{-1}).

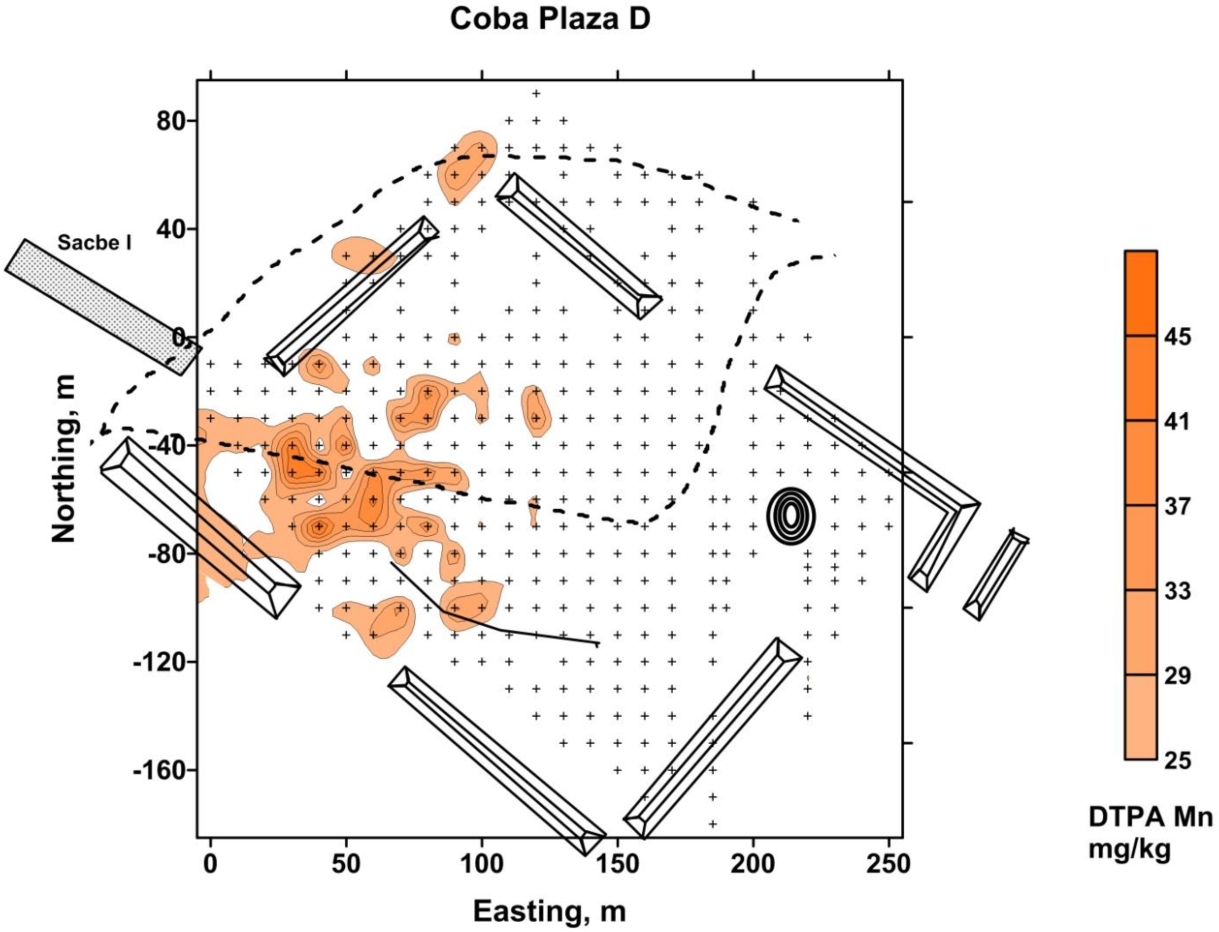
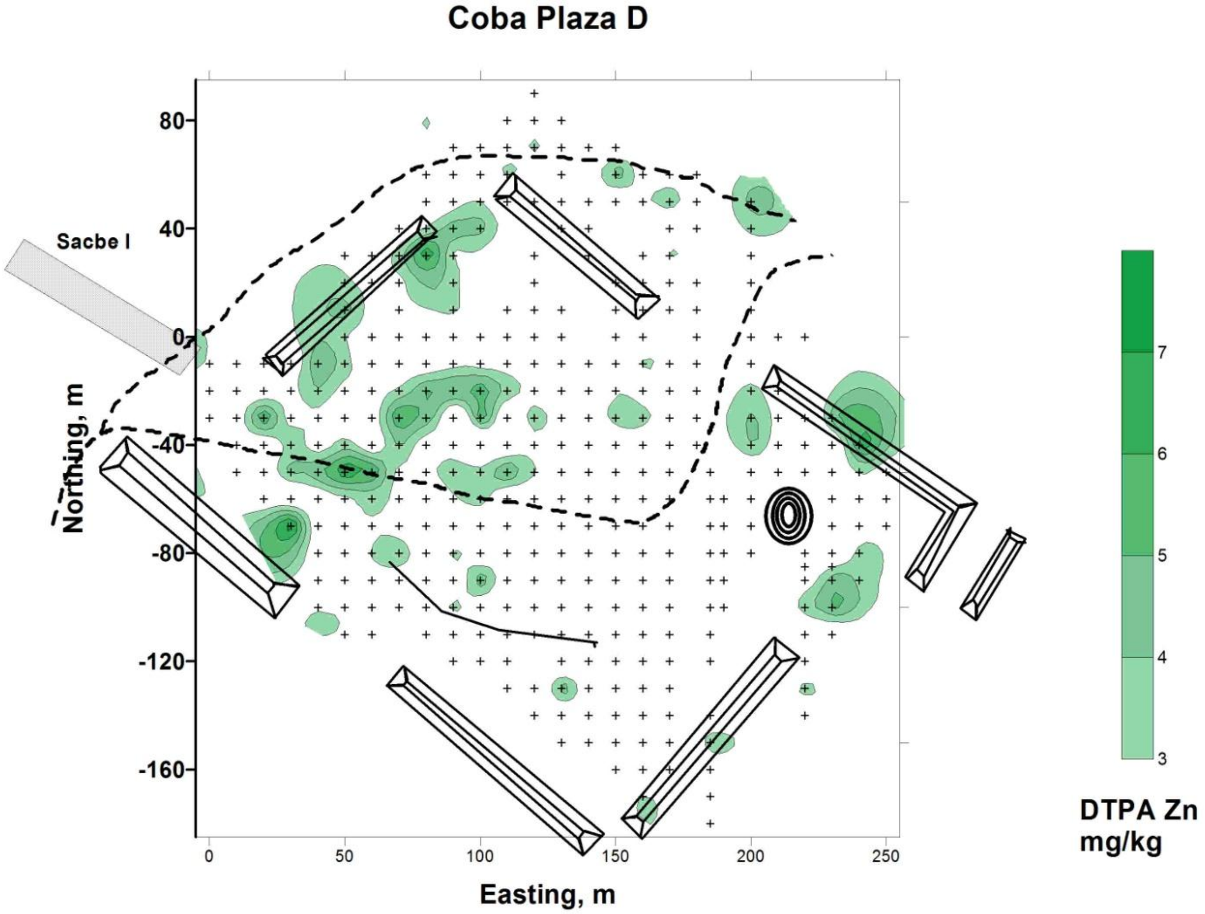


Figure 14. Plaza D samples associated with structures and other features, along with modeling of Zn concentrations (mg kg^{-1}).



Chapter 2

SUITABILITY OF PORTABLE X-RAY FLUORESCENCE FOR TESTING OF ANCIENT ACTIVITY AREAS

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Abstract

Portable X-Ray Fluorescence (PXRF) technology could be implemented at the Soil and Plant Analysis Laboratory at Brigham Young University for faster and more efficient testing of trace metals in soils, such as iron (Fe), copper (Cu), manganese (Mn), zinc (Zn), titanium (Ti), strontium (Sr), and zirconium (Zr), among others. A description of the instrument is provided in the present study, as well as analysis to test its capabilities under several routine circumstances that are present during field work. The PXRF instrument is tested for accuracy at different levels of soil moisture, granule size, and comparisons are made with certified soil samples using samples from the National Institute of Standards and Technology (NIST) and other sources. The PXRF showed good correlations with the certified soil standard reference materials for copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), titanium (Ti), strontium (Sr), zirconium (Zr), and lead (Pb). The attenuation and contamination of the X-Ray signal by plastic films and Whirl-Pak soil bags were also analyzed, with Pearson's correlation coefficients of up to 0.999. The results obtained in the current study showed that a field laboratory would be useful to air-dry, ground and sieve soil samples to a #10 mesh size (< 2 mm) for better accuracy and reproducibility.

Keywords: portable X-Ray fluorescence, geochemistry, DTPA, activity areas, Cobá

Introduction

Over the last few decades, geology, chemistry, and soil sciences have been of great help in the discovery and interpretation of archaeological features. Geochemistry is usually applied to determine when a specific pattern in the soil is manmade or natural. As a consequence, the chemical signatures of ancient human activities can be identified more precisely. Geochemistry helps in the identification of elements and its concentrations. Soil science includes all the testing for organic and inorganic elements that can help to determine if an area has been influenced by human activities (Revenko, 2002; Shibata et al., 2009).

However, the addition of these sciences to support archeological research is expensive, since laboratory work and trained individuals are critical. The current methods for soil testing are time-consuming, and the work involved in taking soil samples from the field into the laboratories is a burden (Zhu and Weindorf, 2009). Since many archeological studies are done outside the U.S., mounting shipping costs and the cumbersome permitting processes to import quarantined soils are specifically challenging in these times.

Cutting-edge technology could be used to ameliorate the burden of soil chemical analyses and may facilitate the analysis in a field laboratory. The application of Portable X-Ray fluorescence (PXRF) to perform analyses in a field laboratory or on-site can be a great tool to make the work easier, cheaper, and faster than by the conventional soil testing methods (Radu and Diamond, 2009).

If the Portable XRF device yields useful results in the field laboratory testing, the work of scientists could be greatly accelerated because laboratory work would be reduced, results obtained faster, and there would be no need for shipping soil samples.

It is anticipated that the research protocol proposed in this report will be used by the scientific community related to soil geochemistry, geology, archaeology, and environmental testing fields. Establishing the reliability of the results of the PXRF device can only be done by extensive research and statistical analyses of the results obtained from comparative analyses.

Portable XRF instrument

The PXRF instrument used in this study is a S1 Tracer IV-SD produced by Bruker AXS (Kennewick, WA). It has a rhodium (Rh) target X-Ray tube excitation source and a silicon (Si) Pin diode detector. The instrument, weighing ~ 1.5 kg, is powered by both a rechargeable Li-ion battery or by an AC adapter. The instrument can also use a vacuum system to capture the signals of elements as light as magnesium (Mg). The PXRF instrument can be run using a factory-provided personal digital assistant (PDA) or a laptop computer, where calibration method and elapsed time per sample are pre-programmed.

Although the instrument itself looks quite simple, the mechanism portion is complex. The device is equipped with a probe window and X-Ray tube that irradiates the sample and the X-Rays can either scatter or be absorbed by atoms in the sample and re-radiated as X-Rays of specific energy in a photoelectric effect. A rearrangement of electrons happens as a consequence of X-Ray irradiation, and every specific atom gives off energy during the process. X-Ray fluorescence is the emittance of X -Rays by the atoms, since the atoms fluoresce at determined levels of energy when irradiated with X -Rays (Jang, 2010; Kalnicky and Singhvi, 2001). The concentration of elements is determined using an internal X -Ray fluorescence spectrometer. The determined energy of the radiation by the atoms is specific for each element, and the amount of radiation is proportional to concentration (Juvonen, 2009).

The characteristics of the device allow for two forms of sample analysis: on-site and intrusive. When samples are analyzed on-site, the probe window of the device is placed in contact with the surface to be examined (soils, metals, or other solids). The capacity to study samples on-site is one of the great advantages of the PXRF instrument. Samples can also be analyzed by the intrusive mode. For this mode, soils or sediments are collected in the field or study area, ground, sieved, and place in a container to be analyzed. The container is then placed on top of the probe window with the aid of a protective film (Potts and West, 2008). The present study will focus on intrusive soil samples after being air-dried, sieved, and bagged.

The sampling time can vary depending in the desired accuracy. Quick scanning for so-called hot spots or high concentrations of an element of interest is usually performed in 60 seconds. If enhanced precision and accuracy are desired or required, the extended times for analyzing can be up to 300 seconds as replicate scans are analyzed (Kalnicky, 2001; Juvonen, 2009).

Soil Sampling

The precision of the device is not the most significant source of error. Human errors or interferences in the sampling are generally the causes of concern. Soil samples to be tested need to be prepared in the same manner to avoid the introduction of errors. The physical character of the samples is necessary to consider so both accuracy and precision in the sampling process are achieved. There are ways to eliminate or at least ameliorate errors in measuring elemental concentrations due to physical characteristics of various samples, such as grinding and homogenizing the samples. Factors such as distribution uniformity and granule size need to be the same to be able to compare one sample to another. One principle to consider is that the PXRF results will most likely vary according to the degree of mixing of the sample and the size of the granules (from coarse to very fine particles and aggregates). For this purpose, grinding, sieving, and mixing soils samples to the same degree will yield reproducible results. However, the grinding and sieving to fine granule size comes at the cost of preparation time, labor, and equipment. Minimal sample preparation in a field laboratory is limited to air-drying, crushing and sieving samples to pass a 10 mesh sieve (< 2 mm). The grinding and sieving of soil samples to much smaller sieves is beyond the scope and capabilities of a field laboratory due to time and funding constraints.

Due to the nature of soils, another concern is the moisture content of the samples. It has been reported that when water content is lower than 20-25 percent, the results obtained from PXRF will not be affected (Lopez Avila et al., 1998; Potts and West, 2008). However, if moisture content is greater, the source of error could be magnified.

PXRF and soil studies

Soil studies have greatly benefited with the capabilities of PXRF instruments. In the last 20 years, PXRF has evolved into a major tool that has the ability to provide quantitative analytical data for workers in science and industry areas (Potts, 2008). A very common use of the PXRF is to perform environmental assessment of contaminated sites due to past mining activities, military use, or any other human activity that has left dangerous levels of pollutants in the soil (Bernick et al., 1995; Carr et al., 2008; Crook et al., 2006; Hurkamp et al., 2009; Kodirov and Shukurov, 2009; Jang, 2010; Melquiades et al., 2011; Peinado et al., 2010; Potts and West, 2008; Stark et al., 2008; Taylor et al., 2005; Vancott et al., 1999; Vanhoof et al., 2004; Weindorf et al., 2011). However, traditional methods of soil testing require taking a considerable number of soil samples, hauling or shipping them to a laboratory for wet chemistry analyses that are expensive and complex, and it takes a substantial amount of time to receive and process the data (Jang, 2010; Taylor et al., 2005; Weindorf et al., 2011). Often, the factors of time and expenses can reduce the number of collected samples, and the resolution of the contamination in soils in a determined site is decreased; therefore, the true distribution of pollutants in the soil is not entirely known. The capacity to take the PXRF instrument to the sample or to a field laboratory is one of the most important capabilities of the device (Potts and West, 2008). The PXRF allows for higher intensity analysis of soil samples in the field, with the results modeled on-site, and work completed in a shorter period of time (Jang, 2010; Taylor et al., 2005; Potts and West, 2008; Weindorf et al., 2011). Crook et al. (2006) reported that PXRF measurements are comparable to the accuracy shown by samples also analyzed with ICPAES for dried and ground samples. Weindorf et al. (2011) found reasonable correlations between PXRF and National Institute of Standards and Technology (NIST) standard reference materials [except for cobalt (Co) and mercury (Hg)]. It must be mentioned, nonetheless, that some soil guidance values or regulatory toxicity levels are below the limits of detection of the PXRF (EPA 1998, Crook et al., 2006; Peinado et al., 2010). This flaw may be corrected in future PXRF models that display even lower limits of detection. Yet, Potts and West (2008) reported that the PXRF has levels of detection low enough for elements such as barium (Ba), Co, chromium (Cr), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb), strontium (Sn), and zinc (Zn), among others. Researchers have reported analytical precision of ~ 1% to up to 12% (Potts et al., 2008; VanCott et al., 1999), but the precision of the PXRF readings can be affected by sample homogeneity and moisture content found in the sample (Potts and West, 2008; Melquiades et al., 2011; Crooks et al., 2006). Crooks et al. (2006) proposed that a mobile laboratory could be used to dry and sieve soil samples for analysis if a more complete quantitative investigation is desired; however, results will not be obtained in one day if samples are dried overnight.

In summary, the PXRF offers practical, comprehensive, and economical screening of elemental concentrations on-site or at nearby field laboratory facilities.

Analysis of Soil Samples at Cobá, Mexico

The Classic Maya are one of the most intensively studied ancient states and are remarkably absent from comparative study of ancient state economies. Geochemical analyses of soils have helped delineate activity areas within households by means of prospection and site interpretation (Fernandez et al., 2002; Oonk et al., 2009; Terry et al., 2004), but this limited context cannot tell us how soil chemical residues were deposited by ancient people. Mapping patterns of soil chemical residues in other public spaces will also help identify economic exchanges affected through redistribution and feasting (Dahlin et al., 2007; Dahlin et al., 2009).

The present study extended the use of geochemical techniques to two plazas of Cobá, one of the largest and most heavily urbanized Maya cities in the Yucatan peninsula. Emphasis was placed on phosphorus (P) as it is a component of marketed foodstuffs, and on several metallic residues such as Cu, iron (Fe), manganese (Mn), and Zn, common constituents of mineral paints and pigments that were highly prized and widely traded among the Maya. These P and metallic residues became fixed to the soils and floors of ancient plazas and households and may represent important exchange items of this ancient civilization at that specific location.

For the past twelve years, Richard Terry and his students have measured the extractable P content of thousands of soil and floor samples in a field laboratory. The portable field laboratory is equipped with battery-operated balances and colorimeters for measurement of Mehlich II extractable P. However, the samples must be brought to the Soil and Plant Analysis Laboratory at Brigham Young University for DTPA (diethylenetriaminepentaacetic acid) chelate extraction and metallic elements concentration analysis by ICPAES (Inductively Coupled Plasma Atomic Emission Spectrometer) (Parnell et al., 2002; Radu & Diamond, 2009; Weindorf et al., 2008). Parnell et al. (2002) have compared these procedures with sample digestion by nitric and perchloric acid and reported positive correlations. The transport of hundreds of soil samples in airline luggage and by express delivery has become very difficult and expensive in the past few years. The airlines have become much more restrictive on excess baggage and the costs have skyrocketed. In addition, soil import permits are becoming more difficult to obtain as security concerns increase.

Objectives

The overall objective of this study was to develop an analysis protocol for the sampling and PXRF analysis of trace residues in the soils and floors of ancient activity areas, including marketplaces. We compared the results of DTPA extraction for both Plaza B and D samples with the PXRF instrument readings for the same soil surface samples. Elemental concentrations were geospatially plotted with Surfer Software (Golden, CO) to compare the elemental distribution within Plaza B and Plaza D.

Specific objectives included:

- Test the soil PXRF calibration against eight certified standard reference materials obtained from NIST and other sources.
- Compare total digestion values of the certified standard soil samples by nitric and perchloric acid to PXRF analysis of the same soil samples. The elemental concentrations of the total

digestion procedure were determined by Inductively Coupled Plasma Spectroscopy (ICPAES).

- Test the attenuation of signal and contamination of results of the Whirl-Pak soil bags against the plastic film recommended by Bruker (SpectroMembrane® Mylar® Polyester film, 3.6 µm).
- Test for any differences related to soil granule size. While Bruker recommends analyzing samples that were passed through a 100 mesh sieve (<149 µm), the grinding time required to pass most soils through such a sieve size would limit the number of samples analyzed in the field. We compared the differences in results in samples passed through a 10 mesh (<2 mm), 40 mesh (<425 µm), 60 mesh (<250 µm), and 100 mesh (<149 µm).
- Test for any differences in elemental PXRF concentrations in relation to soil moisture content at the time of analysis. Soil samples were tested at four moisture levels: oven-dry, air-dry, field capacity, and saturation.

Methodology

The PXRF analysis of soil P is not adequate to differentiate soils with subtle differences in human sources of P. The energy emitted by P is low; therefore, the error in P analysis by PXRF is large. For this reason, Olsen extractable P (Olsen et al., 1954) analysis was performed in the field for samples within Plaza B. Samples within Plaza D were extracted with Mehlich II solution and P concentrations determined at the Soil and Plant Analysis Laboratory at Brigham Young University. The soils were air dried, crushed to pass a 2-mm sieve, and placed in plastic bags prior to analysis procedures. The trace metal levels of soil samples were determined by DTPA extraction and ICPAES analysis. The research allowed us to compare the results of PXRF and DTPA analyses in the identification of ancient Maya activities in plazas. It was hoped that in the future, use of the portable P laboratory and the PXRF will provide useful information on ancient activity areas and eliminate the need to transport hundreds of pounds of quarantined soil samples to distant laboratory facilities.

All the surface soil samples were analyzed using the "Soils with Calcium Carbonate" calibration developed by Bruker, and the fluorescence signal was collected for 120 seconds. In regards to the calibration, it was developed by Bruker using 102 standards from various sources. The calibration employs filter #1 (25 µm Ti, 300 µm Al), an excitation voltage of 45 kV, and a current of 30 µA.

For the analysis performed to compare PXRF values to the standard reference materials provided by NIST and other sources, and with the values obtained from the total nitric-perchloric acid digestion, the soil standards were placed in a plastic vial (2.5 cm diameter and 5 cm long) and covered by a Mylar film (SpectroMembrane® Mylar® Polyester film, 3.6 µm). The samples were placed on top of the PXRF window probe. The elapsed time for each sample was 120 seconds, and the analysis was repeated four times and the values averaged. The double acid digestion procedure (Entwistle et al., 1997, 1998) was used to determine total trace metals. Standard soil samples were already ground to pass a 60-mesh polyester sieve. Five ml of concentrated nitric acid was used to digest a measured portion of the soil sample. The sample was allowed to sit overnight in a ventilating hood and then heated in a digestion block at about 200^{o} C to digest the organic material for about 15 minutes. One ml of concentrated perchloric acid was added to the cooled solution. The mixture was again heated in the digestion block at approximately 200^{o} C for 1 hour. The solution was diluted, shaken, and allowed to settle prior to ICPAES analysis. Distilled water was used as a blank. The reference materials included were:

1. NIST SRM 1645: River sediment.
2. NIST SRM 1646: Estuarine sediment.
3. NIST SRM 2704: Buffalo river bed.
4. GXR-2: Soil from Park City, Utah. United States Geological Survey.
5. NIST SRM 2710: Montana soil.
6. NIST SRM 2711: Montana soil.
7. GFS 403: Dolostone. Reference carbonate rock.
8. NIST NBS 1b: Argillaceous limestone.

To study the attenuation of signal and contamination of results, the plastic films of the standard soil samples were replaced with a circular film cut from the soil Whirl-Pak bags, and repeated four times per sample, replacing the film with an unused one every time. Also, samples of the protective SpectroMembrane film and soil Whirl-Pak bag films were analyzed by themselves to determine what kind of contamination to the results could be introduced by the films. If the attenuation and contamination are not significant, analyzing samples on the PXRF without the need to transfer the soil samples out of the Whirl-Pak soil bag would increase productivity.

For the soil granule size study, four surface soil samples (laboratory-coded A7, B10, B21, and D4) were selected at random from the pool of samples obtained from Plaza B in Cobá. All four soil samples were passed through a 10 mesh (<2 mm), 40 mesh (<425 µm), 60 mesh (<250 µm), and 100 mesh (<149 µm). These four granule size fractions were placed in plastic vials and covered with a plastic film (SpectroMembrane) for further PXRF analysis. At the time of the analysis, the soil samples were already air-dried.

In developing the sampling protocol, we wanted to know if in the case of analyzing samples in the field, it would be necessary to determine the soil moisture content to possibly develop a correction factor. If the variability in results is too great with varying degrees of moisture, then the sampling protocol would have to include air-drying the samples before PXRF readings. To study any elemental concentration differences related to moisture content, the following five soils were used: sand, clay, loam, high organic matter, and low organic matter. Four plastic soil cores with a mesh screen in the bottom were filled for each of the five soils. The PXRF readings were performed under four moisture levels: oven-dry, air-dry, field capacity, and saturated. Field capacity was reached by means of a pressure plate (5-bar pressure plate extractor, Soil Moisture Equipment Co., Santa Barbara, CA) where all the soil cores were under -1/3 bar of pressure for 24 hrs, while oven-dry soil samples were placed in an oven at 110^{o} C for 24 hrs. All the soils were air-dried at the time of the analysis, and the PXRF readings were done first for this moisture level. To reach saturation, soil cores were left in a pan with sufficient water to soak from the bottom up for one day. A plastic film was placed on the other end of the soil core and set on top of the PXRF probe for analysis. Soil cores were weighed to calculate the water content in the soil at the time of analysis.

For the analysis of the soil samples taken within Plazas B and D in the archaeological site of Cobá, Mexico, the samples were collected at the intersection of a 5-m or 10-m grid. The surface litter was removed and soil samples were taken using a plastic trowel from the first 10 cm, and subsequently stored in a sterile Whirl-Pak plastic bag. At the laboratory, the samples were air-dried and sieved (< 2mm), and then placed on top of the PXRF window probe. The samples were analyzed directly from the Whirl-Pak soil bag for time and funding constraints. All the statistical analyses were performed using the software JMP (SAS Institute Inc., Cary, NC).

Results and Discussion

Portable XRF values comparison with Standard Reference Materials and Total Digestion values

Pearson's correlation coefficients (also known as r values) for PXRF and total digestion by nitric-perchloric acid analysis correlated to the certified values for the standard reference materials were calculated (Table 1). The element with the lowest correlation with both reported values and total digestion values was titanium (Ti). The Ti PXRF had a correlation of r = 0.962 with the reference materials (certified values), and r = 0.6494 with the total digestion values. In the case of zirconium (Zr), the correlation with the standard reference material was r = 0.9871 but r = 0.1097 with the total digestion values. For the rest of the elements (Mn, Fe, Cu, Zn, Sr, and Pb), the r with the reference materials ranged from 0.9871 to 0.999, and the r with the total digestion values ranged from 0.9763 to 0.9997. In general, these results show that the PXRF performed well using the calibration "Soils with Calcium Carbonate" to analyze soil standard reference materials with a wide range of characteristics. The elements most widely used by the Soil and Plant Analysis laboratory were reported in this study.

Attenuation and Contamination by Protective Films

Percent changes, Pearson's correlation coefficient, and mean percent changes between the PXRF readings of the certified standard reference materials using the SpectroMembrane and the Whirl-Pak soil bag as protective films were compiled (Table 2). This study compared the results from the standard reference materials analyzed with two different covers: the plastic film recommended by Bruker (SpectroMembrane® Mylar® Polyester film, 3.6 µm) and a plastic film cut from the Whirl-Pak soil bags normally used at this laboratory.

The task to transfer soil samples to a plastic vial and then to cover it with the SpectroMembrane is time-consuming, and it would restrict how many samples could be analyzed under the limited time in the field. In general, the values are very encouraging for our purposes. All elements presented good correlations for the PXRF readings under both plastic films. The lowest r value was shown by Fe (r = 0.95999). These correlations allow analysis of soil samples directly through the Whirl-Pak soil bag as the elemental concentrations of samples were not greatly affected.

Soil bags and the SpectroMembrane were also analyzed to quantify the amount of contamination found in the chemical composition of these materials. Table 3 shows a summary of the elements found in these supplies. In addition, the soil bag paint strip was analyzed, and high concentrations of various elements were found (data not shown). The painted area of the soil bags should not be placed on top of the windows probe while performing analysis. In regards to the non-painted area of the Whirl-Pak soil bag, it also presents various elements in different concentrations, being the most notorious Ca (605 mg kg^{-1}), Ti (71 mg kg^{-1}), Fe (114 mg kg^{-1}), and Zn (145 mg kg^{-1}). The SpectroMembrane contained high levels of most elements reported for the Whirl-Pak bag. However, when most of our soil samples from Yucatan contain several thousand mg kg^{-1} of Ca, Fe, and several hundred mg kg^{-1} in Zn and Ti, the low concentrations found in these materials are relatively insignificant and do not represent a serious source of contamination. The PXRF readings were done on a single layer of a SpectroMembrane, Whirl-Pak soil bag, and the windows probe with nothing placed on top of it (Table 3). The correlation between the SpectroMembrane with the Whirl-Pak bag and no sample was of r= 0.9866 and r=0.9945, respectively. The correlation between the Whirl-Pak soil bag and no sample was of r=0.9833. Also, these differences were not statistically significant, and these interferences do not pose a serious problem in the integrity of the data. However, the PXRF windows probe should not face the paint strips or metal ties in the Whirl-Pak soil bags. The PXRF allows for measurements with both SpectroMembrane and Whirl-Pak soil bags with high levels of confidence in the results.

Granule Size Analysis

Tables 4 through 7 summarize the data obtained from the granule size study. Each one of the four samples (laboratory-coded A7, B10, B21, and D4) was sieved to four mesh sizes. The tables present the mesh number, letters to denote significant differences among the results obtained for each sieve, and the standard deviation (SD) of the four replicates.

For the soil sample A7 (0 E 35 N Plaza B; 19% sand, 47% clay), sieve sizes made a significant difference in measurements of five elements (Ti, Mn, Fe, Sr, and Zr) but not for two elements (Cu and Zn) (Table 4). The impact varied among elements, but generally lower concentrations were measured for the coarser granule sizes. Both Sr and Zr presented greater concentrations with smaller sieve size.

On the values obtained from soil sample B10 (-5 E 50 N Plaza B; 8% sand, 50% clay), there were no significant differences between any of the sieves for elements Ti and Cu, but there were significant differences for Mn, Fe, Zn, Sr, and Zr (Table 5). For Sr and Zr, the concentrations increase with smaller mesh size.

Table 6 presents the data obtained from the PXRF analysis of sample B21 (-5 E 105 N Plaza B; 25% sand, 42% clay), one of four samples chosen at random to represent the types of soils analyzed from Plaza B and D in order to test the effect of granule size in the PXRF elemental concentrations. The elements titanium, manganese, iron, copper, and zinc presented no significant differences between the results obtained from the four sieves. However, Sr and Zr presented significant differences between the different sieve sizes. The pattern of increasing PXRF values with finer granule size for Sr and Zr is displayed as before.

The last soil sample to be analyzed as part of the granule size study was sample D4 (-15 E 20 N Plaza B; 22% sand, 45% clay) (Table 7). The elements Ti, Fe, Cu, and Zn showed no significant differences between the four treatments. On the other hand, manganese, Sr and Zr, presented significant differences among the measurements with different sieve sizes. Moreover, both elements Sr and Zr showed increasing PXRF concentrations with finer granule size.

In summary, the granule size study showed that, for the soil samples included in this study, the PXRF concentrations for strontium and zirconium increased with finer granule size. The results for Ti, Mn, Fe, Cu, and Zn were fairly reliable, and the spread of the range of concentrations was never extremely high, particularly for Cu and Zn. Grinding soil samples to pass a 100 mesh (<149 µm) in the field would be very time-consuming and restrict the amount of samples analyzed per field season. However, samples analyzed after passing a 10 mesh (<2 mm) showed reliable results for most elements of interest, and it would be more practical for field work.

PXRF results attenuation or enhancement of signal at different moisture levels

Moisture content could easily impact the PXRF instrument readings and this study tests the impacts of four soil moisture levels on five unique soils. This knowledge would help determine whether soil drying in the field is needed – a time consuming factor which would slow field analyses. The four moisture levels were oven-dry, air-dry, field capacity, and saturated. Elemental concentrations of the elements Mn, Fe, Cu, Zn, Sr, and Zr for the five soils at four moisture levels showed significant differences among the moisture levels (Tables 8-12). The statistical significance of differences among the four moisture levels (denoted with letters), and the percent change of the means in comparison to the oven-dry level are shown (Tables 8-12). Water content at the time of analysis is shown in kg kg^{-1} of H_2O in the top right corner of Tables 8-12. The mean of the four repetitions and the percent change of the air-dry, field capacity, and saturated moisture levels in comparison to the oven-dry levels are displayed to discern if there are any departures from the reference value (the oven-dry moisture level), and if this departure is either an enhancement (a larger value) or an attenuation (a smaller value) of the PXRF signal in comparison to the oven-dry mean levels.

The PXRF readings for the elements Mn, Cu, Zn, and Sr presented significant differences among the moisture levels for the sand soil (90% sand, 6% clay) (Table 8). The measurements of Fe and Zr showed no significant differences between the moisture levels. Moreover, oven-dry, air-dry, and field capacity moisture levels were not significantly different for any of the six elements read in this study at any given moisture level. In general, the air-dry moisture levels showed an enhancement of the X-Ray signal in comparison to the reading for the oven-dry level, except for Cu.

Table 9 shows the results of the PXRF readings under four moisture levels for the clay soil (19% sand, 54% clay). Except for Zr, all the other elements (Mn, Fe, Cu, Zn, and Sr) showed significant differences between the moisture levels. In addition, the oven-dry and air-dry moisture levels were significantly different for Mn and Sr, presenting the air-dry moisture level lower values than oven-dry for both elements. In the case of Mn, the air-dry moisture level was 60 percent lower than the oven-dry moisture level PXRF reading. The remaining elements presented moderate variations.

Table 10 shows the PXRF readings for the four moisture levels in a soil with high organic matter content (5.5% organic matter, 20% sand, 42% clay). Only the PXRF readings for manganese presented no significant differences between the four moisture levels. This soil also showed significant differences between the oven-dry and air-dry PXRF readings for the element Zn. Percent changes between the oven-dry and air-dry measurements presented relatively low variations.

Table 11 presents the PXRF reading results for the soil with low organic matter (1.2% organic matter, 45% sand, 35% clay). While Mn and Fe presented no significant differences between all four moisture levels, the other elements (Cu, Zn, Sr, and Zr) showed significant differences between the moisture levels. Oven and air-dry levels showed statistical differences for the Sr readings only. In general, the percent changes are quite low between the oven-dry and air-dry PXRF readings.

The last soil analyzed in this study was a loam soil (51% sand, 19% clay) (Table 12). The elements Mn, Cu, and Zr showed no significant differences between the readings of any moisture level. Percent changes were also relatively low, except for Cu, where the oven-dry PXRF readings gave a Cu level more than twice as high in comparison to the other moisture levels. Significant differences were seen for iron, zinc, and strontium; the greatest attenuations were seen for the saturated moisture level. Moreover, no significant differences were detected for the oven-dry and air-dry, except for the Sr PXRF readings, where the air-dry measurement was six percent lower than the oven-dry PXRF readings.

This study has shown that different elements react in various manners under changing moisture contents, and the PXRF readings for various elements most likely had a strong dependence on factors such as soil type and texture. It is not possible to suggest or encourage an ideal method to run the PXRF on-site, since the needs of various researchers may not be similar. The method of analysis used on-site will depend on the elements desired to read, the precision and accuracy required, and the speed at which results are wanted. Oven-dry and air-dry samples will require an extra day to achieve these moisture levels, plus the need of an oven and the collection and transport of soil samples to a field laboratory. It is clear that soil samples should not be analyzed under saturated conditions, while the field capacity moisture levels produced results comparable to the oven-dry and air-dry readings. From our field experiences, most soils will be between field capacity and air-dry moisture levels, thus allowing the researchers to perform on-site PXRF analysis with a high level of confidence on the results.

PXRF total concentrations for Plaza B and Plaza D

Plaza B

There were 299 samples collected using a plastic trowel from Plaza B in a combination of a 5-m and 10-m grid after the surface organic litter was removed. Soil samples were then stored in sterile Whirl-Pak bags.

The Cu concentration isopleths within Plaza B was plotted (Figure 1). These concentrations showed a minimum PXRF Cu level of 35, a maximum of 63, and a mean of 44 mg kg^{-1}.The location of the highest values in the southwest corner of the plaza was the same as the high spot identified using the DTPA extractable Cu isopleth (see Chapter 1, Figure 7). However, the PXRF Cu concentrations were higher (~ 1 mg/kg of DTPA extractable Cu vs ~ 60 mg/kg PXRF Cu). The Cu was also semi linearly distributed in the east side of the plaza.

The Fe concentration isopleths is shown in Figure 2. The minimum, maximum, and mean PXRF Fe concentrations were 1561, 16170, and 4777 mg kg^{-1}, respectively. The PXRF Fe isopleths and the isopleths created from the DTPA extractable Fe were almost opposite images of each other (see Chapter 1, Figure 6). DTPA extractable Fe was persistent throughout the east side of Plaza B, while PXRF Fe was found mostly on the west side of Plaza B. We believe that this sharp difference may be due to the form of Fe in the soil. The east side of the plaza is regularly swept of organic materials using metallic rakes; plants and trees are also chopped or trimmed using machetes. Overtime, these activities will likely increase Fe concentrations, and it appears that DTPA is better at extracting this fraction of Fe. The high PXRF Fe levels found in the west side of the plaza may probably be due to the natural constituents of the soils, and not related to human activities.

The Mn concentration isopleths created with the distribution of PXRF Mn is shown in Figure 3. These concentrations showed a minimum of 67, a maximum of 614, and a mean of 296 mg kg^{-1}. The distribution of PXRF Mn was very similar to the distribution found for DTPA extractable Mn (see Chapter 1, Figure 8), although the range of PXRF Mn levels was much higher as would be expected since it represents total Mn concentrations. DTPA extractable Mn concentrations never exceeded ~ 28 mg kg^{-1}. The PXRF Mn distribution was prevalent in the west side of the plaza, and less predominant along the east side. As observed in the DTPA Mn concentration isopleths (see Chapter 1, Figure 8), there was a high spot of PXRF Mn in the southwest area of Plaza B. Another high spot was located about 10 m east of the debris line in the area cleaned up of understory vegetation.

The PXRF Zn concentration isopleths was plotted (Figure 4). The minimum, maximum, and mean averages for PXRF Zn were 40, 171, and 72 mg kg^{-1}, respectively. There were two similarities in the distribution of Zn between the PXRF and the DTPA extractable Zn (see Chapter 1, Figure 9). Two hot spots were identified in both concentration isopleths, one being located in the southwest side of Plaza B, and the other about 20 m east of the debris line, in the area that is swept clean regularly. However, PXRF Zn showed a much more interesting pattern. In the north half of the plaza, there was a very clear difference in concentration distribution. In the very east side, there was a linear pattern of Zn concentration that went from the northeast corner to about half of the plaza, stopping right at the feet of the stairs of the structure called La Iglesia. Then, there was an absence of high Zn content between coordinates 0 and -20 East. After -20 East, the high Zn content increased and drew a rectangle in the north side of the plaza with very distinct linear concentrations, especially in the south side. The cause of these sharp patterns could be related to many things: if the plaza floor at this area ever had stucco floors, if there were any construction period differences between the north and south sides of Plaza B, if the material obtained to stucco the north and south sides came from the same quarry, and if a specific human activity caused this distinct Zn loading in the north side of the plaza. We do not believe that these Zn concentrations were due to ancient or modern anthropogenic activities, since no other element analyzed in this study followed a similar pattern. However, we suggest that, in the most conservative sense, this PXRF Zn pattern was due to differences in the stucco floor of the plaza, or the lack of it. It could be that the materials used to build or repair the north side of La Iglesia were also used to fill, fix, or consolidate the north side of Plaza B.

Plaza D

Soil surface samples collected within Plaza D totaled 376 samples. The entire plaza was sampled on a 10-m grid, and transects were cut along the vegetation to gain access to the soil surface. Isopleths were created with the distribution of the elemental concentrations of PXRF Cu, Fe, Mn, and Zn.

In regards to Cu, Figure 5 shows the concentration isopleths with the PXRF readings. The pattern of DTPA extractable Cu and PXRF Cu slightly overlapped in the middle of the plaza (see Chapter 1, Figure 12). However, there was little resemblance between each other. Copper analyzed with the PXRF presented a minimum, a maximum, and a mean concentration of 24, 53, and 42 mg kg^{-1}, respectively. The DTPA extractable Cu did not exceed ~ 2 mg/kg, and had less spots with high Cu. The PXRF Cu presented a somewhat linear pattern in the southwest side of the plaza. The conical structure El Xaibe also presented high PXRF Cu in the east side and to the north of it. Other spots with high PXRF Cu were visible throughout the plaza, with no identifiable pattern.

Iron concentration isopleths was plotted (Figure 6). Portable XRF Fe levels ranged from 2632 to 86800 mg kg^{-1}, with a mean of 15887 mg kg^{-1}. While DTPA extractable Fe was relatively high close to El Xaibe (see Chapter 1, Figure 11), the PXRF Fe concentrations near the structure were not high. The high PXRF Fe spots were ~ 20 m south of El Xaibe, off the center of the site about 10-20 m south, and in a group of samples in the north corner of Plaza D. These distributions of PXRF Fe did not represent a very clear pattern, and we believe that the differences encountered here were due to natural Fe levels in the soil constituents.

Figure 7 shows the PXRF Mn concentration isopleths. The readings for PXRF Mn in Plaza D presented a minimum Mn level of 111, a maximum of 1870, and a mean of 484 mg kg^{-1}. The DTPA extractable Mn ranged from 1 to 50 mg kg^{-1}, and its distribution within Plaza D was quite different from the patterns shown by PXRF Mn (see Chapter 1, Figure 13). The area with the highest PXRF Mn enrichment was located on the north corner of the plaza, with a considerable PXRF Mn spot off the center of the plaza about 10-20 m south. These two high PXRF Mn spots actually resembled the pattern presented by PXRF Fe.

Concentrations of PXRF Zn are shown in Figure 8. There was some overlapping between PXRF and DTPA extractable Zn close to the middle of the plaza, but no other similarities were found between these two isopleths (see Chapter 1, Figure 14). Portable XRF Zn presented a more or less linear pattern that almost completely divided Plaza D in two. This linear pattern ran north-south, and it is 20-50 m wide. The minimum, maximum, and mean PXRF Zn concentrations were 38, 171, and 70 mg kg^{-1}. It is very unlikely that these concentrations of PXRF Zn were related to ancient or modern human activities, but rather related to the natural constituents of the mineral fraction of the soil.

Cluster Analysis of DTPA and PXRF concentrations for both Plazas

A cluster analysis of elements was created and plotted on Surfer Software to compare the trace metal concentrations by DTPA extraction and PXRF measurements of the soil samples collected within Plazas B and D of Cobá (Figures 9-12). It is important to notice that on top of Cu, Fe, Mn, and Zn, the PXRF measurements included Sr, Zr, Rb, and Ti, while the DTPA extraction did not. All P levels were measured using Mehlich-II extraction method for Plaza D and Olsen extraction method for Plaza B. Three hierarchical clusters were determined with JMP Software and plotted.

The PXRF elemental clusters within Plaza B were plotted on Surfer Software (Figure 9). Cluster 1 included low levels of P, Cu, Mn, Zn, Fe, and high levels of Sr and Zr. Cluster 2 consisted of high concentrations of Ti, Cu, Mn, Zn, Fe, and low P, Sr, and Zr. Cluster 3 presented high P and Zn, and low Ti, Mn, Fe, Cu, Sr, and Zr. Cluster 1 was found mostly in the southeast corner of Plaza B. Cluster 2 was predominant in the south portion of the plaza, west of the debris line. In regards to cluster 3, it was found in the majority of the area west of the debris line, and on the northeast portion of the surface close to the structure.

The three hierarchical clusters for DTPA concentrations for Plaza B were also plotted in Surfer (Figure 10). The patterns identified for the DTPA clusters were similar to the ones presented by the PXRF clusters. Cluster 1 was still found mostly on the east side of Plaza B. Cluster 2 was identified in the south portion of the plaza, but slightly shifted to the west in comparison to the PXRF cluster. Lastly, cluster 3 was predominant in the soil surface west of the debris line, as seen in the PXRF cluster.

In regards to the PXRF clusters for Plaza D (Figure 11), cluster 1 included high levels of Cu, and medium P, Sr, Zr, and Zn. Cluster 2 showed high PXRF Ti, Mn, Fe, Zn, Rb, Zr, and low P, and cluster 3 presented high P, medium Zn, and low trace metal concentrations. Cluster 1 was found along the southern edge at the foot of structures. Cluster 2 was identified close to the southern corner of Plaza D, and was also found outside the plaza in the northernmost edge, while cluster 3 was predominant in the north corner of Plaza D.

The DTPA extracted elements clusters for Plaza D were plotted (Figure 12). Cluster 1 consisted of medium P, and high Cu, Mn, and Zn. Cluster 2 included high Fe and Zn, and low P, while cluster 3 showed high P and medium Zn. Cluster 1 was not very predominant, but it was identified in the southwest area within Plaza D. Cluster 2 was found in the south corner and outside of the plaza in the northernmost corner, and cluster 3 was predominant in the north corner, as with the PXRF clusters.

In summary, although the PXRF and DTPA methods showed a different elemental fraction, these results hint that future geochemical studies could potentially include analysis of soil samples in the field for phosphates and PXRF concentrations, without the need to take the soil samples to a distant laboratory. Clusters for PXRF and DTPA concentrations in Plaza B (Figures 9-10) showed low P, Cu, Mn, Zn east of the debris line, and medium-high Cu, Mn, Zn, and Fe in the south area west of the debris line. Clusters for PXRF and DTPA concentrations within Plaza D (Figures 11-12) presented high P and medium Zn in the north corner, and low P and high trace metals in the south portion of Plaza D.

Conclusions

The PXRF instrument worked well and produced reliable results for the elements included in this study, except for very few values. There were no significant differences in the results of the readings using different protective films. Results from both the SpectroMembrane and the Whirl-Pak soil bags were reliable and did not present a serious source of contamination. The granule size study results showed that samples could be passed through a #10 mesh (< 2 mm) and still produce reliable PXRF reading values. In regards to moisture content in soil samples, the data showed that for the archaeological site of Cobá, it was necessary to have soil moisture at or drier than field capacity. However, soil texture has to be taken into consideration also. A field laboratory is recommended to aid with minor preparation of samples, such as air-drying and sieving soil samples to pass a #10 mesh size.

The PXRF study of the soil samples collected at both Plaza B and D in the site of Cobá also showed that the PXRF analysis captures a different fraction of trace elements in comparison to DTPA extraction. However, the cluster analysis presented that the areas of high and low concentrations presented very similar distributions for the PXRF and DTPA methods, although the PXRF levels were much higher for all elements. In addition, the PXRF total elemental concentrations could help to interpret sources of stucco, spatial differences in the chemical constituents of plaza floors, and possibly different construction periods if sharp elemental concentration differences are found in the soils or plaza floors.

References

Bernick, M., Kalnicky, D., Prince, G., & Singhvi, R. (1995). Results of field-portable X-ray fluorescence analysis of metal contaminants in soil and sediment. *Journal of Hazardous Materials, 43*, 101-110.

Carr, R., Zhang, C., Moles, N., & Harder, M. (2008). Identification and mapping of heavy metal pollution in soils of a sports ground in Galway City, Ireland, using a portable XRF analyser and GIS. *Environ. Geochem. Health*, *30*, 45-52.

Crook, V., Simpson, P., Rawson, B., & Wake, D. (2006). Investigation of PXRF procedures for measuring contaminated land. Health & Safety Laboratory 2006/102.

Dahlin B.H., Jensen C.T., Terry R.E., Wright D.R., Beach T. (2007). In search of an ancient Maya market. *Latin American Antiquity* 18:363-385.

Dahlin B.H., Bair D., Beach T., Moriarty M., Terry R. (2009). The dirt on food: ancient feasts and markets among the Lowland Maya, in: J. E. Staller and M. Carrasco (Eds.), Pre-Columbian Foodways: Interdisciplinary Approaches to Food, Culture, and Markets in Ancient Mesoamerica, Springer, New York. pp. 191-232.

Entwistle, J., & Abrahams, P. (1997). Multi-element analysis of soils and sediments from Scottish historical sites. The potential of inductively coupled plasma-mass spectrometry for rapid site investigation. *Journal of Archaeological Science*, *24*, 407-416.

Entwistle, J., Abrahams, P., & Dodgshon, R. (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.

Fernández F.G., Terry R.E., Inomata T., Eberl M. (2002) An ethnoarchaeological study of chemical residues in the floors and soil of Q'eqchi' Maya houses at Las Pozas, Guatemala. *Geoarchaeology: An International Journal* 17:487-519.

Hurkamp, K., Raab, T., & Volkel, J. (2009). Two and three-dimensional quantification of lead contamination in alluvial soils of a historic mining area using field portable X-ray fluorescence (FPXRF) analysis. *Geomorphology*, *110*, 28-36.

Jang, M. (2010). Application of portable X-ray fluorescence (pXRF) for heavy metal analysis of soils in crop fields near abandoned mine sites. *Environ. Geochem. Health*, *32*, 207-216.

JMP, Version 9. SAS Institute Inc., Cary, NC, 1989-2011.

Juvonen, R., Parviainen, A., & Loukola-Ruskeeniemi, K. (2009). Evaluation of a total reflection X-ray fluorescence spectrometer in the determination of arsenic and trace metals in environmental samples. *Geochemistry: Exploration, Environment Analysis*, *9*, 173-178.

Kalnicky, D., & Singhvi, R. (2001). Field portable XRF analysis of environmental samples. *Journal of Hazardous Materials*, *83*, 93-122.

Kodirov, O., & Shukurov, N. (2009). Heavy Metal Distribution in Soils near the Almalyk Mining and Smelting Industrial Area, Uzbekistan. *Acta Geologica Sinica* , *83*(5), 985-990.

Lopez Avila, V. L., Barcelo, D., Beckert, W., Goheen, S., Jinno, K., Keith, L., et al. (1998). Determination of metals in soils by field-portable XRF spectrometry. *Current protocols in field analytical chemistry* (pp. 3B.1.1-3B.1.8). New York: J. Wiley.

Melquiades, F., Bastos, R., Biasi, G., Parreira, P., & Appoloni, C. (2011). Granulometry and Moisture Influence for In Situ Soil Analysis by Portable EDXRF. *AIP Conf. Proc.*, *1351*, 317-320.

Olsen, S.R., Cole, C.V., Watanabe, F.S. & Dean, L.A. (1954). Estimation of available phosphorus in soils by extraction with sodium bicarbonate. *U.S. Department of Agriculture*, Circular 939.

Oonk, S., Slomp, C., & Huisman, D. (2009). Geochemistry as an aid in archaeological prospection and site interpretation: current issues and research directions. *Archaeological Prospection*, *16*, 35-51.

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

Peinado, F., Ruano, S., Gonzalez, M. B., & Molina, C. E. (2010). A rapid field procedure for screening trace elements in polluted soil using portable X-ray fluorescence (PXRF). *Geoderma*, *159*, 76-82.

Potts, P. J., & West, M. (2008). *Portable x-ray fluorescence spectrometry: capabilities for in situ analysis*. Cambridge, UK: RSC Pub.

Potts, P., Ellis, A., Kregsamer, P., Streli, C., Vanhoof, C., West, M., et al. (2005). Atomic spectrometry update. X-Ray fluorescence spectrometry. *Journal of Analytical Atomic Spectrometry*, *20*, 1124-1154.

Radu, T., & Diamond, D. (2009). Comparison of soil pollution concentrations determined using AAS and portable XRF techniques. *Journal of Hazardous Materials*, *171*, 1168-1171.

Revenko, A. (2002). X-ray fluorescence analysis of rocks, soils and sediments. *X-Ray Spectrometry*, *31*, 264-273.

Shibata, Y., Suyama, J., & Kitano, M. (2009). X-ray fluorescence analysis of Cr, As, Se, Cd, Hg, and Pb in soil using pressed powder pellet and loose powder methods. *X-Ray Spectrometry*, *38*, 410-416.

Stark, S., Snape, I., Graham, N., Brennan, J., & Gore, D. (2008). Assessment of metal contamination using X-ray fluorescence spectrometry and the toxicity characteristic leaching procedure (TCLP) during remediation of a waste disposal site in Antarctica. *J. Environ. Monit*, *10*, 60-70.

Taylor, P., Ramsey, M., & Potts, P. (2005). Spatial contaminant heterogeneity: quantification with scale of measurement at contrasting sites. *J. Environ. Monit.*, *7*, 1364-1370.

Terry R.E., Fernández F.G., Parnell J.J., Inomata T. (2004) The story in the floors: chemical signatures of ancient and modern Maya activities at Aguateca, Guatemala. *Journal of Archaeological Science* 31:1237-1250.

U.S. EPA, 1998. Field portable x-ray fluorescence spectrometry for the determination of elemental concentrations in soil and sediment. Method 6200.

VanCott, R., McDonald, B., & Seelos, A. (1999). Standard soil sample preparation error and comparison of portable XRF to laboratory AA analytical results. *Nuclear Instruments and Methods in Physics Research Section A*, *422*, 801-804.

Vanhoof, C., Corthouts, V., & Tirez, K. (2004). Energy-dispersive X-ray fluorescence systems as analytical tool for assessment of contaminated soils. *J. Environ. Monit.*, *6*, 344-350.

Weindorf, D., Zhu, Y., Chakraborty, S., Bakr, N., & Huang, B. (2011). Use of portable X-ray fluorescence spectrometry for environmental quality assessment of peri-urban agriculture. *Environ. Monit. Assess.*

Weindorf, D., Sarkar, R., Dia, M., Wang, H., Chang, Q., Haggard, B., et al. (2008). Correlation of x-ray fluorescence spectrometry and inductively coupled plasma atomic emission spectroscopy for elemental determination in composted products. *Compost Science and Utilization*, *16*(2), 79-82.

Zhu, Y., & Weindorf, D. (2009). Determination of soil calcium using field portable X-ray fluorescence. *Soil Science*, *174*, 151-155.

Tables

Table 1. Pearson's correlation (r) for the comparison of eight soil standard reference materials (certified values) against values obtained from PXRF readings and total nitric-perchloric acid digestion. All of the r values are positive.

	---------------------Pearson's correlation coefficient (r)------------------	
Element	PXRF with certified values	PXRF with total digestion
Ti	0.962	0.6494
Mn	0.9999	0.9986
Fe	0.9942	0.9832
Cu	0.9998	0.9996
Zn	0.9996	0.9847
Sr	0.9958	0.9763
Zr	0.9871	0.1097
Pb	0.999	0.9997

Table 2. The percent change between individual certified standards comparing the PXRF values analyzed through the Whirl-Pak soil bag and the SpectroMembrane plastic film. The average percent attenuation or enhancement of values per element and Pearson’s correlation coefficients (r) are listed. All of the r values are positive.

	Certified Standard Reference Materials									
Element	403	2710	1646	GXR-2	NBS 1b	2704	1645	2711	Average	Pearson's correlation
	- Percent Change -									r
Ti	-1	-31	-25	-8	-27	-26	0	-30	-18	0.98195
Mn	-13	6	44	63	-11	16	13	17	17	0.9961
Fe	-12	23	32	34	-7	23	-17	22	12	0.95999
Cu	-6	-13	-20	-36	-10	-12	-14	-23	-17	0.99995
Zn	4	-9	-8	-2	-3	-11	-9	-5	-6	0.99996
Sr	-9	-11	-8	-5	-11	-6	-11	-7	-9	0.99995
Zr	44	-3	-11	-3	34	3	16	-2	10	0.99125

Table 3. PXRF elemental concentrations found in a single layer of a soil bag, a single layer of the SpectroMembrane (protective plastic film supplied by Bruker Elemental), along with PXRF readings without a sample, with a bag, or with a SpectroMembrane placed on top of the PXRF windows probe.

Element	Spectro membrane (mg kg^{-1})	Soil Bag (mg kg^{-1})	No Sample (mg kg^{-1})
K	248	225	226
Ca	817	605	628
Ti	70	71	69
Cr	19	18	20
Mn	1	0	0
Fe	98	114	96
Ni	33	19	28
Cu	218	128	221
Zn	98	145	101
Br	4	3	3
Rb	24	16	22
Sr	27	19	23
Zr	6	4	0
Pb	121	89	129

Table 4. PXRF measurements of Ti, Mn, Fe, Cu, Zn, Sr, and Zr from the readings for soil surface sample A7 testing soils screened with sieve sizes 10, 40, 60, and 100 mesh. The mean concentrations, standard deviations (SD) and significant differences (denoted by letters) are given. Within a given element, values with same letter are not significantly different.

Element	Mesh #		Mean mg kg^{-1}	SD
Ti	10	B	438	44
	40	A	622	65
	60	A	594	88
	100	AB	509	33
Mn	10	A	277	1
	40	A	267	18
	60	B	233	7
	100	C	205	13
Fe	10	B	3371	96
	40	A	3743	257
	60	B	3327	121
	100	B	3203	168
Cu	10	A	55	9
	40	A	46	1
	60	A	49	3
	100	A	50	3
Zn	10	A	61	15
	40	A	53	2
	60	A	50	2
	100	A	51	1
Sr	10	D	3413	71
	40	C	3618	26
	60	B	4173	70
	100	A	4368	57
Zr	10	D	167	4
	40	C	178	2
	60	B	206	4
	100	A	214	2

Table 5. PXRF measurements of Ti, Mn, Fe, Cu, Zn, Sr, and Zr from the readings for soil surface sample B10 testing soils screened with sieve sizes 10, 40, 60, and 100 mesh. The mean concentrations, standard deviations (SD) and significant differences (denoted by letters) are given. Within a given element, values with same letter are not significantly different.

Element	Mesh #		Mean mg kg^{-1}	SD
Ti	10	A	496	78
	40	A	523	66
	60	A	521	70
	100	A	564	104
Mn	10	B	253	16
	40	A	287	9
	60	AB	277	6
	100	AB	266	21
Fe	10	B	3260	138
	40	A	3544	40
	60	A	3535	21
	100	A	3514	100
Cu	10	A	50	3
	40	A	48	1
	60	A	47	1
	100	A	51	3
Zn	10	B	50	3
	40	A	55	1
	60	AB	53	2
	100	B	50	1
Sr	10	C	3360	60
	40	C	3378	28
	60	B	3583	29
	100	A	3728	15
Zr	10	C	162	4
	40	BC	167	3
	60	B	173	3
	100	A	182	1

Table 6. PXRF measurements of Ti, Mn, Fe, Cu, Zn, Sr, and Zr from the readings for soil surface sample B21 testing soils screened with sieve sizes 10, 40, 60, and 100 mesh. The mean concentrations, standard deviations (SD) and significant differences (denoted by letters) are given. Within a given element, values with same letter are not significantly different.

Element	Mesh #		Mean mg kg^{-1}	SD
Ti	10	A	673	60
	40	A	705	50
	60	A	719	54
	100	A	727	60
Mn	10	A	302	17
	40	A	299	14
	60	A	287	15
	100	A	297	18
Fe	10	A	5163	95
	40	A	5086	103
	60	A	5093	50
	100	A	5052	72
Cu	10	A	48	3
	40	A	48	3
	60	A	49	2
	100	A	49	3
Zn	10	A	49	1
	40	A	47	2
	60	A	48	1
	100	A	48	1
Sr	10	B	3030	65
	40	A	3343	43
	60	A	3403	39
	100	A	3415	27
Zr	10	B	150	4
	40	A	167	3
	60	A	170	2
	100	A	170	3

Table 7. PXRF measurements of Ti, Mn, Fe, Cu, Zn, Sr, and Zr from the readings for soil surface sample D4 testing soils screened with sieve sizes 10, 40, 60, and 100 mesh. The mean concentrations, standard deviations (SD) and significant differences (denoted by letters) are given. Within a given element, values with same letter are not significantly different.

Element	Mesh #		Mean mg kg^{-1}	SD
Ti	10	A	419	39
	40	A	418	54
	60	A	318	74
	100	A	401	72
Mn	10	B	143	6
	40	A	171	10
	60	AB	152	20
	100	B	143	9
Fe	10	A	2219	125
	40	A	2443	70
	60	A	2427	226
	100	A	2240	86
Cu	10	A	48	2
	40	A	46	3
	60	A	49	2
	100	A	48	3
Zn	10	A	51	4
	40	A	50	2
	60	A	50	2
	100	A	50	2
Sr	10	C	3393	101
	40	B	3698	95
	60	A	4230	53
	100	A	4243	36
Zr	10	C	163	5
	40	B	182	5
	60	A	205	5
	100	A	205	2

Table 8. Elemental concentrations, significant differences, and percent change for the sand soil for the effect of moisture on PXRF readings. Four readings were performed for each soil moisture level: oven-dry, air-dry, field capacity, and saturated. Moisture levels with same letter are not significantly different at the 0.05 level. The percent change is in comparison to the oven-dry values. Water content in kg kg^{-1} at the time of the analysis is displayed in the top right corner.

	Moisture Level		Mean	% Change
Mn	Oven Dry	B	185	0
	Air Dry	B	208	12
	Field Cap	B	182	-2
	Saturated	A	354	91
Fe	Oven Dry	A	10955	0
	Air Dry	A	14770	35
	Field Cap	A	12005	10
	Saturated	A	14473	32
Cu	Oven Dry	A	36	0
	Air Dry	A	34	-6
	Field Cap	A	36	0
	Saturated	B	24	-33
Zn	Oven Dry	AB	46	0
	Air Dry	A	51	11
	Field Cap	A	50	9
	Saturated	B	42	-9
Sr	Oven Dry	A	306	0
	Air Dry	A	340	11
	Field Cap	A	324	6
	Saturated	B	222	-27
Zr	Oven Dry	A	111	0
	Air Dry	A	161	45
	Field Cap	A	133	20
	Saturated	A	95	-14

Moisture Level	Water Content kg kg^{-1}
Oven Dry	0
Air Dry	0.013
Field Cap	0.055
Saturated	0.28

Table 9. Elemental concentrations, significant differences, and percent change for the clay soil for the effect of moisture on PXRF readings. Four readings were performed for each soil moisture level: oven-dry, air-dry, field capacity, and saturated. Moisture levels with same letter are not significantly different at the 0.05 level. The percent change is in comparison to the oven-dry values. Water content in kg kg^{-1} at the time of the analysis is displayed in the top right corner.

	Moisture Level		Mean	% Change
Mn	Oven Dry	A	1320	0
	Air Dry	B	533	-60
	Field Cap	A	1228	-7
	Saturated	B	537	-59
Fe	Oven Dry	B	74550	0
	Air Dry	B	83825	12
	Field Cap	B	82775	11
	Saturated	A	104125	40
Cu	Oven Dry	AB	133	0
	Air Dry	A	144	8
	Field Cap	B	120	-10
	Saturated	C	76	-43
Zn	Oven Dry	A	87	0
	Air Dry	A	86	-1
	Field Cap	A	81	-7
	Saturated	B	58	-33
Sr	Oven Dry	A	19	0
	Air Dry	BC	12	-37
	Field Cap	AB	16	-16
	Saturated	C	8	-58
Zr	Oven Dry	A	200	0
	Air Dry	A	163	-19
	Field Cap	A	116	-42
	Saturated	A	86	-57

Moisture level	Water Content kg kg^{-1}
Oven Dry	0
Air Dry	0.017
Field Cap	0.323
Saturated	0.629

Table 10. Elemental concentrations, significant differences, and percent change for the soil with high organic matter for the effect of moisture on PXRF readings. Four readings were performed for each soil moisture level: oven-dry, air-dry, field capacity, and saturated. Moisture levels with same letter are not significantly different at the 0.05 level. The percent change is in comparison to the oven-dry values. Water content in kg kg^{-1} at the time of the analysis is displayed in the top right corner.

	Moisture Content		Mean	% Change
Mn	Oven Dry	A	791	0
	Air Dry	A	751	-5
	Field Cap	A	871	10
	Saturated	A	618	-22
Fe	Oven Dry	AB	29645	0
	Air Dry	A	32848	11
	Field Cap	B	26513	-11
	Saturated	B	26600	-10
Cu	Oven Dry	A	55	0
	Air Dry	AB	53	-4
	Field Cap	B	48	-13
	Saturated	C	28	-49
Zn	Oven Dry	A	131	0
	Air Dry	B	117	-11
	Field Cap	C	111	-15
	Saturated	D	62	-53
Sr	Oven Dry	A	251	0
	Air Dry	A	250	0
	Field Cap	B	213	-15
	Saturated	C	106	-58
Zr	Oven Dry	A	184	0
	Air Dry	A	195	6
	Field Cap	B	154	-16
	Saturated	C	77	-58

Moisture level	Water Content kg kg^{-1}
Oven Dry	0
Air Dry	0.123
Field Cap	0.416
Saturated	1.017

Table 11. Elemental concentrations, significant differences, and percent change for the soil with low organic matter for the effect of moisture on PXRF readings. Four readings were performed for each soil moisture level: oven-dry, air-dry, field capacity, and saturated. Moisture levels with same letter are not significantly different at the 0.05 level. The percent change is in comparison to the oven-dry values. Water content in kg kg^{-1} at the time of the analysis is displayed in the top right corner.

	Moisture Level		Mean	% Change
Mn	Oven Dry	A	325	0
	Air Dry	A	243	-25
	Field Cap	A	266	-18
	Saturated	A	264	-19
Fe	Oven Dry	A	14893	0
	Air Dry	A	14805	-1
	Field Cap	A	14368	-4
	Saturated	A	16083	8
Cu	Oven Dry	A	52	0
	Air Dry	A	51	-2
	Field Cap	A	52	0
	Saturated	B	33	-37
Zn	Oven Dry	AB	89	0
	Air Dry	A	102	15
	Field Cap	AB	87	-2
	Saturated	B	65	-27
Sr	Oven Dry	A	296	0
	Air Dry	BC	224	-24
	Field Cap	AB	284	-4
	Saturated	C	162	-45
Zr	Oven Dry	A	190	0
	Air Dry	A	189	-1
	Field Cap	A	188	-1
	Saturated	B	139	-27

Moisture level	Water Content kg kg^{-1}
Oven Dry	0
Air Dry	0.015
Field Cap	0.187
Saturated	0.373

Table 12. Elemental concentrations, significant differences, and percent change for the loam soil for the effect of moisture on PXRF readings. Four readings were performed for each soil moisture level: oven-dry, air-dry, field capacity, and saturated. Moisture levels with same letter are not significantly different at the 0.05 level. The percent change is in comparison to the oven-dry values. Water content in kg kg^{-1} at the time of the analysis is displayed in the top right corner.

	Moisture Level		Mean	% Change
Mn	Oven Dry	A	390	0
	Air Dry	A	374	-4
	Field Cap	A	326	-16
	Saturated	A	377	-3
Fe	Oven Dry	AB	21053	0
	Air Dry	AB	22120	5
	Field Cap	B	17868	-15
	Saturated	A	23678	12
Cu	Oven Dry	A	149	0
	Air Dry	A	60	-60
	Field Cap	A	61	-59
	Saturated	A	41	-72
Zn	Oven Dry	AB	86	0
	Air Dry	A	90	5
	Field Cap	B	76	-12
	Saturated	C	65	-24
Sr	Oven Dry	A	280	0
	Air Dry	B	263	-6
	Field Cap	AB	279	0
	Saturated	C	184	-34
Zr	Oven Dry	A	211	0
	Air Dry	A	199	-6
	Field Cap	A	172	-18
	Saturated	A	142	-33

Moisture level	Water Content kg kg^{-1}
Oven Dry	0
Air Dry	0.019
Field Cap	0.174
Saturated	0.413

Figures

Figure 1. Concentration isopleths of Cu in surface soils collected on a gridded area of Plaza B, Cobá, and analyzed by PXRF.

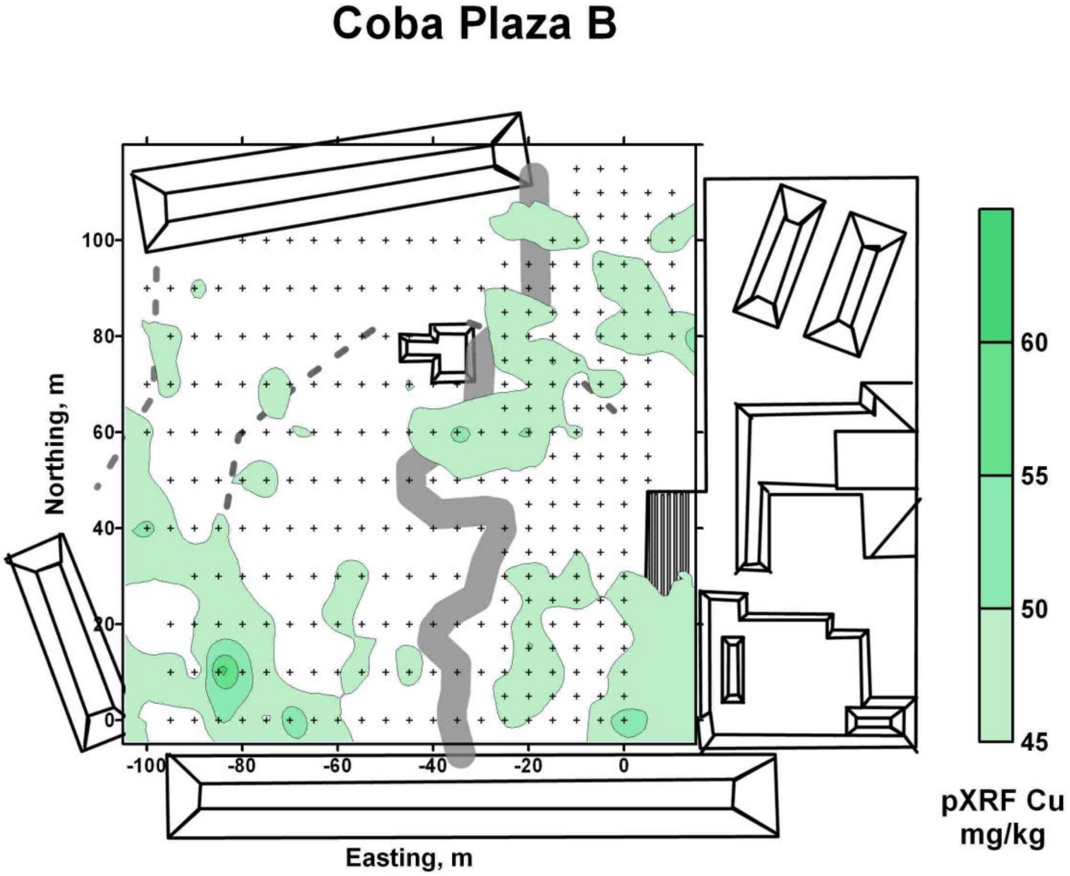

Figure 2. Concentration isopleths of Fe in surface soils collected on a gridded area of Plaza B, Cobá, and analyzed by PXRF.

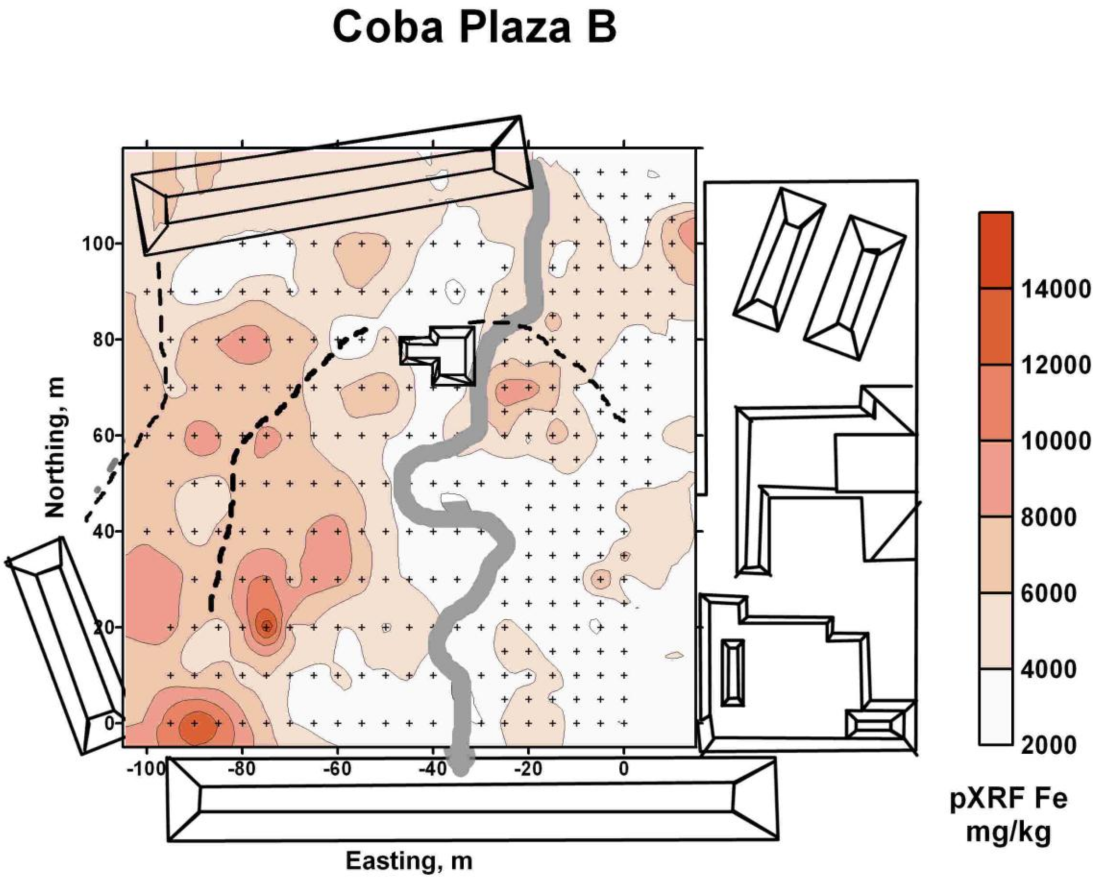

Figure 3. Concentration isopleths of Mn in surface soils collected on a gridded area of Plaza B, Cobá, and analyzed by PXRF.

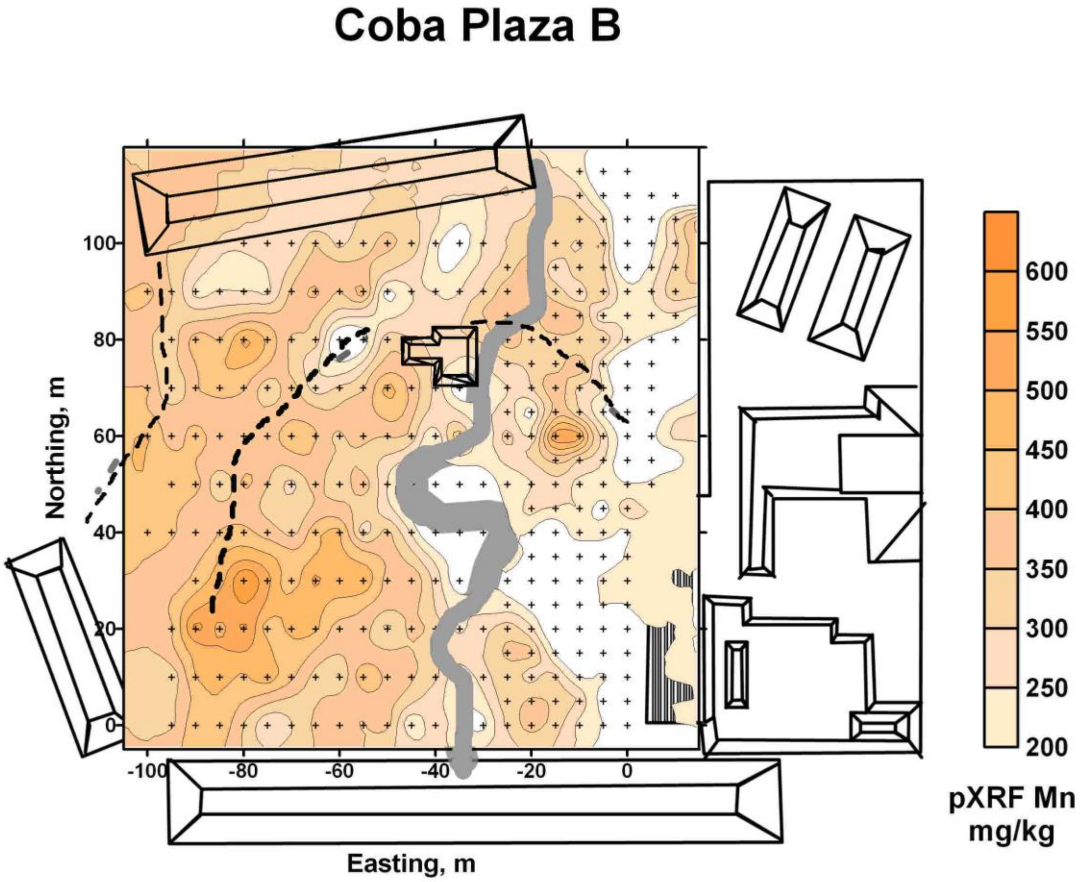

Figure 4. Concentration isopleths of Zn in surface soils collected on a gridded area of Plaza B, Cobá, and analyzed by PXRF.

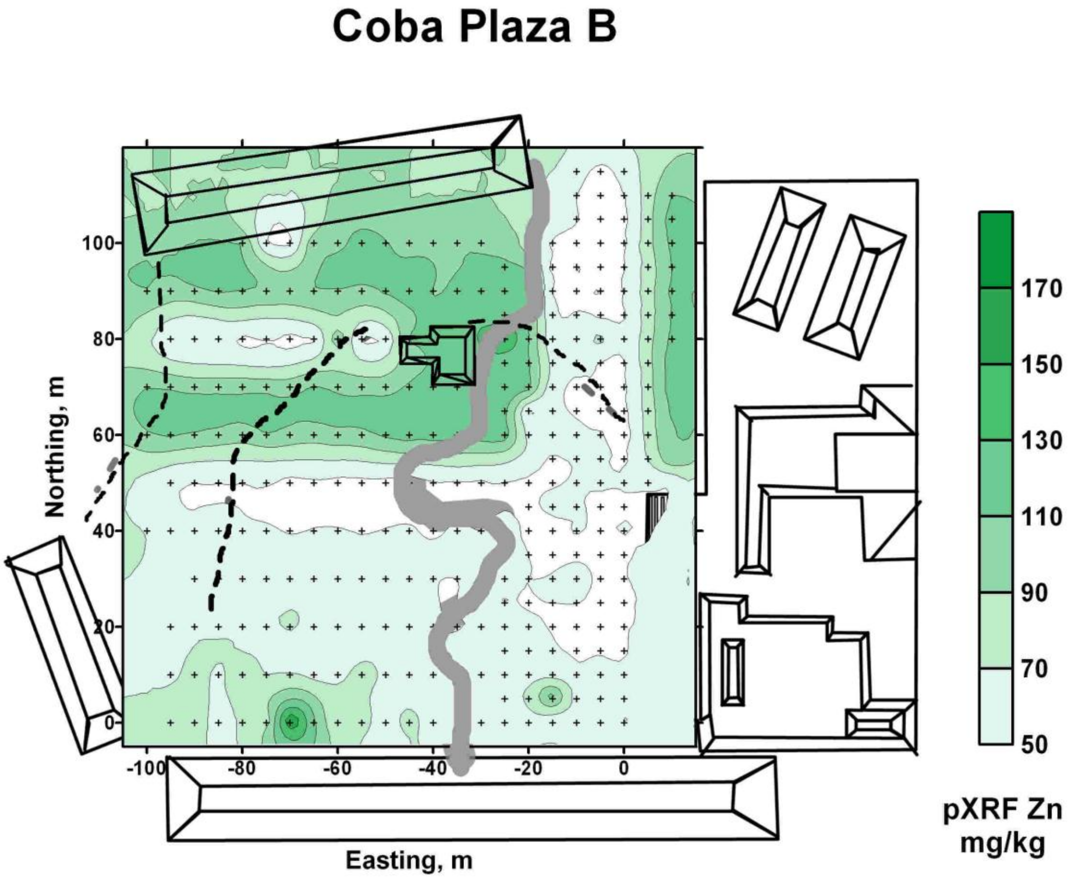

Figure 5. Concentration isopleths of Cu in surface soils collected on a gridded area of Plaza D, Cobá, and analyzed by PXRF.

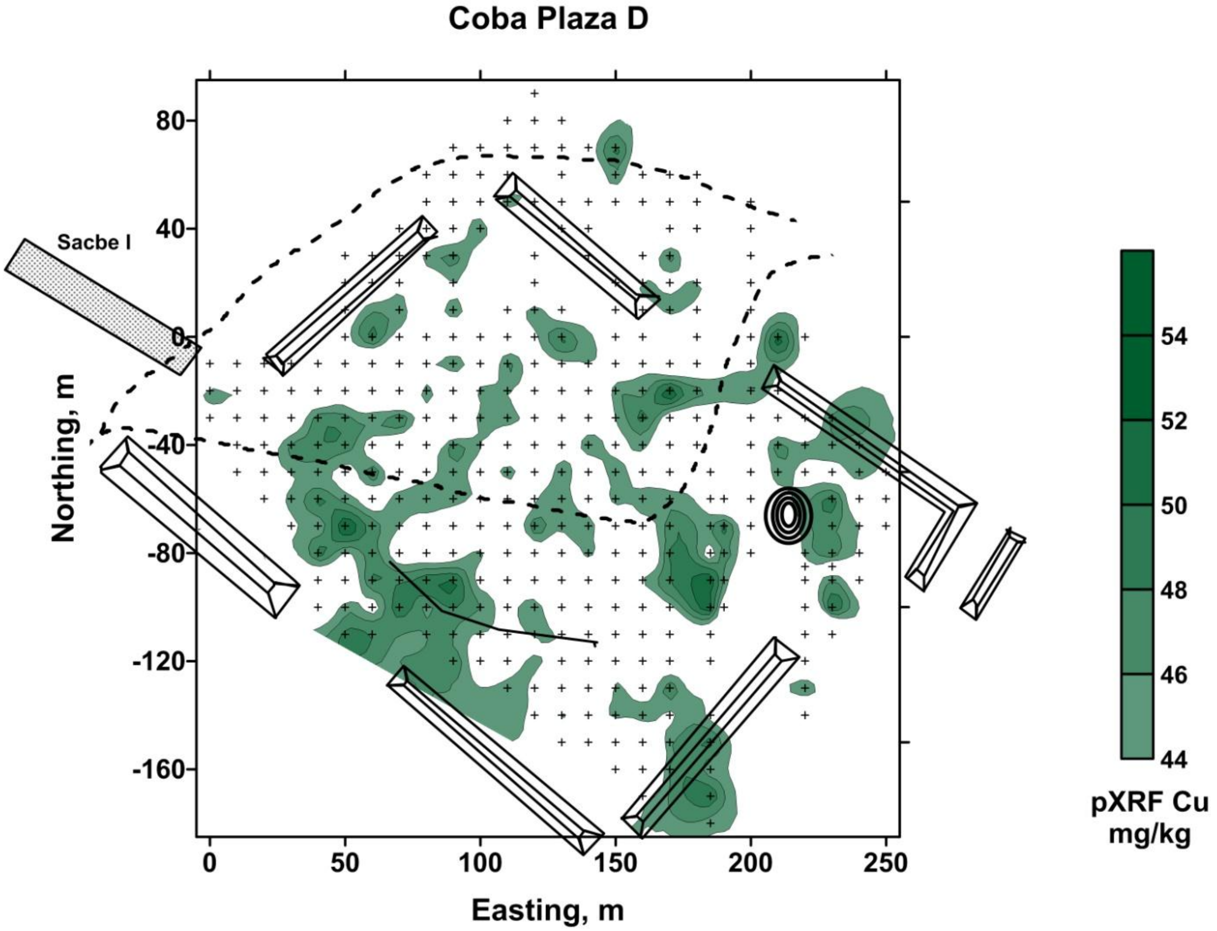

Figure 6. Concentration isopleths of Fe in surface soils collected on a gridded area of Plaza D, Cobá, and analyzed by PXRF.

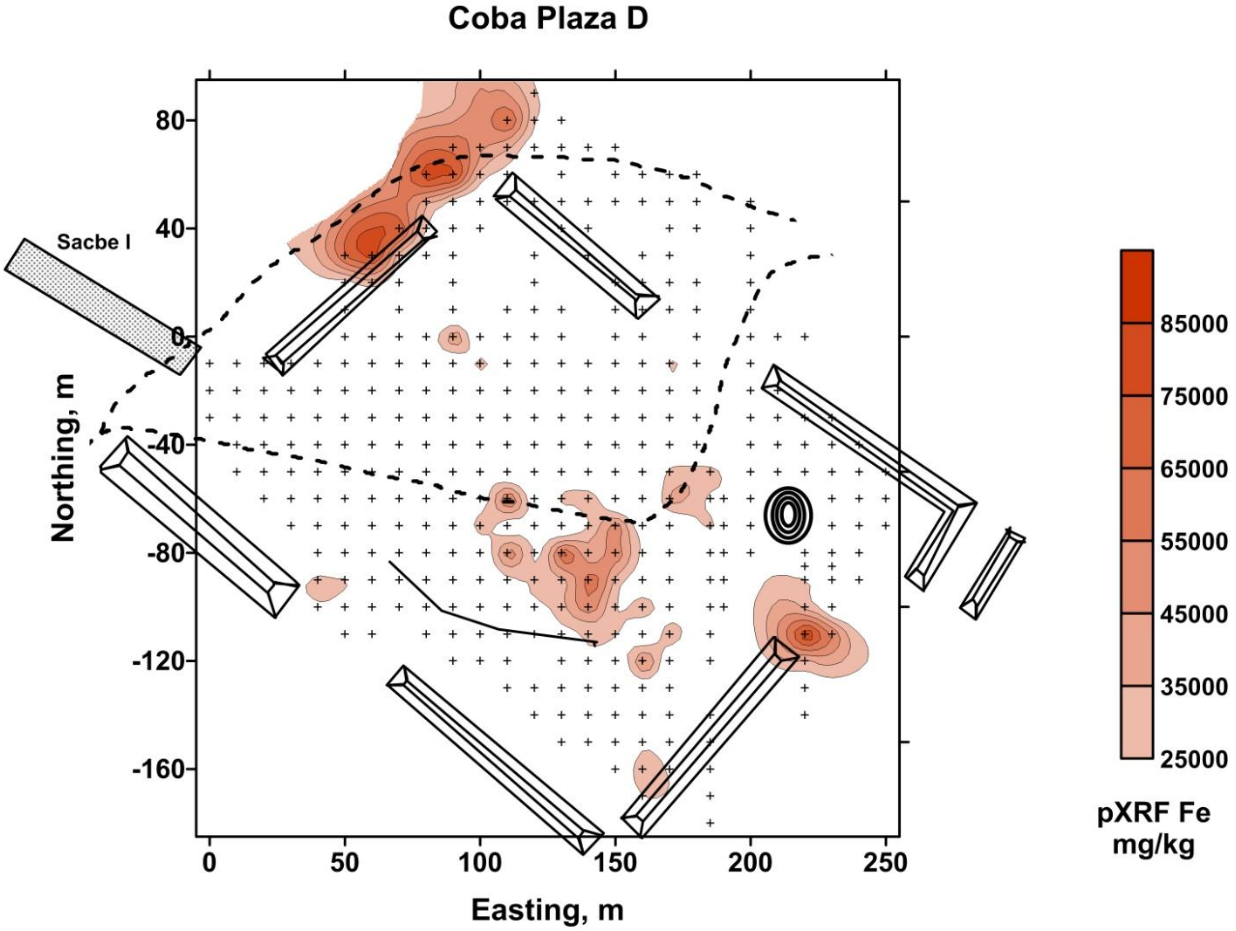

Figure 7. Concentration isopleths of Mn in surface soils collected on a gridded area of Plaza D, Cobá, and analyzed by PXRF.

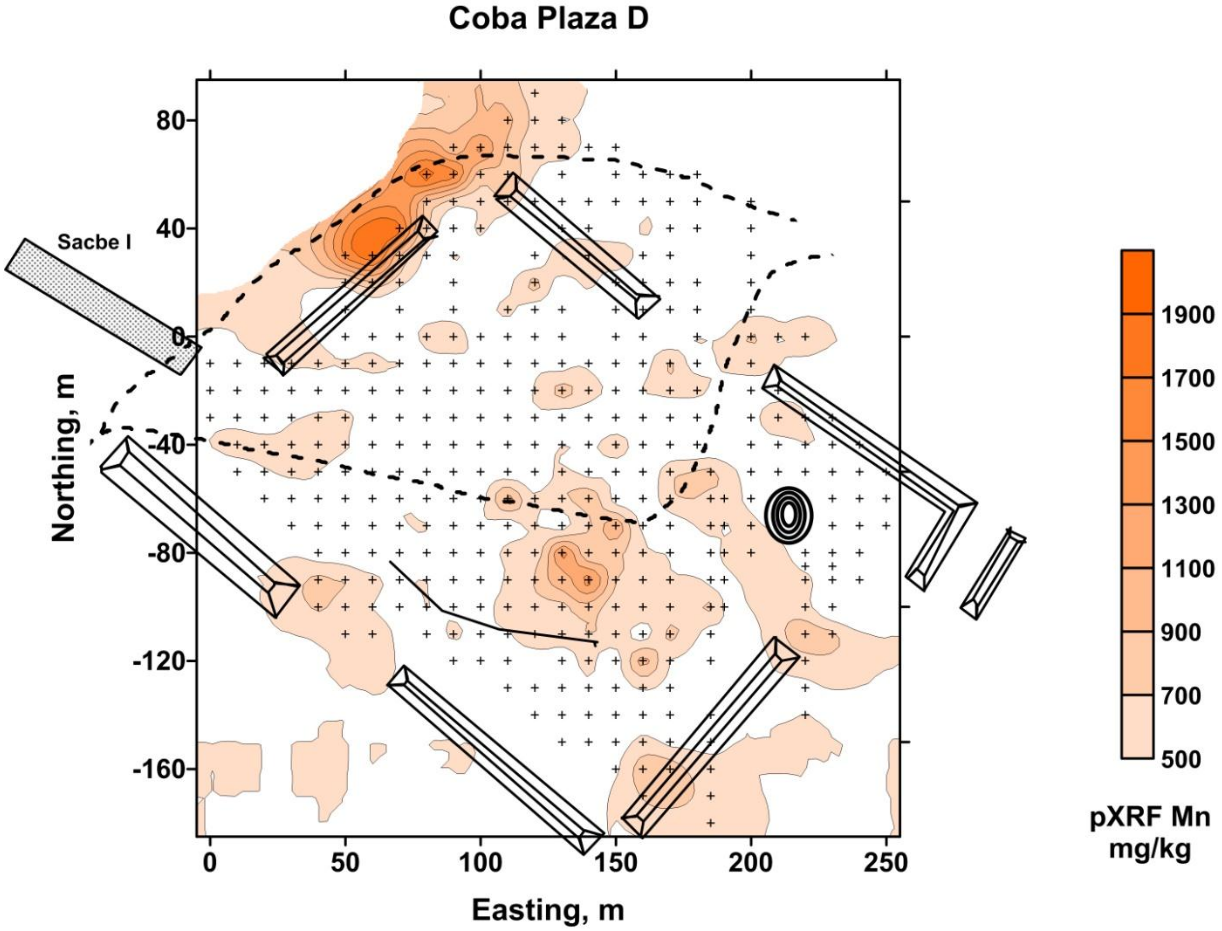

Figure 8. Concentration isopleths of Zn in surface soils collected on a gridded area of Plaza D, Cobá, and analyzed by PXRF.

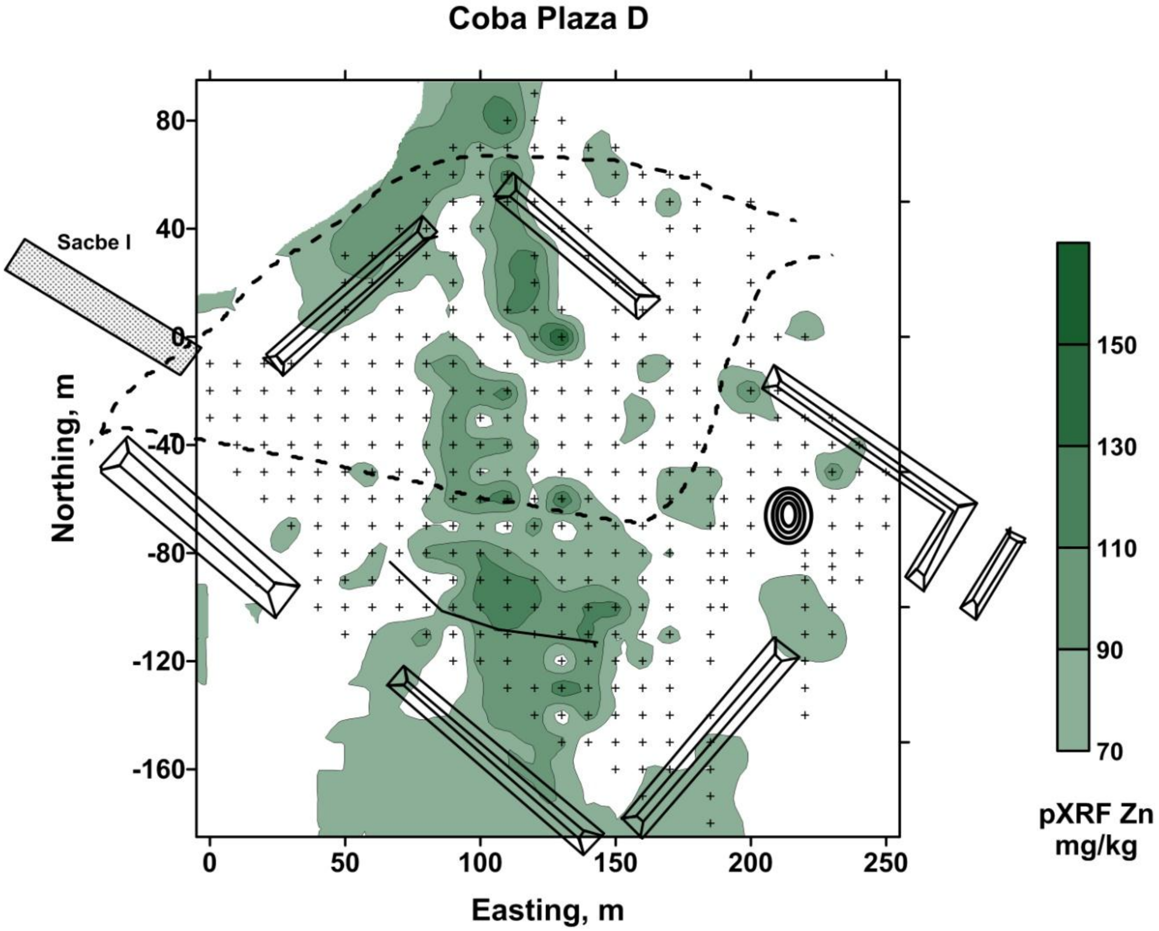

Figure 9. Plot of three clusters of PXRF elements created for Plaza B, Cobá. The elements included in the clusters were P, Ti, Cu, Mn, Zn, Fe, Sr, and Zr.

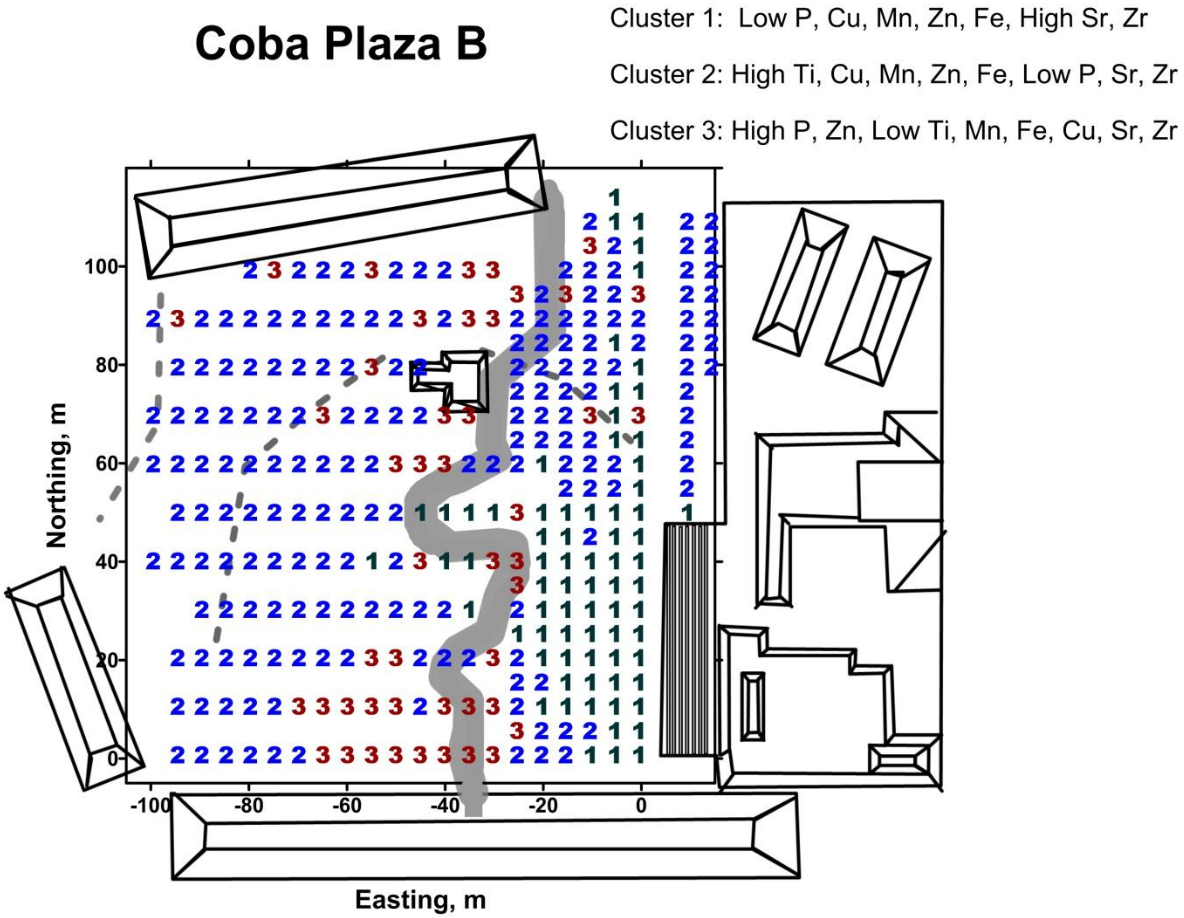

Figure 10. Plot of three clusters of DTPA Extractable elements created for Plaza B, Cobá. The elements included in the clusters were P, Cu, Mn, Zn, and Fe.

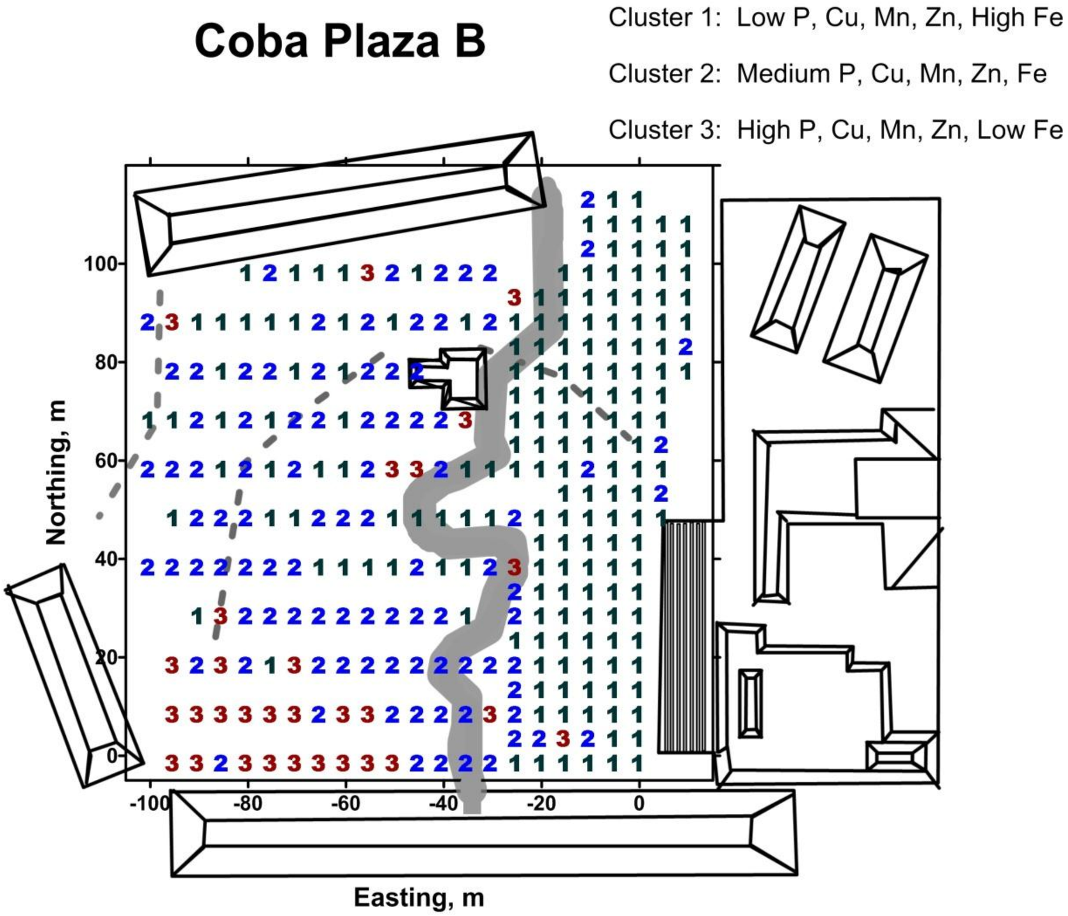

Figure 11. Plot of three clusters of PXRF elements created for Plaza D, Cobá. The elements included in the clusters were P, Ti, Cu, Mn, Zn, Fe, Sr, Rb, and Zr.

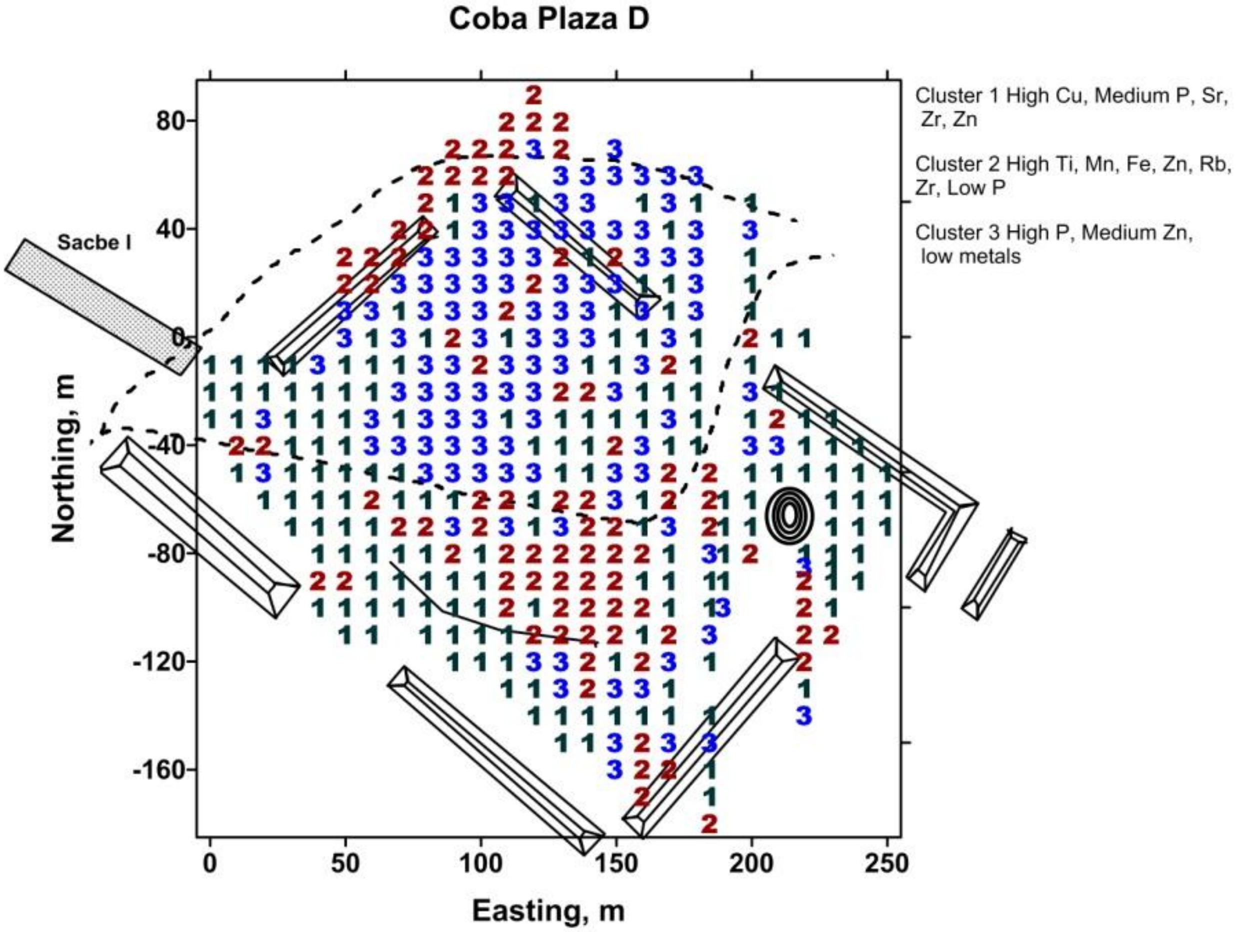

Figure 12. Plot of three clusters of DTPA Extractable elements created for Plaza D, Cobá. The elements included in the clusters were P, Cu, Mn, Zn, and Fe.