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FROM THE BRONZE AGE TO THE "LEAD AGE": OBSERVATIONS ON SEDIMENT ANALYSES AT TWO ARCHAEOLOGICAL SITES IN THE JEZREEL VALLEY, ISRAEL

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ABSTRACT

This paper reports on a study conducted on archaeological sediments from two sites in the Jezreel Valley, Israel: the Roman military camp of Legio, dating to the 2nd-3rd centuries CE, and the Bronze Age village of Tel Megiddo East, dating to Early Bronze I. The primary purpose of the study was to test the assumption that chronologically-specific metallurgical production and consumption would be evident through trace elements within archaeological sediments. Sediment samples were analyzed using a portable X-ray fluorescence (pXRF) device, as well as conventional wet chemistry techniques in order to compare the results between bulk element analysis and readily leachable cations, and to assess the feasibility of field-based pXRF for such study. Samples taken from various contexts at each site were analyzed specifically for concentrations of lead, copper, and zinc, which should hypothetically differ between a Roman Period site utilizing lead and brass (a copper/zinc alloy), versus an Early Bronze Age site participating in primarily copper metallurgy. Results demonstrate quantitative differences in the sediments between both sites, as well as the capability of pXRF to detect and quantify such trace elements. The implications of these results are discussed in terms of the archaeo-metallurgical context of the two sites.

KEYWORDS: XRF, Metals, Legio, Megiddo, Jezreel Valley, Roman, Elemental Analysis.

1. INTRODUCTION

This paper reports on a series of exploratory chemical analyses conducted on archaeological sediments from two sites in the Jezreel Valley, Israel, during the summer of 2013 (Figure 1). The research was conducted by the Jezreel Valley Regional Project (JVRP)[i] at the Roman military camp at Legio, dating to the 2nd-3rd centuries CE (hence RC; for historical and archaeological background, see Tepper 2007; Adams et al. 2013; Tepper et al. Forthcoming), and at the Bronze Age village at Tel Megiddo East, dating to the Early Bronze Ib period (ca. 3200 – 3000 BCE; hence BAV; see Adams et al. 2014; forthcoming).

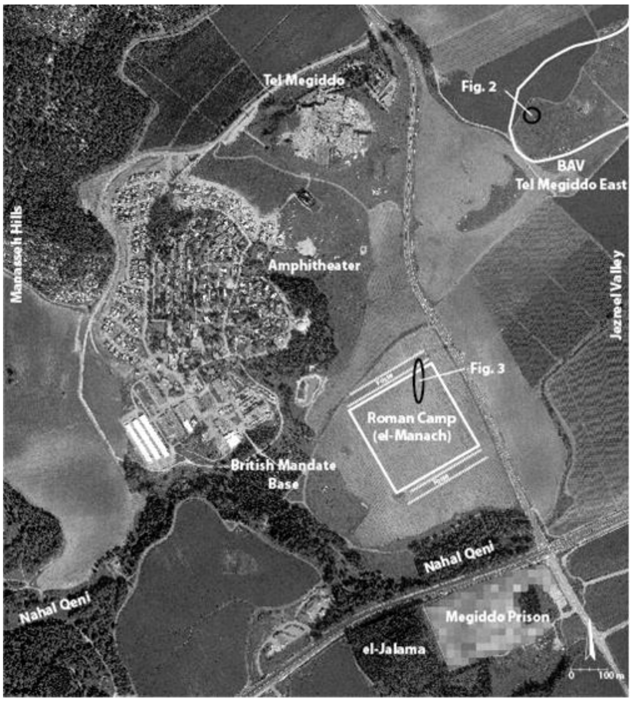

Figure 1. Map of the immediate region showing the site of Tel Megiddo East (BAV) and Legio (RC).

The purpose of the study was to explore methodological approaches toward quantifying concentrations of certain metals in sediments from two sites belonging to significantly different time periods in order to test the assumption that such elements may be interpreted as indicators of period-specific metallurgical production and consumption. These sediment tests were devised and planned heuristically during the excavations of the two sites, and were primarily aimed at analyzing the sediments for concentrations of Lead (Pb), Copper (Cu), and Zinc (Zn).

It is known that the use of Pb and its presence in the environment increased during the Roman Period (Montgomery et al. 2010). In the same period, the use of brass (Cu + Zn) increased in the region of the southern Levant relative to the use of bronze (Cu + Sn) (Ponting 2002), which had already been utilized to varying degrees throughout the region for more than two millennia. On the basis of these general patterns, chemical analyses of sediment samples should reveal distinct chemical signatures for Roman-era sites versus pre-Roman-era sites. In the case of a strong positive correlation between expected metallurgical norms and trace element concentrations, this method may be employed as a useful survey technique for dating archaeological sites by types of metals present, and possibly for determining spatially significant patterns of metallurgical activity within sites.

Multiple techniques may be used for elemental analysis of materials in sediment and other materials, particularly Neutron Activation Analysis (NAA) and Inductively Coupled Plasma (ICP) Spectrometry. NAA uses gamma-rays to measure a wide variety of elemental concentrations with good precision, but requires a nuclear reactor and measurements over duration of time. Variations of ICP (i.e. ICP-AES, ICP-OES, ICP-MS) heat plasma containing a sample to high temperature, causing elements to emit energy according to individual wavelengths that are quantitatively measured according to elemental abundance. Although such techniques are commonly employed in archaeometric analysis (e.g. Dirix et al. 2013; Misarti et al. 2011; Salisbury 2013; Wilson et al. 2008), they may be costly, time consuming, and ultimately destroy the sample under study, rendering it unavailable for further analysis.

Two alternative analytical methods were used in this investigation: (1) a portable X-ray fluorescence (pXRF) device and (2) conventional wet chemistry tests by Flame Atomic Absorption Spectroscopy (SM 3111B). These two methods utilize the same sampling strategy, but comprise considerably different analytical approaches. Whereas conventional wet chemistry techniques are destructive and must be completed using specialized equipment in a laboratory, but at relatively low cost, pXRF is a particularly attractive technology since it is non-destructive and expedient. Furthermore, pXRF has become an increasingly obtainable and common part of the archaeologist's toolkit (e.g. Frahm 2012; 2013; Frahm and Doonan 2013; Hunt and Speakman 2015; Liritzis and Zacharias 2011; Shackley 2011; Speakman and Shackley 2013), and general XRF technologies (including Energy Dispersive-XRF) have been used effectively in similar studies analyzing anthropogenic traces in archaeological sediments (e.g. Abrahams et al. 2010; Eliyahu-Behar et al. 2012). This study intends to elaborate on the practical uses of this technology by experimenting with a comparative analytic technique suited for archaeological fieldwork.

Although both techniques have the potential to measure the same general phenomena, they do so in different ways: pXRF is a bulk analysis technique, whereas the wet chemical analysis detects the readily leachable cations. Both techniques serve as broadly independent verification of the results, whereas the ratio of cations to bulk concentrations of elements may yield patterns of further significance to the study by indicating whether variation can be explained by naturally occurring oxides or some type of anthropogenic contamination.

The primary aims of these exploratory sediment analyses were: (1) to assess the feasibility and desirability of conducting tests related to the above assumptions at the two sites; (2) to obtain preliminary information on the local sediments, archaeological and others, and on peculiarities of the macro- and micro-environment that may bear on such tests; (3) to compare the results between the conventional wet chemistry techniques and pXRF analysis as a methodological query, including evaluating the ratio of cations to bulk concentrations; (4) to acquire qualitative and quantitative information that, in conjunction with previously published information, will help in planning future archaeological prospection. General distinctions between the two sites rely on statistical relationships among Pb, Cu, and Zn, as well as the wider range of data derived from the pXRF analysis, which may help indicate other significant elements worth future consideration.

The results detailed below indicate that quantitative differences do exist in the chemistry of the local sediments at each site. On the one hand, the RC contained higher concentrations of Pb than the BAV, supporting the hypothesis that Pb-related metallurgy and use during the Roman Period may be traced in the archaeological sediments from the site. On the other hand, the BAV contained notably higher concentrations of Cu than the RC, which may be expected from a site comprised of phases belonging to a period of known Cu exploitation. The data also indicate that the two different analytical methods are both capable of measuring the same broad patterns of distribution across both sites.

1.1. Archaeological and Geological Context

The two archaeological sites are situated only ca. 600 meters from one another and overlie limestone bedrock. The RC is situated on a moderate northeast-facing slope of the Lower-Middle Eocene Adulam Formation (Sneh et al. 1998). Basalt flows that intruded in the later Miocene can be found in various places in the Jezreel Valley, particularly in the ridge stretching from Givat Yoshiyau (northwest of the study area) eastward across the valley to Nazareth. One such intrusion marks the northern edge of the RC and is within 15 meters of some of the samples taken there. Historical studies indicate that the area of the RC was occupied by the Roman army, primarily *Legio VI Ferrata*, for nearly 200 years during the 2nd and 3rd centuries CE (Isaac and Roll 1982; Isaac 1990), and preliminary survey and excavation results indicate an architectural layout largely typical of Roman military camps of the period (Tepper 2007; Pincus et al. 2013; Adams et al. 2013; Tepper et al. Forthcoming). More recently, the area was occupied by the British army for only a few years during the end of WWII. From ca. 1950 to the present (probably also previously throughout the Ottoman Period), the area of the RC was fertilized and cultivated by the farmers of Kibbutz Megiddo. The topsoil and modern plow-zone covering the RC is not more than 30 cm in most places.

The BAV likewise sits upon Eocene chalk surrounded on one side by Pleistocene and Holocene clay deposits. During its occupation, the BAV was a significant agricultural village and regional center on the verge of urban development, ca. 3000 BCE. This settlement underwent at least four architectural phases during the terminal stages of the Early Bronze I, paralleling major changes at the nearby site of Tel Megiddo, which was the site of a cultic complex linked to the BAV (Adams et al. 2014). While the modern hillside on which the BAV is located has not been cultivated in more than 30 years, it was formerly a citrus orchard (ca. 1960s), and appears to have been part of an agricultural terrace in the Roman Period. The topsoil covering the BAV varies in thickness from 30 cm to more than 1 m in places.

The individual ancient and modern histories of these sites affected the composition of the local sediment. Beyond broader geomorphological processes in the area throughout the Holocene (cf. A. Rosen 2006), the magnitude of anthropogenic interferences and the exact identity of the interfering agents are not known, hence the nature of this study.

1.2. Sampling Strategy

Sediment samples were collected from stratigraphically secure contexts as determined by the excavation team, accompanied by appropriate documentation.[ii] From the BAV 15 samples were collected from archaeological sections (Figure 2), including all possible occupational layers within the four strata, as well as the topsoil horizon. The RC is a single-period site, and thus the 11 samples were collected from specific excavation contexts, such as floors, water pipes, and topsoil. Figure 3 shows the locations in the RC from which these samples derive, and Table 1 lists all samples with descriptions of their contexts.

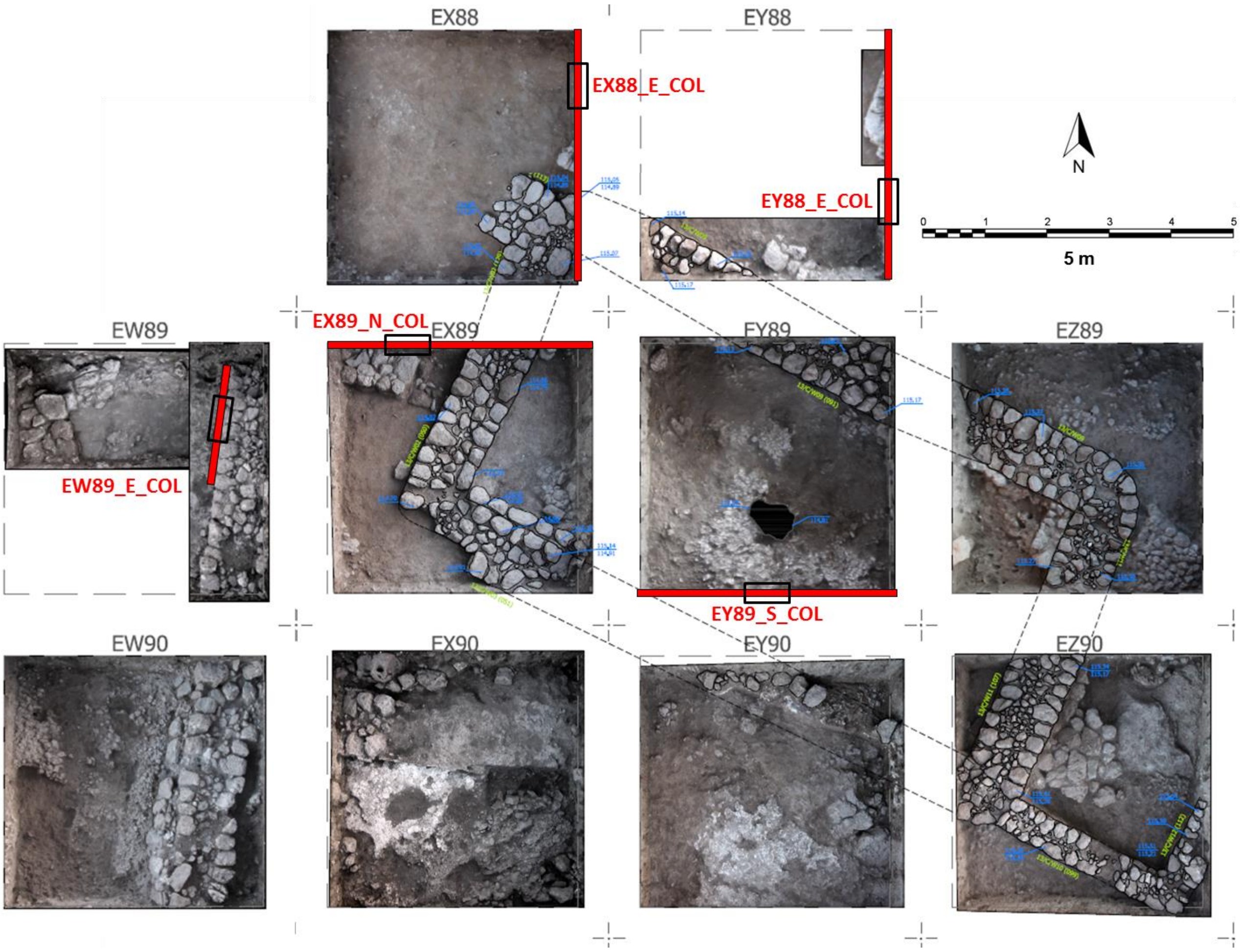

Figure 2. Locations of samples taken from archaeological sections (marked in red) from Tel Megiddo East (BAV).

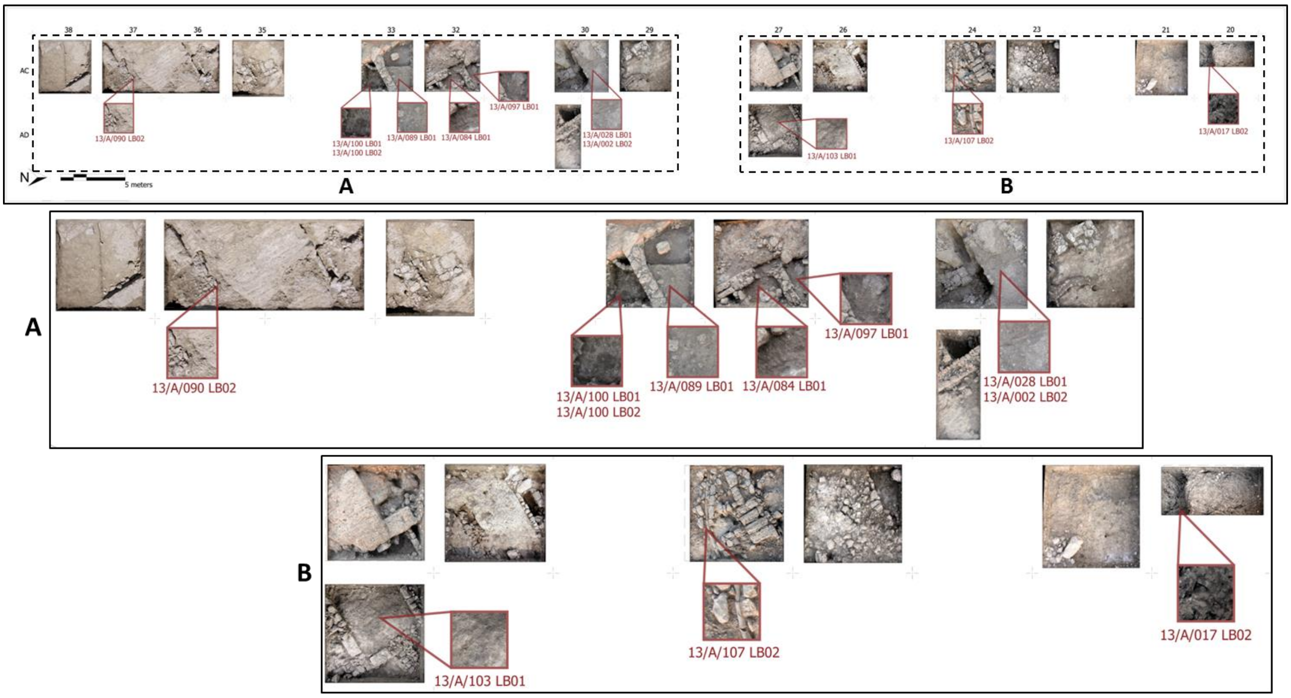

Figure 3. Locations of samples taken from archaeological contexts from Legio (RC).

Table 1. List of sediment samples from the BAV and the RC.

Sediment Samples from BAV			
Square	Column	Sample	Context Description
EY88	EY88_E_COL	S01	Upper alleyway
EY88	EY88_E_COL	S02	Lower alleyway
EY89	EY89_S_COL	S01	Topsoil
EY89	EY89_S_COL	S02	Occupational debris
EY89	EY89_S_COL	S03	Plaster surface + below
EX89	EX89_N_COL	S01	Occupational debris
EX89	EX89_N_COL	S02	Outside debris
EX88	EX88_E_COL	S01	Topsoil
EX88	EX88_E_COL	S02	Occupational debris
EX88	EX88_E_COL	S03	Below upper alleyway
EX88	EX88_E_COL	S04	Below lower alleyway
EW89	EW89_E_COL1	S01	Below outside alleyway
EW89	EW89_E_COL1	S02	Middle occupational debris
EW89	EW89_E_COL1	S03	Lower occupational debris
EW89	EW89_E_COL1	S04	Early (natural?) sediment
Sediment samples from RC			
Square	Locus	Sample	Context Description
AD27	13/A/103	LB01	Plaster floor
AC37	13/A/090	LB02	Topsoil (upslope)
AC20	13/A/017	LB02	Topsoil (downslope)
AC24	13/A/107	LB02	Water Pipe
AC30	13/A/028	LB01	Water Pipe
AC33	13/A/100	LB01	Floor
AC32	13/A/097	LB01	Floor
AC33	13/A/100	LB02	Floor
AC32	13/A/084	LB01	Floor
AC33	13/A/089	LB01	Floor (?)
AC30	13/A/002	LB02	Topsoil (mid-slope)

Samples were extracted using a standard steel trowel and immediately put into 1 L sediment sampling paper bags supplied by the Neve Yaar laboratory (hence NYL) in Israel, which subsequently conducted the conventional sediment chemistry analyses. Sample bags were labeled with identification numbers according to the recording standards of the excavation and parallel data recorded in the excavation database (Table 1). After non-destructive pXRF analysis was conducted in the excavation field laboratory (see below), the bagged samples were kept in a closed cardboard box and transferred to NYL.

While a random sampling strategy has its place in studies in which the territory is not known, both sites were well understood in terms of their nature, stratigraphy and chronology, and the types of contexts available. Having prior knowledge of the site, our sampling strategy was able to target specific, stratigraphically secure contexts (such as floors) and controls (such as topsoil and occupational layers, where possible). Furthermore, the objective of this study was to gather exploratory data in order to test the feasibility of comparative chemical studies, thus non-random judgment samples seemed justified. The need for solid controls, verified analytical treatments, and base lines still exists, and the results of the exploratory sediment tests reported here will help in designing more thorough studies in the future.

It should be noted that our sample size is rather limited, both in terms of quantity and distribution/control. Consequently, our observations and interpretations are only preliminary in nature. However, this study was implemented precisely as a preliminary study in order to explore analytical methods and, preliminary though they may be, the results constitute a methodological contribution that is well contextualized in an archaeological and historical context. Future study will be carried out by more intensive and extensive sampling, including additional archaeological sites representing different periods and functions, as well as geological controls from bedrock and sediments for the present purpose and further environmental research.

2. ANALYTICAL METHODS

2.1. *pXRF Analysis*

Once collected, the bulk sediment samples were first analyzed by pXRF before being sent to the NYL laboratory for conventional wet chemistry analyses. The handheld pXRF device used was a Bruker Tracer III-SD,[iii] and the samples were analyzed for 120 seconds at 40.00 kiloelectronvolts (keV) and 30.00μA, using a Yellow Filter (300 μm Al + 25 μm Ti). These parameters were optimized for measuring Copper (Cu), which has a Kα fluorescence at 8.05 keV, to Bromine (Br), which has a Kα fluorescence at 11.92 keV. In this process, the depth of analysis is contingent upon the energy of photons being sent into the material matrix (in this case, sediment), and can be expressed as $I/I_0 = e[-(\mu/\rho)x]$, where I is the quantity of photons returning from the sample, I_0 is the quantity of photons entering the sample, μ/ρ represents the mass attenuation coefficient of a given element for a particular matrix, and x represents the density of the object. Assuming a limit of 1% returning photons from a silicate matrix, the depths of analysis of key elements are shown in Table 2.

Table 2. The XRF depth of measurement for the analysis of Cu, Zn, and Pb elements.

Element	Fluorescence	Depth of Measurement
Cu	Kα = 8.05 keV	0.52 mm
Zn	Kα = 8.64 keV	0.71 mm
Pb	Lα = 10.55 keV	1.49 mm

When using pXRF to analyze conglomerate materials, such as sediment, a common challenge is the potential variability of constituent materials within the narrow X-ray field. As a result, individual readings may be skewed and may not necessarily represent the desired sample as a whole. A preferred method to overcome the inherent heterogeneity of sediment entails grinding the sample into a homogenized powder that is subsequently pressed into a pellet or fused into a disk, producing a uniform material for analysis (e.g., Hein et al. 2002; cf. Speakman et al. 2011). However, the present experimental application of the pXRF in a field laboratory lacked the means to prepare the samples in such a manner. As an alternative measure to ensure a comprehensive reading of each sample, three sub-samples (A, B, C) were quartered from each bulk sample and then analyzed.

The pXRF data for Cu, Zn, and Pb were quantified using an empirical reference set of 26 samples developed via the coring of multiple geological layers (Rowe et al. 2012). All data were normalized to background reflection of the spectra between 9.8 - 10.35 keV. These data were used to generate multiple linear models, following the Lucas-Tooth equation (1961)[iv]: $C_i = r_0 + I_i[r_i + \Sigma(r_{in}I_n)]$.

Following quantification, the three sub-samples were averaged, providing a mean value for the concentrations of the elements within each sample. Across the entire set of samples, the mean value of relative standard deviation between the three sub-samples was 6.6 percent, indicating that the procedure described above for pXRF analysis of sediment proved viable for the present study. In order for direct comparison with the NYL results, the pXRF concentrations of Cu, Zn, and Pb are calculated as parts per million (ppm).

2.2. *NYL FAA Analysis*

The detection and interpretation of heavy metals in anthrosols has been an area of growing interest in recent decades (e.g., Aston et al. 1998; Bintliff et al. 1990; Entwistle et al. 1998; Lewis et al. 1993; Linderholm and Lundberg 1994; Lambert et al. 1984; Parnell et al. 2002; Wells et al. 2000; Wilson et al. 2005). In calcareous sedimentary environments, metals are readily adsorbed or precipitated on the mineral surfaces, and the resulting metallic ions remain stable for long periods of time in the form of ions on clay surfaces, as well as insoluble oxides, sulfides, and carbonates (Wells et al. 2000; Lindsay 1979; Alloway 2013). Different extraction techniques and total analysis procedures yield divergent quantities of trace metals: total analysis digestion techniques essentially yield total elemental concentrations in sediments (similar to the bulk data of pXRF), whereas dilute acid or chelate extraction procedures remove soluble and easily labile trace elements absorbed on particle surfaces. The NYL analysis followed that latter approach, which mainly detects the readily leachable cations of these metals.

Preparation of the sediment samples at NYL comprised drying at 65 – 70° C for 24 – 48 hours to constant weight, after which the sediment was ground and sieved through a 2 mm sieve. Once prepared, aliquots were divided for the subsequent analyses. For analyzing the content of Zn, Cu, and Pb, the trace elements were extracted from the sediment using a DTPA – TEA (diethylenetriaminepentaacetic acid – triethanolamine) solution, which was filtered by gravity through Whatman #42 filter paper (after Lindsay and Norvell 1978). A chelate (DTPA) extraction was appropriate for the calcareous sediments used in this study because the procedure avoids the complete dissolution of $CaCO_3$, removing only the trace elements that were deposited in the sediment and adsorbed on the surfaces of particles (Wells et al. 2000). Samples of this process were then subjected to atomic absorption by Air – Acetylene Flame method (FAA, SM 3111B) using an instrument calibrated according to Merck standards. NYL also determined the total concentration of P using SM 4500-P E.

3. RESULTS

Generally, the NYL and pXRF data correlate moderately well, and highest for Pb (see Figure 4). Although the numeric values vary between the two methods, the relative patterns of distributions are quite similar, thus both methods appear to be fairly precise in terms of representing the concentrations of elements. The mean difference between NYL and pXRF values for each element are: Pb = 7.4 ppm, Cu = 30.5 ppm, and Zn = 100.7 ppm. Figure 5 shows pXRF data plotted NYL data, which demonstrates the overlap of Pb concentrations between sites and methods, whereas there are greater differences in Cu and Zn values.

The NYL data provide values for Cu, Zn, and Pb of only 1 – 5 ppm. These concentrations are much lower than would be expected in normal sediment deriving from the Earth's crust, which would be closer to 68, 79, and 10 ppm, respectively (Winters n.d.). In particular, the NYL values for Pb are quite low considering the metallurgical traces at the RC that would presumably result in values higher than in typical natural sediments, not lower (see below). However, since the NYL data represent dissolved cations rather than bulk elemental concentrations, the ratio between pXRF and NYL data appears to represent leachable metals.

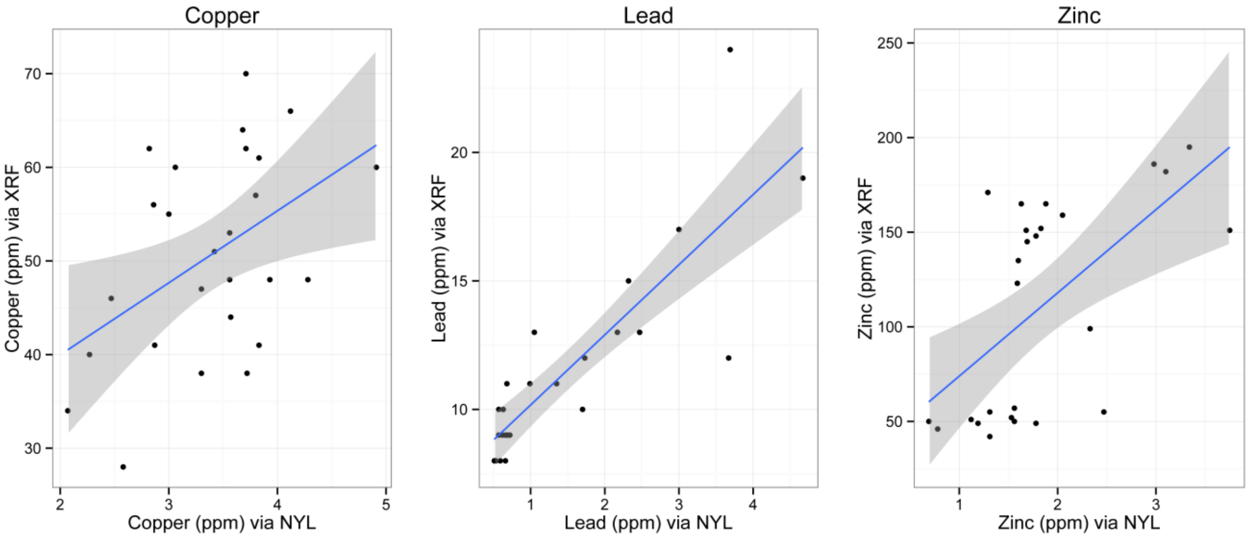

Figure 4. Linear regressions between NYL and pXRF results for Cu (left), Pb (center), and Zn (right). The statistical correlations between NYL and pXRF data are moderate for each element: Pb $r^2 = 0.65$ ($p < 0.0001$); Zn $r^2 = 0.38$ ($p < 0.001$); and Cu $r^2 = 0.33$ ($p = 0.002$).

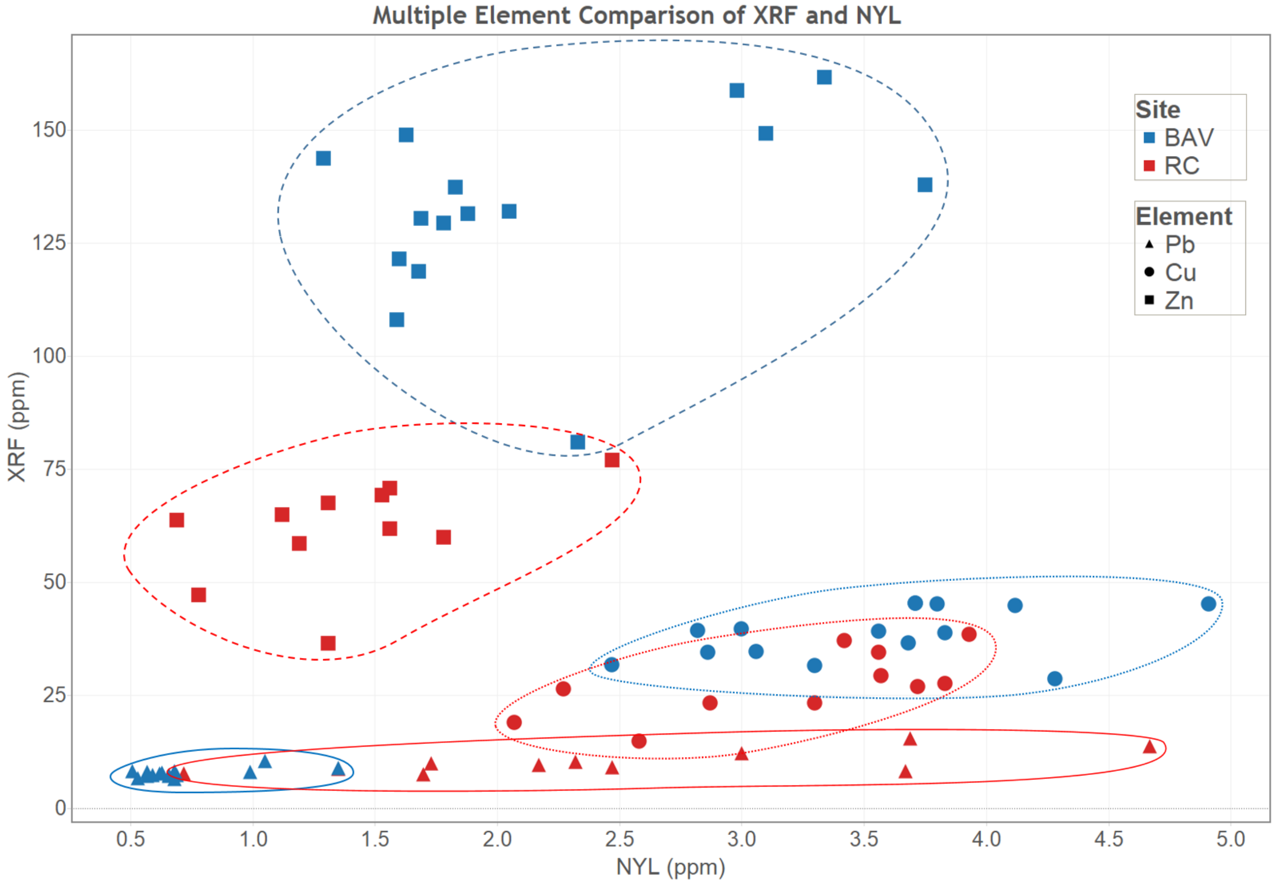

Figure 5. Comparison of Pb, Cu, and Zn via NYL and pXRF. NYL estimates vary between only 0.5 to 5.0 ppm, whereas pXRF estimates are considerably higher.

As determined by linear regression, the statistical correlations between NYL and pXRF results (Fig. 4) are moderate for each element: Pb $r^2 = 0.65$; Zn $r^2 = 0.38$; and Cu $r^2 = 0.33$. Whereas the correlations for Zn and Cu are fairly low by comparison with Pb, itself only a moderately-high correlation, these statistics demonstrate that both methods are measuring the same overall phenomena with a fair degree of precision, while also indicating notable departures, which we discuss below as relating to leachable metals.

We suggest that the primary reason for the different values and only moderate correlations derives from the fact that the NYL data represent dissolved cations, which are only a portion of the bulk elemental concentrations represented by the pXRF data (which do not discriminate the molecular state of an element). Some of the discrepancy between the two methods may also derive in part from different detection limits, which should theoretically be much more sensitive for the NYL method (parts-per-billion) than the pXRF (ppm).[v]

3.1. *Lead*

According to both the NYL and pXRF data, there is more Pb at the RC than at the BAV, as shown in the area histogram (Figure 6), but it is only a difference of ca. 2.5 ppm according to the pXRF data (difference of ca. 1.8 ppm using NYL data). It is certainly probable that the slightly higher concentrations of Pb at the RC derive from anthropogenic factors, yet the magnitude of difference is much lower in comparison to Pb directly associated with metallurgical contexts in the Levant (cf. Eliyahu-Behar et al. 2012).

pXRF spectral data for Pb are derived from the L-alpha line (10.55 keV, 1.49 mm estimated depth), which fluoresces at about 11% efficiency (e.g., 11 out of 100 atoms would be expected to fluoresce). The hypothetical pXRF detection limit for Pb in a pure silicate is around 3 ppm. However, the NYL results indicate that Pb concentrations vary between 500 ppb and 5 ppm. If these had been the concentrations in the present samples, there would have been no relationship between the NYL and pXRF results since Pb would fall below the detection limit for pXRF and thus be driven largely by Poisson variation in the spectrum (noise resulting from the reflection of high-energy photons off lighter elements). However, the correlation ($r^2 = 0.65$) between the two results suggests that both pXRF and NYL are in agreement on the variation of Pb in the sediments despite being in disagreement on the actual concentrations. Since the pXRF data in this study are consistent with known reference standards (e.g., RTC-W-205, see Rowe et al. 2012) measured on the same device, it would seem that the NYL concentrations are far below the detectable limits for Pb, and are therefore not representative of bulk composition.

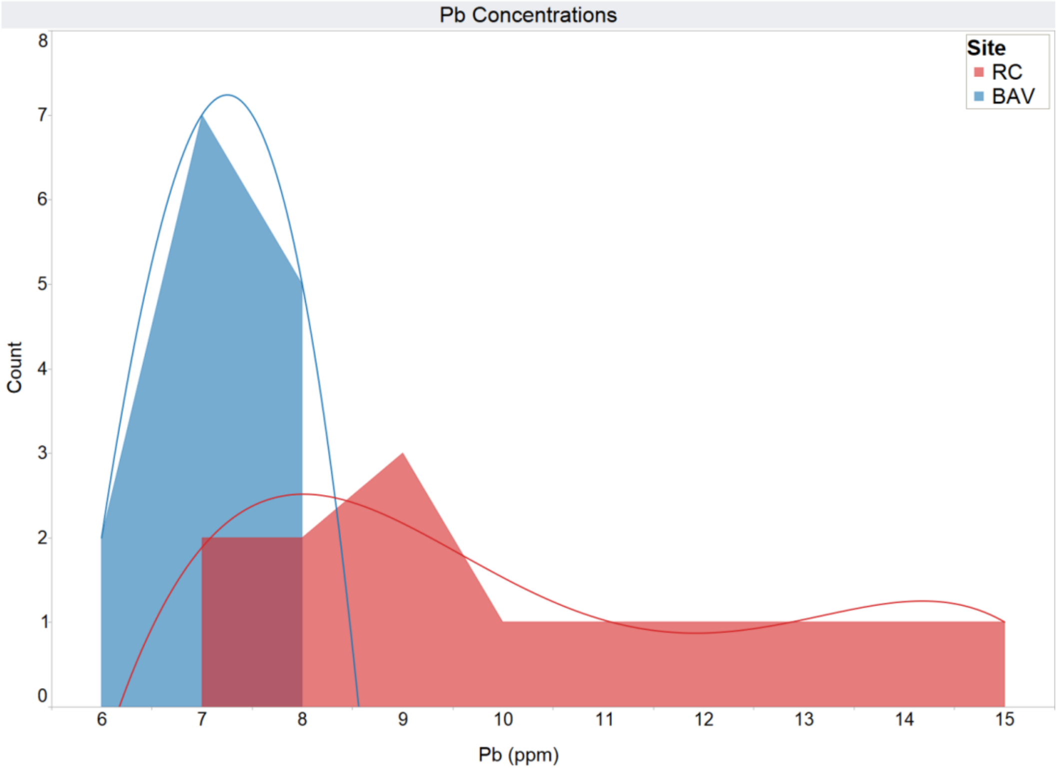

Figure 6. Comparison of the pXRF concentrations of Pb (ppm) between the RC (red) and the BAV (blue). The area histogram shows that the majority of BAV samples fall between 7-8 ppm, whereas RC samples are distributed between ca. 7-15 ppm.

The earliest (pre-settlement) stratigraphic layer at the BAV has the highest Pb concentration within that site. This result suggests that as a trace element, Pb here mostly derives from geological rather than anthropogenic factors. Other samples from the BAV with high Pb concentrations derive from the topsoil, which probably relates to Pb contamination from modern farming or by aerosols from the nearby roads (Erel et al. 1997; Erel 1998).

At the RC, the three samples from topsoil have the highest Pb content, particularly those from the middle and upper slope of the site. These latter two locations also represent the shallowest archaeological material on the site, and thus the highest probability of topsoil formation from archaeo-sediments. The sediment samples from within the in situ ceramic water pipes also have a fairly high Pb concentration, and are perhaps the most secure contexts, having been protected from potential exogenous contamination. Lead pipes are known from other Roman contexts (Hodge 1981; Hirschfeld 1993; Covello-Paran 2007) and may also have been in use elsewhere in the water-supply and drainage systems at this site. Of all the sampling contexts, floors were found to have the lowest Pb concentration. Thus, it seems that the non-random sampling strategy of collecting from specific archaeological contexts managed to capture a fairly wide range of variation of Pb, considering the relatively small sample size.

If the Pb concentrations from the RC derive from metallurgical activity, as supposed, then the residues would have more Pb cations than oxides (i.e., a high ratio of cations to bulk Pb). Interpreting the ratio of the FAA cation data to the pXRF bulk data as leachable Pb, there seems to be a significant pattern. The RC has a mean Cation : Bulk Pb Ratio of 0.25, whereas the BAV has one of only 0.09, with both sites yielding very different distributions ($p < 0.0001$), as illustrated in Figure 7. Therefore, not only does the RC generally comprise higher concentrations of Pb than the BAV, it also suggests much more Pb demonstrably derived from metallurgy rather than geological factors. Thus, it is possible to identify anthropogenic activity from Pb despite low concentrations (< 20 ppm) by using mixed FAA and XRF approach.

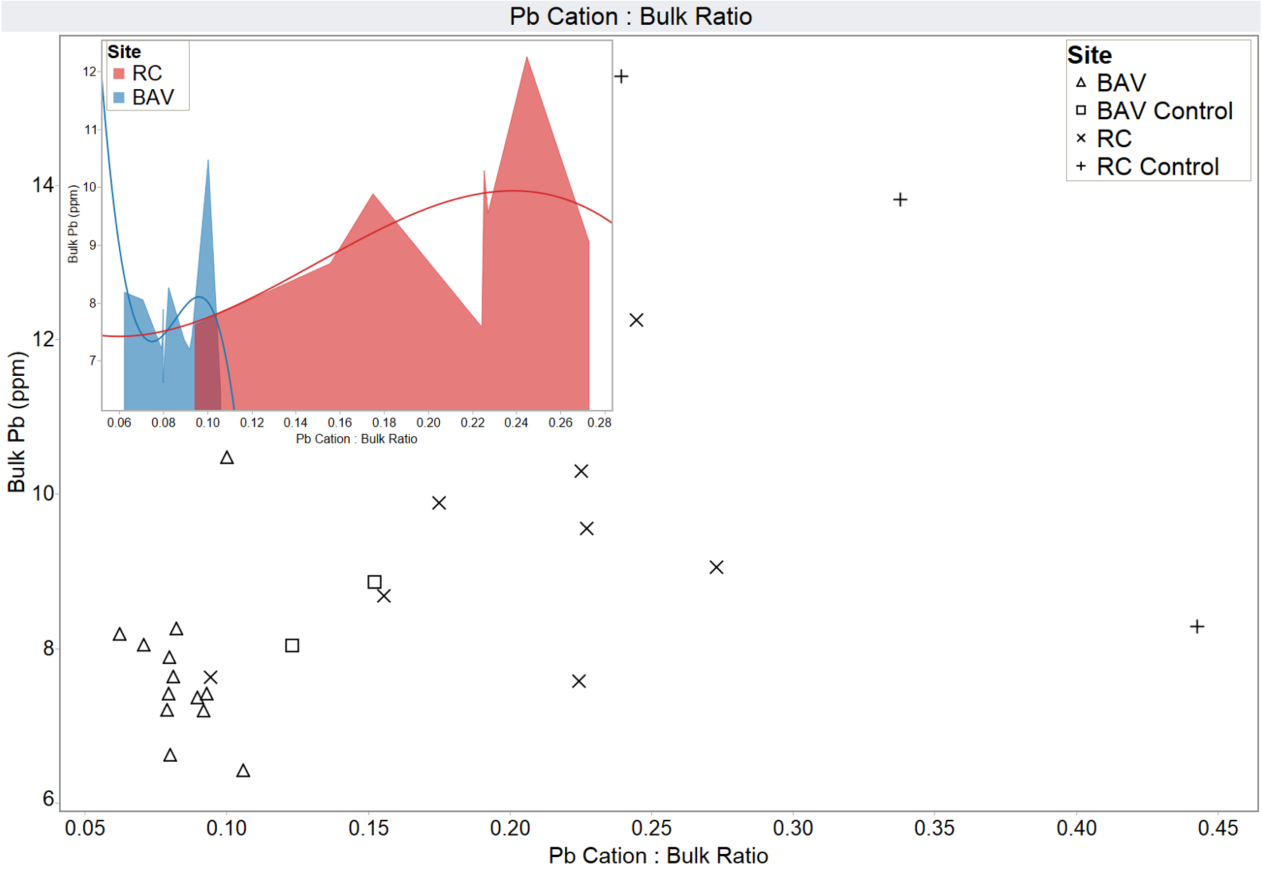

Figure 7. 7 Pb Cation : Bulk Ratio between the RC and the BAV, including topsoil control samples from each site. There is a notably higher quantity of leachable Pb at the RC than at the BAV.

3.2. Copper and Zinc

Based on both types of analysis, the two sites both yielded concentrations of Cu and Zn (Figure 8 and Figure 9). It was anticipated that the RC would have higher concentrations of Zn than the BAV due to the presumed increase in the use of brass at a Roman-period site. Such a scenario should have affected the ratio of Cu/Zn, a correlation successfully demonstrated in a study in Silchester, UK (Cook et al. 2005). However, the BAV yielded considerably higher concentrations of Zn than the RC, suggesting the possibility that Zn concentrations may derive primarily from geological rather than anthropogenic factors.

The BAV samples contain notably higher concentrations of Cu than those from the RC, which is to be expected since the former site is comprised of multiple phases belonging to a period of known Cu exploitation (see discussion below).

The Cation : Bulk Ratio for Cu (BAV = 0.091 [mean]; RC = 0.117 [mean]) and Zn (BAV = 0.016 [mean]; RC = 0.023 [mean]) do not show the same magnitude of difference as does Pb (Figure 10 and Figure 11). Zn does have a more significant difference in distribution ($p < 0.001$) than Cu ($p = 0.002$. Based qualitatively on the distributions, the cases for leachable Cu and Zn are not as clear as for Pb.

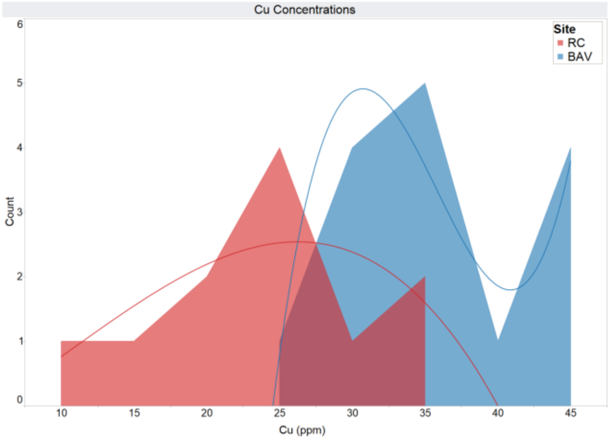

Figure 8. Comparison of the pXRF concentrations of Cu (ppm) between the RC (red) and the BAV (blue). The area histogram shows that the majority of RC samples are distributed between ca. 20-30 ppm, whereas BAV samples demonstrate a somewhat bi-modal distribution grouping around ca. 30-35 and 45 ppm.

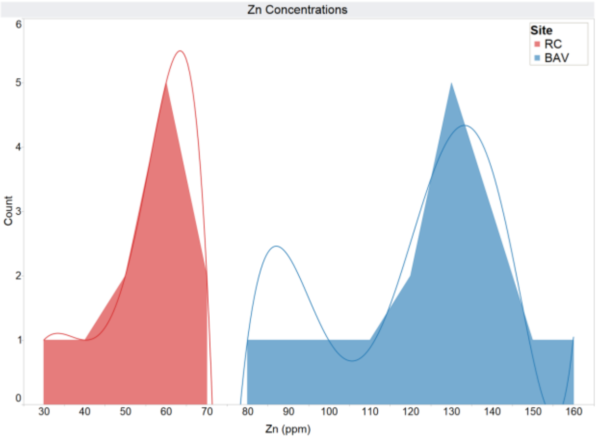

Figure 9. Comparison of the pXRF concentrations of Zn (ppm) between the RC (red) and the BAV (blue). The area histogram shows that the majority of RC samples are distributed between ca. 50-70 ppm, whereas BAV samples demonstrate considerably higher concentrations, particularly between ca. 120-140 ppm.

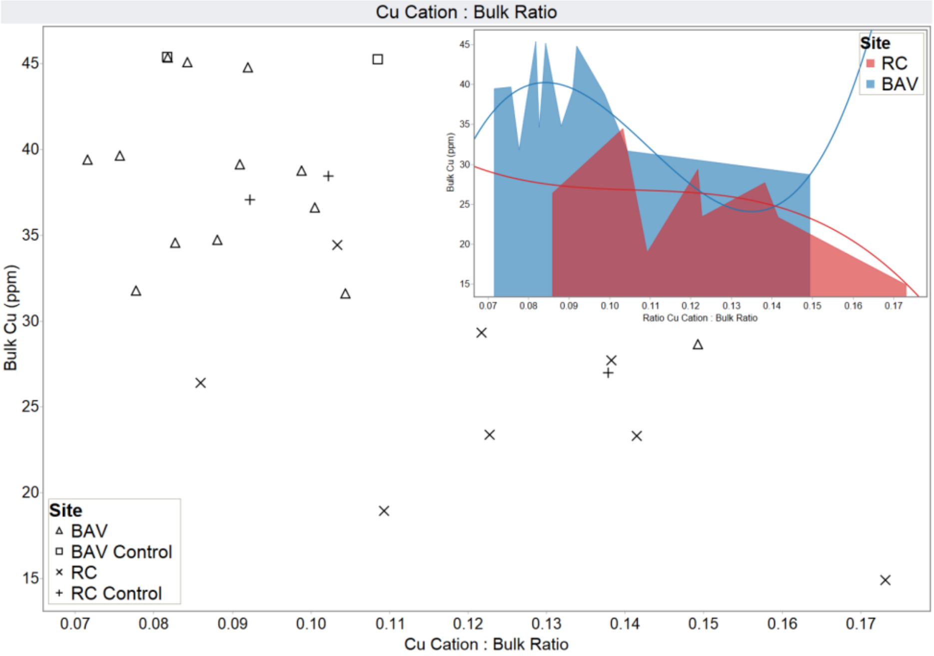

Figure 10. Cu Cation : Bulk Ratio between the RC and the BAV, including topsoil control samples from each site. There is little difference in leachable Cu between the two sites.

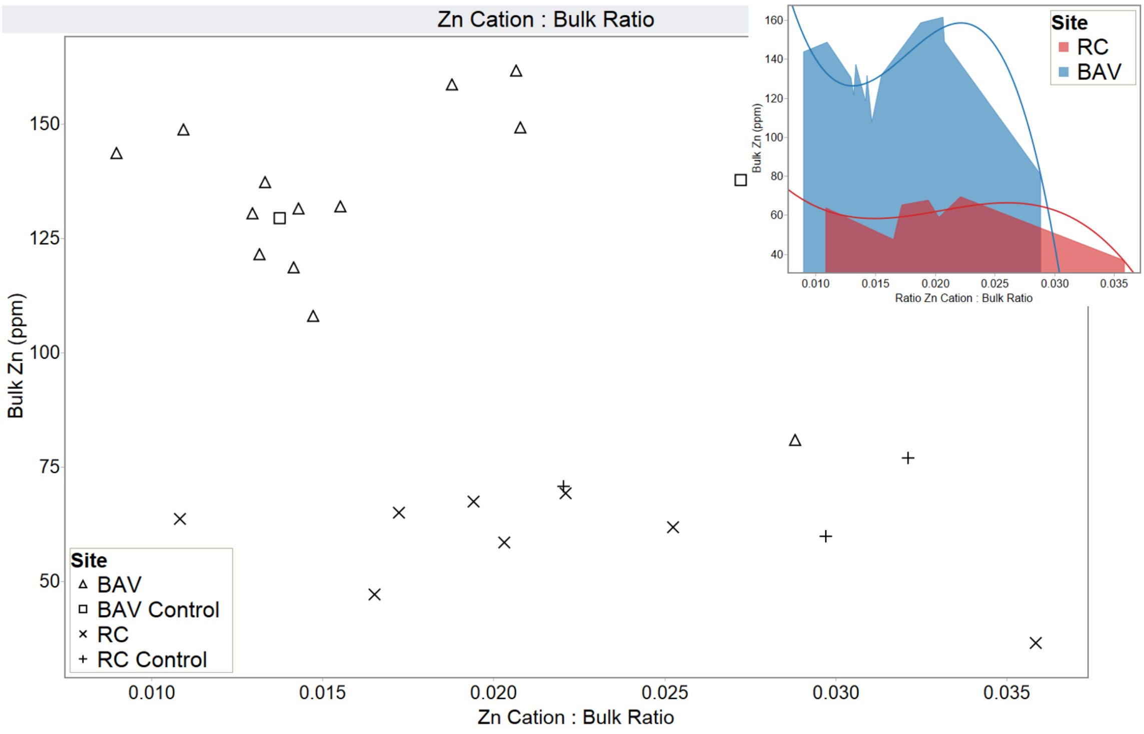

Figure 11. Zn Cation : Bulk Ratio between the RC and the BAV, including topsoil control samples from each site. Although there are higher concentrations of Zn at the BAV, there is little difference in the leachable Zn between the two sites.

4. DISCUSSION

4.1. *Lead*

Based on both the present study and previous research, three primary sources of Pb concentrations in the local sediments may be expected: (1) anthropogenic, from ancient metallurgical activity and/or utilization of metal artifacts; (2) modern contamination, from sources appearing after the mechanical-industrial developments in the region following the mid-nineteenth century (Erel 1998; Erel et al. 1997; Teutsch et al. 2001); (3) geological, derived from native limestone bedrock (Foner 1992; Teutsch et al. 2001).

The widespread utilization of Pb during the Roman Period is widely known (e.g., Boulakia 1972; Weiss et al. 1999; Montgomery et al. 2010). As was the case in many areas of the broader Empire, in the Levant there was a dramatic increase in Pb during Roman dominion, as is evident in remains of baths and of ships off the Levantine coast having structural Pb and carrying Pb utensils (Rosen and Galili 2007). Pb was utilized in a variety of objects, such as pipes in local vineyards (Ayalon and Rosen 2007) and human burials in Pb coffins (Rahmani 1999). The notable increase of Pb metallurgy in Judea during the Roman Period is an important change to consider, as it raises the question of the interface between imperial influence and the reception of technological innovation among subordinates within the Empire.

Pb concentration in the world atmosphere rose during the flourishing of the Roman Empire and the causal relationship between the rise of Rome and the rise of Pb concentrations is generally accepted (Weiss et al. 1999). The effects of Pb on Roman society have been well studied (e.g., Nriagu 1983; Montgomery et al. 2010), and are known to have had major negative consequences (lead poisoning or saturnism) on both individuals and whole populations (Needleman 2004; Lessler 1988).There are numerous macro-archaeological studies on Pb in the Roman Empire (e.g., Nriagu, 1983), and the longstanding question about the Pb in Roman wine (i.e., *defrutum* and *sapa*) still remains (Scarborough, 1984).

Recently, comprehensive osteological studies of Pb in samples from Roman Britain in the first centuries BCE and CE showed a thorough exposure to Pb (Montgomery et al. 2010). However, contrary to notions that the dangers of Pb were unknown or ignored by the Romans, in part contributing to the decline of the Roman Empire (Nriagu 1983), the dangers of Pb were probably well known by this time (Scarborough 1984; Lessler 2009). Already in the 4th century BCE, Hippocrates had described the symptoms of multiple cases of Pb poisoning (*contra* Waldron 1973; Waldron 1978), yet not noting the cause

(*Epidemics* 3.2.8), and the 2nd century BCE poet Nicander of Colophon diagnosed Pb as the culprit explicitly in his *Alexipharmaca* (1.600). Vitruvius (8.6.10-11) and Pliny the Elder (*Natural History* 34.50) noted the harmful/lethal effects of both breathing fumes from Pb smelting and drinking water from Pb pipes, and Dioscorides also wrote of this in his *Materia Medica* (5.103).

In recent times, Pb contamination has been shown to be a major human health problem, and numerous studies have been conducted on Pb pollution in order to address its consequences, behavior in sediments, and appropriate preventative courses of action (e.g., Needleman 2004; Montgomery et al. 2010). Accordingly, the issue of modern contamination of soils in Israel by Pb has been studied over recent decades (e.g., Erel et al. 1997). As a general observation, the amount of Pb found in sediments in the present study seems to be consistently lower than those reported in previous studies of Pb in Israel. Typical concentrations of Pb in "uncontaminated" sediments developed on carbonate bedrock are 17-19 ppm (Foner 1992; Teutsch et al. 2001), and the sampling undertaken by such studies generally occurred close to the surface, within the topsoil. This so-called "carbonate derived" sediment type characterizes both the BAV and the RC, yet, compared to these other studies, the Pb concentrations are lower than expected.

Figure 12. A sample of Pb objects collected at the RC during excavation and a metal-detector survey.

Several Pb objects were collected at the RC during excavation and a metal-detector survey (Figure 12), the results of which will be presented elsewhere (cf. Tepper et al. Forthcoming). In particular, three hemispherical Pb objects were recovered during excavation, resembling something akin to an ingot or "pig" (Figure 13). It is possible that these objects represent either imported raw material, recycling of Pb objects, or some other metallurgical activity within the site, and they are in the process of being studied. Together with these artifacts, the preliminary findings from the sediment study constitute quantitative evidence for the exploitation of Pb within the Roman military Camp at Legio.

Figure 13. One example of the three Pb ingots recovered from the RC, bottom (left) and top (right).

The degree to which modern Pb contamination of sediments obscures the concentrations attributable to human activities in the past at these archaeological sites presents a major challenge. The data from studying Pb in the environment of Israel over a long period of time (e.g., Erel 1998; Erel et al. 1997) is probably the best measure of modern contamination. Such studies should be considered alongside other factors affecting local environmental contexts. For example, during the last years of the British Mandate, there was a British military base just to the west of the RC. Likewise, the RC is situated within an agricultural field that has been cultivated using machinery for many decades in the recent past. The immediate area of the BAV has not been actively cultivated in recent years, but is situated on the margin of active agricultural fields. In the basic (high pH), carbonate-rich sediment characteristic of these two sites, Pb mobility should be reduced to some extent (Erel 1998; Allison and Allison 2005). As a result, such modern contamination of the topsoil over a relatively short period of time should theoretically not contaminate the sub-facies nearer bedrock, including archaeo-sediments and the bedrock itself. This scenario may be represented by the Cation : Bulk Pb ratios from topsoil samples at each site being higher (BAV = 0.14, RC = 0.34) than the securely archaeo-sediment samples (BAV = 0.08, RC = 0.20).

Whether from modern or ancient contamination, the Cation : Bulk Pb Ratio suggests that the comparison between our NYL and pXRF data seem to indicate anthropogenic Pb contamination in the sediment at the RC, and much more so than at the BAV. From a stratigraphic standpoint, the present topsoil horizon at the RC is nearly indistinguishable from the archaeo-sediment belonging to the site. In the southernmost upslope units excavated *in situ* architectural foundations of the RC were encountered a mere 5 cm below the modern surface, increasing to only as much as 30 cm downslope (north), with hardly discernible gradations between the topsoil and underlying sediments. Thus, modern Pb contamination in the topsoil of the site is plausible, and would likely derive from fuel exhaust from nearby busy roads (Erel 1998) and farm equipment. These contributing factors may result in contamination to a considerable depth (Foner H.A. 1992, Teutsch et al. 2001). Also, anthropogenic contamination via exogenous sources associated with agricultural fertilizers (e.g., manure, compost) remains a possibility (Erel et al. 1997). In future study, the relatively high Pb concentration on the surface of the RC should be further investigated, including more spatial controls both onsite and in the surrounding vicinity. If the Pb concentrations derive mostly from modern contamination, then the fact that there is less Pb at the BAV than the RC may have implications for understanding recent agricultural practices.

With a modern military base having been nearby, there may also be a compelling record of Pb contamination of local environments deriving from various military activities over time. Such modern environmental contamination is certainly a contemporary issue, and the impact of ancient human activities awaits more in-depth study. If a Roman military site with little modern interference were sampled (perhaps somewhere in the Negev, Judean desert, or in Transjordan), its use as a control in such research could prove to be a considerable contribution.

Nevertheless, preliminary investigation by the JVRP at the RC seems to indicate both quantitative and qualitative evidence for the exploitation of Pb within the Roman military camp at Legio (cf. Tepper et al. Forthcoming). The samples from the RC, particularly the most secure samples from the intact water pipes, demonstrate higher Pb concentrations than those from the BAV. Moreover, direct evidence for the exploitation of this metal was discovered in the form of objects, including the Pb ingots noted above, which were presumably intended for further utilization.

4.2. *Copper and Zinc*

Although the beginnings of Cu exploitation in the region may be traced to earlier periods (Garfinkel et al. 2014), it was in the Chalcolithic period (ca. 4500 – 3700/3600 BCE) that major technological innovations occurred in metallurgy in the southern Levant (Golden 2010; Shugar and Gohm 2011). In addition to the use of "pure" Cu, some of the earliest complex metallurgical activities utilized arsenical copper (Cu-As), which contains concentrations of As ranging 1 – 5% (Eaton and McKerrell 1976; Garfinkel et al. 2014; Golden 2009). The purposes of alloying Cu are essentially (1) to harden the metal (by deoxidization), making it easier to work without fracture, (2) to alter the color to a silvery hue (with As), (3) to decrease the melting temperature, and/or (4) to improve casting capability (Shugar and Gohm 2011).

The extent to which such alloying was intentional, that is, whether complex metals were actively combined from distinct materials or passively derived from ores naturally containing other elements, remains somewhat unclear. Based on the especially high quantity of Cu-As objects found in parts of the southern Levant during the late Chalcolithic period onward, it would seem that even if ores containing natural alloys were being utilized, it was probably by choice (or predetermined by trade sources). There are no known sources of ores containing significant amounts of As and/or antimony (Sb) in the southern Levant, whereas there are many local "pure" Cu ores, necessitating long-distance importation of the former. Cu naturally occurring with As is known from Anatolia, Armenia, the Transcaucasus, and Azerbaijan (Hauptmann 2007), with possible sources of Cu containing As and Sb in Syria (Golden 2009; Shalev 1996).

Based on the pXRF data, concentrations of As at the RC and the BAV were quite low (5.6 and 3.0 ppm, respectively). However, a single fragmentary artifact of a presumably metallurgical function (possibly a mold or crucible) was recovered from the BAV, containing Cu relatively high in As (1.54% As/Cu)[vi]. The concentration of As in this object is 70 times more than As in the sediments at the RC and 130 times more than at the BAV. These data indicate that, while Cu metallurgy incorporating As was probably not a widespread activity at the BAV, the concentration of As in the artifact was probably due to the manufacture of the alloyed object itself, whether intentional or not. Based on the generally higher concentrations of Cu at the BAV than at the RC, as well as the presence of the artifact containing Cu-As, the BAV settlement appears to reflect common fourth millennium metallurgical activity (Thornton 2009; Golden 2009; 2010).

Throughout the third millennium BCE, societies in the Near East increasingly began to use copper in the form of tin-bronze, which is a binary alloy of Cu (~ 90%) and Sn (~10%) (Ponting and Segal 1998). The practice of complex metal alloying became widespread in the southern Levant during the Middle Bronze Age at the beginning of the second millennium BCE (Shalev 2009). Despite the fact that Sn ore had to be imported from sources outside the region, concentrated mostly in a narrow geological belt stretching from Europe to southeast Asia (Roberts et al. 2009; Eaton and McKerrall 1976), the practice of alloying Cu with Sn brought with it many technological advantages in metallurgy.

Thus, due to the long-term metallurgical practices using Cu, elevated concentrations of Cu should be reflected in archaeological sediments dating to the Chalcolithic period through the Bronze Age, if not a much broader span of time. This scenario appears to be corroborated by the present study. The pXRF data demonstrate nearly equal concentrations of Sn (ca. 2.5 ppm) at the two sites, and so such levels are probably due to local geological factors. Moreover, there was presumably no tin-bronze metallurgy occurring at the BAV, which is to be expected given the chronological development of alloying practices summarized above.

By the Roman Period, Cu was actively used in brass, a binary alloy of Cu (~75%) and Zn (~ 25%), first appearing in the southern Levant at that time (Ponting 2002). Again, the fact that the data demonstrate higher concentrations of Zn at the BAV than at the RC suggests an absence of brass, or at least brass metallurgical activity at RC, whereas the relatively higher concentrations of Zn at the BAV appear to derive from geological rather than anthropogenic factors. Nonetheless, analyses of objects previously sampled from Legio and the village just to its south (Kefar 'Othnay) do indicate the local presence of brass objects as early as the first century CE (M. Ponting, pers. comm.).

5. CONCLUSIONS

This study investigated trace elements in sediments from two chronologically and functionally distinct archaeological sites in the Jezreel Valley. The RC was a military camp occupied for ca. 200 years (2nd-3rd centuries CE) and the BAV was an agricultural village occupied for ca. 200 years (3200 – 3000 BCE). The primary purpose of the study was to determine the concentrations of Pb, Cu, and Zn in sediments to test the assumption that such elements may be interpreted as chronological indicators of period-specific metallurgical production and consumption.

It was found that notable quantitative differences do exist in the chemistry of the archaeological sediments. Overall, the RC contained higher concentrations of Pb than the BAV, particularly leachable Pb, which supports the hypothesis that Pb-related metallurgy and use of Pb objects during the Roman Period may be traced in the archaeological sediments from the site. These analytical results were also corroborated by the recovery of Pb artifacts during excavation, including ingots. Although external influences might also have affected the concentrations of Pb in at least the topsoil horizon of both sites, it seems that the higher amount of Pb in the RC most likely relates to archaeologically relevant factors, meriting further study and verification.

The BAV contained notably higher concentrations of Cu than the RC, which was expected from a site comprised of multiple phases belonging to the Early Bronze I, a period of known Cu exploitation. The BAV also yielded considerably higher concentrations of Zn than the RC, suggesting the possibility that Zn concentrations may derive primarily from geological rather than anthropogenic factors. This result was rather unexpected, since we anticipated evidence for the utilization of brass (Cu + Zn) at the RC. In addition to metal elements, P concentrations analyzed (as part of a secondary study) were higher at the BAV than the RC, presumably due to (1) better (and deeper) preservation of archaeological remains, and (2) a longer duration of more intense anthropogenic factors than at the RC.[vii]

The two analytical methods used in this investigation (FAA and pXRF) generated data indicating that they were capable of measuring similar overall patterns of distribution across both sites, and that the pXRF technique proved to be reasonably accurate despite concerns about the conglomerate nature of sediment and limited preparation of the samples. Thus, pXRF provides an expedient method for broad characterization of target elements in archaeological sediments. Although the resolution of the data might be vastly improved by further sample preparation (e.g., pulverizing the samples and creating homogenous pellets), the present field-based method did capture a range of elemental variation useful for archaeological prospection on various scales of inquiry. Furthermore, the comparison between the cation (NYL) vs. bulk (pXRF) data of the two methods presents a potentially viable method to determine the leachable proportions of bulk elemental concentrations, which should help to distinguish between anthropogenic contamination (e.g., archaeometallurgy, modern pollution) vs. geological derivation.

Although preliminary, the general correspondence between expected metallurgical norms and trace element concentrations suggests that these methods may be employed as a useful survey technique for determining spatially significant patterns of metallurgical activity within sites. Future work at these two archaeological sites, and others investigated by the JVRP, will apply this general method as a component of intensive survey, incorporating off-site environmental and spatial controls in addition to context-specific sampling strategies derived from excavation. Spatially-oriented sampling strategies (e.g., systematic sampling, stratified unaligned systematic sampling) should elucidate areas of intensive metallurgical activity. A future inquiry will be the degree to which metallurgical traces in buried archaeological contexts may be represented in the topsoil horizon, which may be determined from controlled sampling of stratigraphic profiles. Together with geophysical survey techniques, this method may also contribute to non-invasive means of archaeological prospection.

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[i] The JVRP (www.jezreelvalleyregionalproject.com) is a long-term, multi-disciplinary survey and excavation project investigating the history of human activity in the Jezreel Valley from the Paleolithic through the Ottoman period. The project is directed by Matthew J. Adams, with Assistant Directors Jonathan David and Robert S. Homsher. Under these auspices, the excavations at Tel Megiddo East were directed by Matthew J. Adams and those at Legio by Yotam Tepper, Jonathan David, and Matthew J. Adams.

[ii] The sampling occurred during the course of excavation, under excavation permit G-59/2013.

[iii] Detector: 10 mm^2 XFlash® SDD; peltier cooled; typical resolution 145 eV at 100,000 cps full width maximum at the manganese K-alpha1 line. X-ray tube: Rh target; max voltage 45 kV.

[iv] Here, C_i represents the concentration of a given element of the sample in weight % or ppm, r_0 is the intercept/constant, r_i is the slope of photons for element i, r_{in} is the slope of photons for element n that influence the fluorescence of element i, I_i is the quantity of photons for element i, and I_n is the quantity of photons for element n.

[v] FAA (SM 3111B) detection limits, where mg/L equates to ppm (American Public Health Association 2005):

Element	Wave-length *nm*	Detection Limit *mg/L*	Sensitivity *mg/L*	Optimum Concentration Range *mg/L*
Cu	324.7	0.01	0.1	0.2 – 10.0
Pb	283.3	0.05	0.5	1.0 – 20.0
Zn	213.9	0.005	0.02	0.05 – 2.0

[vi] Based on pXRF net photon data calculated using Bayesian Deconvolution.

[vii] It may be worth considering the intensity of occupation in terms of such factors as population density, animal husbandry, agricultural processing, and other specialized activities at a given site that may also be reflected in the relative concentrations of P. Most of these factors probably vary according to the overall function and demographic makeup of the site, which for the BAV is multiple-phase domestic and agricultural but for the RC is primarily military occupation during a single period.