CHEMOSTRATIGRAPHIC ANALYSES OF LEGACY AND LATE HOLOCENE, PRE-SETTLEMENT DEPOSITS, UPPER STICK ELLIOTT CREEK, NORTH CAROLINA

A thesis presented to the faculty of the Graduate School of Western Carolina University in partial fulfillment of the requirements for the degree of Masters of Science in Chemistry.

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April 2020

ACKNOWLEDGEMENTS

I would like to thank, from the bottom of my heart, Dr. Carmen Huffman for helping me through these last 5 years. Without her, I would not be completing this thesis today. I am truly indebted to her and I am grateful that I was able to work with her and learn from someone with so much to give me. She has been the greatest advisor and mentor.

I would also like to thank Dr. Jerry Miller. Without his geology expertise, I would have not been able to ever comprehend any of my concepts. He has taught me more than I thought was possible and I am thankful to be able to work beside him.

A debt of gratitude is owed to Gina Carney. She was the person who helped me with the lab work and the person who made the work go by faster. I would not have been able to complete all the lab work without her.

I would also like to acknowledge the Department of Chemistry and Physics along with the Department of Geosciences & Natural Resources for allowing me to use their instruments and providing funding towards this research.

Lastly, I would like to thank my support system, my family and friends.

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LIST OF ABBREVIATIONS

YBP: Years before present

H: hours

USE: Upper Stick Elliott

ED-XRF: Energy Dispersive X-ray Fluorescence

PSDA: particle size distribution analysis

PCA: principle component analysis

cm: centimeters

km: kilometers

LOD: limit of detection

LOQ: limit of quantification

ABSTRACT

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Chemostratigraphy is a technique that defines and spatially correlates stratigraphic units using subtle variations in the elemental composition of the sediments. A collaborative study of Upper Stick Elliott Creek within the Big Harris River basin near Polkville, NC was conducted to determine the occurrence of chemostratigraphic units in floodplain sediments. Field studies showed that the alluvial floodplain deposits primarily consisted of organic rich, pre-settlement deposits dating between approximately 3460 YBP and 210 YBP. The legacy sediments were produced in response to basin wide changes in land use from predominantly forest cover to cotton farming. The changes in land use resulted in extensive upland erosion and gully formation as well as channel and valley floor aggradation. Depositional rates during aggradation of the legacy deposits were an order of magnitude higher than those associated with pre-settlement deposits. Beginning in the late 1940s and early 1950s, erosion control methods were implemented, and cotton farming was replaced by pasture and turkey farming, which in combination led to channel incision and the exposure of legacy and pre-settlement deposits in the channel banks. These deposits were described in detail at four sites located along Upper Stick

Elliott Creek. At each site, between 26 and 39 samples were collected at approximately 5 cm increments from the ground surface to the base of the channel banks. The samples were subsequently analyzed for 45 elements by XRF as well as their grain size distribution. More than 120 samples were collected and analyzed in total. The geochemical data showed that legacy and pre-settlement deposits exhibited significant differences in elemental concentrations. In addition, concentrations varied systematically as a function of depth with these two deposit types. Thus, multivariate statistical techniques including hierarchical cluster analysis and principle component analysis (PCA) were used to define chemostratigraphic units at each of the sampling sites. Hierarchical cluster analysis was able to identify chemostratigraphic units within the lithostratigraphic sites. However, it was not able to separate different stratigraphic sections clearly. PCA of normalized metal concentrations to a conservative element (Al, Fe, or Ti) proved to be most effective at defining chemostratigraphic units within legacy deposits at a site. These units could be correlated along the stream, thereby providing information needed to more fully understand sediment transport and depositional processes within the drainage basin. While pre-settlement deposits exhibited distinct chemostratigraphic units at a site, these units were more difficult to correlate between sites. Differences in the ability to correlate units along the channel may reflect differences in the rates and processes of sediment transport and deposition before and after significant changes in land use.

CHAPTER ONE: INTRODUCTION

Watersheds (drainage basins) have simplistically been divided into three major zones, including the zone of sediment production, transport, and deposition (See Figure 1).[1] The zone of sediment production includes headwater and upland (hillslope) areas where sediment is created by various weathering processes and delivered to low-order channels. The zone of transport is dominated by the movement of sediment from headwater areas downstream to the ultimate zone of deposition, such a lake, a delta, or an alluvial fan. The movement of sediment along the zone of transport is not temporally constant, but varies in terms of quantity and rate as a function basin hydrology and other environmental conditions (e.g., vegetation cover). Nor are sediments moved without interruptions from the zone of sediment production to deposition. Rather, a fraction of the sediment load is deposited and stored along the channel where it is incorporated into channel bed, floodplain, and other types of alluvial (riverine) deposits.[2,3] These alluvial deposits contain a record of the spatial and temporal variations in the quantity and rate at which sediment is transport through the river system and can provide important insights into the degree to which natural and anthropogenic activities have impacted the aquatic environment. For example, as far back at the mid- to late 1800s and early 1900s, the analysis of alluvial deposits in the southwestern U.S. were used to assess the role of short-term (event- to decadal-scale) changes in climate (rainfall totals and intensity) and land use (cattle grazing, mining, roads) on the catastrophic formation of arroyos (deep, flat-floored, trenches with near vertical banks) cut in the valleys' alluvial fill.[4–11]

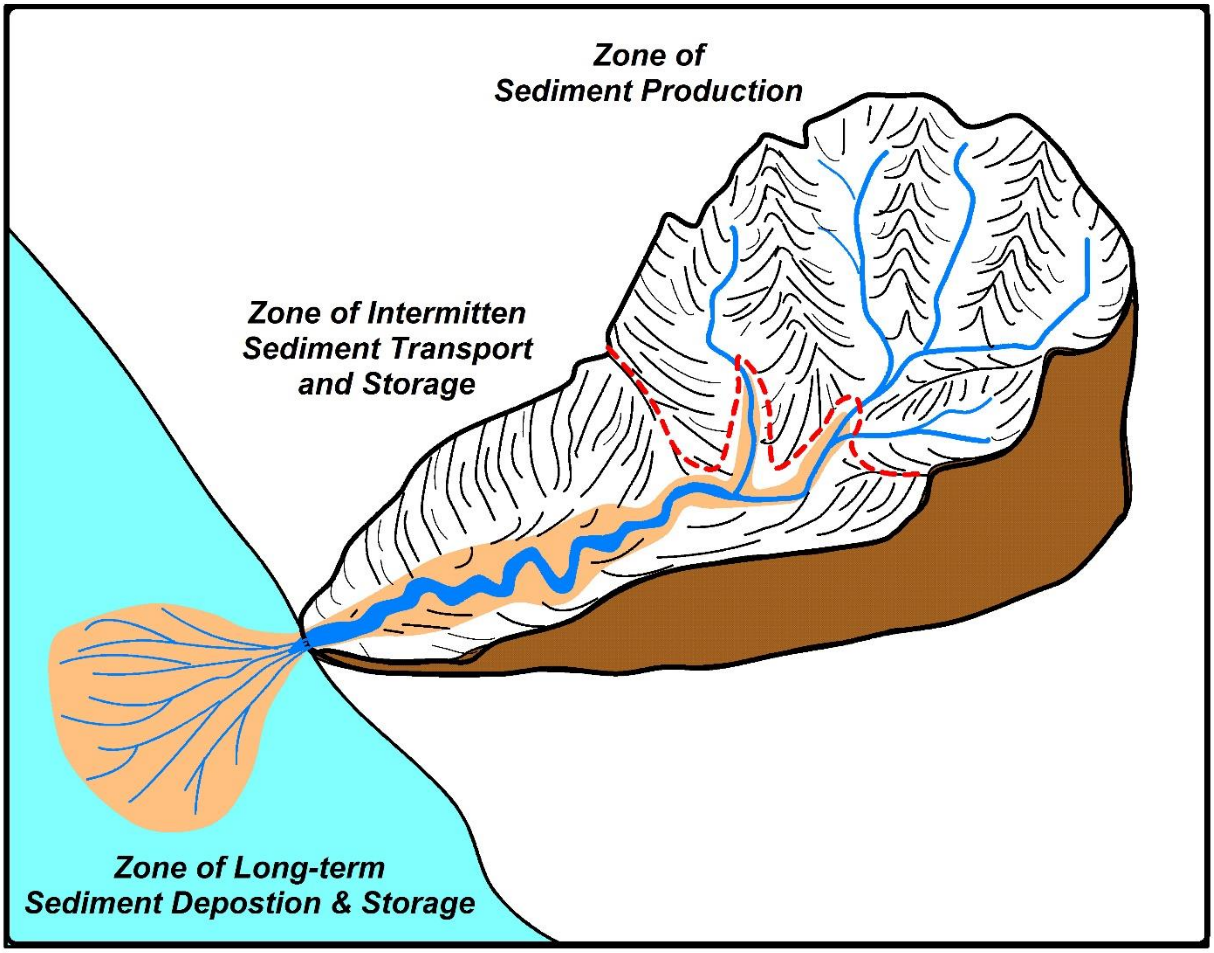

Figure 1. Sediment transport and production model (modified from Schumm, 1977)

Studies which use alluvial deposits to reconstruct the erosional and depositional events that occur in response to natural and anthropogenic disturbances typically include five major steps: (1) the delineation of distinct stratigraphic units found in the valley's alluvial landforms (e.g., floodplains and terraces), (2) the sedimentologic characterization of the deposits in terms of sediment color, induration, size, mineralogical composition, and bounding surfaces, among a host of other parameters, (3) the correlation and mapping of the deposits within the basin to determine their spatial distribution, (4) the relative and absolute dating of the deposits to determine the sequence in which they were deposited and the timing of their deposition relative to natural and anthropogenic changes within the watershed, and (5) the compilation and interpretation of the data to construct the desired geomorphic history. All of these steps are closely inter-twinned and can be extremely difficult to carry out. The correlation of distinct alluvial deposits can be particularly difficult in basins where the deposits are not physically continuous.

Unit delineation and their correlation along a river has historically been performed on the basis of the physical properties of the sediment (e.g., grain size, color, depositional structures, and topographic position).[1] These stratigraphic packages of sediment are referred to as lithostratigraphic units. In some instances, lithostratigraphic units exhibit unique materials (e.g., volcanic ash) or other characteristics (e.g., anthropologic artifacts) that not only allow them to be easily identified and correlated within a basin, but provide a marker of the timing of their deposition. In many other instances, however, sedimentological differences between lithostratigraphic units are minimal, making their correlation difficult.

An alternative approach to the use of lithostratigraphic analysis is chemostratigraphy. Chemostratigraphy involves the characterization of the chemical nature of the strata, and the use of specific geochemical signatures for the correlation of geographically separated units.[12] Chemostratigraphic methods have been most extensively utilized for the correlation of marine, lacustrine, and lithified strata.[12–15] However, a number of investigations show that the technique holds considerable potential for correlating alluvial stratigraphic units.[16,17]The approach has been particularly useful in analysis of contaminated river systems, where the influx of toxic trace metals from mining operations creates chemically distinct deposits that usually possess elevated levels of trace metals. Because these enriched metal deposits (chemostratigraphic units) can be temporally linked to mining, the deposit not along provides a means of correlating sediments along a river valley, but provides insights into the age of the deposits within the floodplain or terrace. In addition to the application of chemostratigraphy to contaminated rivers, Miller et al. (2019) demonstrated that chemostratigraphic units could be used along the Rio Loa of Chile to correlate sedimentologically similar paleoflood deposits preserved within bedrock channels. Chemostratigraphy, then, had the potential to correlate units that possessed similar physical and chemical characteristics and ages from one site to another increasing the resolution of the paleoflood analysis.

Lithostratigraphic floodplain units reflect local environmental conditions at the site of deposition, and record depositional and erosional changes associated with variations in the hydrologic and/or sedimentologic regime of the basin. In contrast, chemostratigraphic units reflect variations in the source and source contributions of sediments to the depositional site. Chemostratigraphy, then, is a complimentary technique that can help decipher the geomorphic and environmental history of a basin by providing insights into where the sediments found within a lithostratigraphic unit are derived.

In western North Carolina, Wang and Leigh (2015) demonstrated that Pre- and Post-settlement (legacy) deposits along the Little Tennessee River not only differed in terms of sedimentation rates and sediment size, but Ca, Hg, and Pb concentrations. These data suggest that chemostratigraphic methods may be applicable to the analysis alluvial sequences and geomorphic processes throughout the southeastern U.S. where the impacts of European settlement are well-documented and ubiquitous.[18–22]

In this study, a chemostratigraphic method was applied to floodplain deposits along Upper Stick Elliot Creek, a tributary to Big Harris Creek, the site of the largest stream restoration project (~$10 M) in North Carolina (Figure 2). As described in more detail below, the Upper Stick Elliott Creek floodplain is dominated by two stratigraphic units (Figure 3). The lower section of the bank materials is characterized by organic rich pre-settlement sediments that were deposited prior to significant European activity in the area (~1780). Overlying these deposits are post-settlement (legacy) sediments that were primarily deposited in response to the conversion of forested areas to cotton plantations.[23] More specifically, the conversion resulted in severe upland erosion and the formation of gullies that delivered large quantities of sediment to the Big Harris Creek drainage system, including Stick Elliott Creek. In the 1950s, in an attempt to control erosion, the landowners implemented a number of erosion mitigation activities (e.g., the creation of upland terraces) and converted cotton fields into turkey farms and pastures. These activities resulted in channel incision (downcutting of the channel bed) that exposed both the pre-settlement and legacy deposits in the channel banks (Figure 3). In 2017, Big Harris Creek underwent stream restoration as another attempt at erosion control.

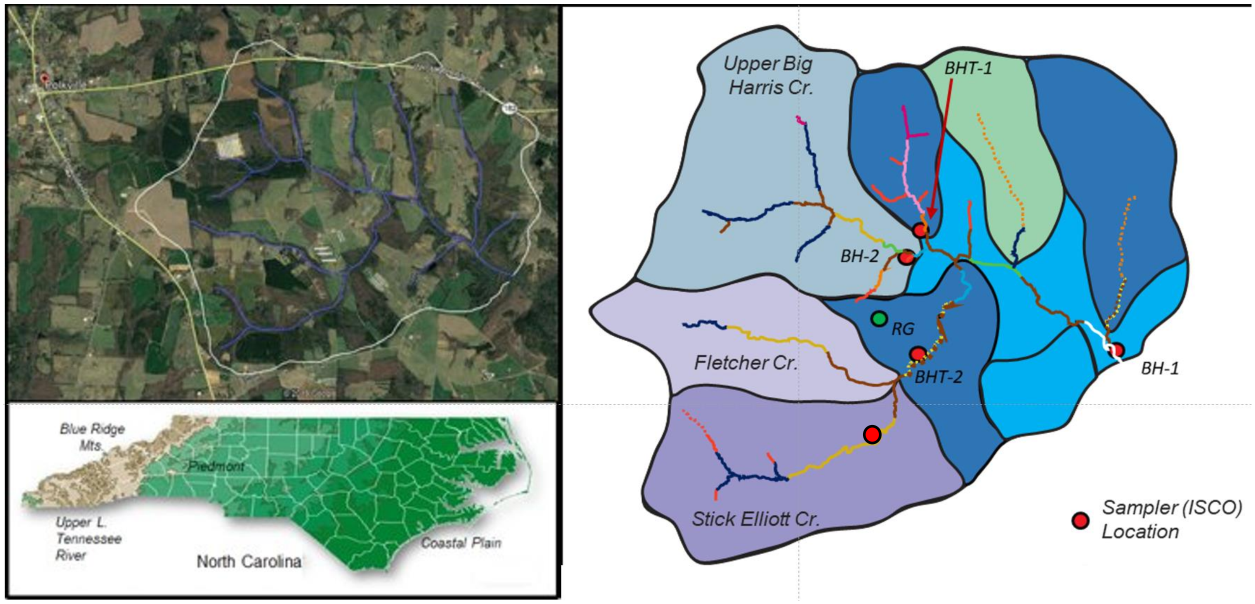

Figure 2. Aerial photograph (left) of the Big Harris Creek drainage system (upper panel) and location of site near Polkville, NC (lower panel). Map of the tributary system (right) labeled with some sample sites marked.

Figure 3. Two sharply delineated stratigraphic units within the floodplain of Upper Stick Elliott Creek. The black, lower layer is the organic rich pre-settlement sediment and the brown top layer is the post-settlement, legacy sediment.

The pre-settlement deposits within the basin were dated using radiocarbon methods and ranged in age from between 290 +/- 30 YBP and 3760 +/- 30 YBP.[23] The first land use by people would have been by the Native Americans. Previous studies suggest that they may have burned the area occasionally to encourage plant growth.[24] In the mid-1700s, the English migrated to the area and used it for hunting and the farming of livestock. In the 1840s, cotton was becoming an important cash crop and the local farms were converted to cotton. Cotton, a row crop that allowed for extensive areas of bare ground, increased erosion within the basin. In the early 1900s, 6-8 inches of topsoil was being lost due to erosion.[24] The erosion also formed numerous deep gullies on hillslopes. In the 1950s, farmers implemented erosion control to reduce the impacts of erosion on the region's soils and stream systems. These efforts, which included the development of upland terraces, were only partially successful.[24] As a result, farmers started to shift from cotton to pastures and turkey farming; cotton was no longer a cash crop. Many upland areas were also re-forested. In 2017, a stream restoration project was implemented within the Big Harris Creek Basin as another attempt to reduce bank and gully erosion and to improve water quality.

The Big Harris Basin possesses two primary sedimentary sections defined within the watershed, legacy, and pre-settlement sediment. The legacy sediments were initially deposited in response to the land-use changes associated with the conversion of forest cover to cotton farms in the mid-to late 1800s. However, the finer-grained, upper-most legacy sediments, which were dated using dendrochronologic methods, were presumably deposited following channel incision that occurred around the early 1950s in response to the conversion of upland areas to pastures and forests.[23] These legacy sediments ranged in depth from 0 to 150 cm in thickness with the basin.[25]

The legacy deposits could be subdivided into three sections on the basis of their sedimentologic characteristics (e.g., grain size, color, induration and mineral composition): the upper, middle, and lower deposits. The upper most deposit tended to be fine grained, was massive (lacked noticeable layers) and was enriched in organic matter relative to other sediments within the legacy deposits (Figure 3). The middle section consisted of coarser grained, fine to medium-sized sand units that were interlayered with silt and clay. The lower-most layer consisted of a interlayers of sand, silt and clay sediments, including dark clumps of pre-settlement sediments that were eroded and re-deposited within the lighter brown legacy sediments.[25]

The deposition of legacy sediments was relatively rapid, reaching rates along Upper Stick Elliott Creek of more than 1.65 cm/yr. Deposition since the 1850's, however, was likely to have varied significantly through time. Field data, combined with historical photographs taken during the early 1900s in other areas suggest that as channels filled with sediments overbank flows became more prevalent.[19,26,27] These flows deposited sediments from gullies and eroded upland areas onto the floodplain where they formed vertical accretion deposits (by the vertical deposition of sediments from flood waters), channel splays (fan shaped, sandy deposits on the floodplain), and deposits associated with distributary channels and bars.[19] Many of these deposits interfingered in complex ways and were discontinuous both downstream and across the valley floor, making it difficult to correlate deposits over significant downstream distances, or to interpret geomorphic histories on the basis of a few locations.[19]

The pre-settlement sediments were deposited prior to the early 1800s and were found through radiocarbon dating to be at least 3760 +/- 30 years old. These deposits are gray and black in color, and possess a higher silt and clay and organic content than the overlying legacy deposits. The depositional rate of the pre-settlement deposits was slower than that of the legacy sediment, measuring 0.027 cm/yr at one site located long Upper Stick Elliott Creek (near USE4). The slower depositional rate was associated with limited upland erosion within forested areas, increased rates of evapotranspiration, and low gradient channels. In fact, the organic rich, massive nature of the upper pre-settlement deposits suggest deposition primarily by vertical accretion within riparian wetlands.

The objectives of this study were to:

(1) Determine if pre-settlement and legacy sediments differ in their chemical composition at several sites along Upper Stick Elliot Creek;

(2) Identify unique chemostratigraphic units within both pre- and post-settlement (legacy) deposits at selected sites along the stream using several multivariate statistical approaches;

(3) Compare the chemostratigraphic and lithostratigraphic units to assess their vertical and longitudinal (downstream) differences; and

(4) Determine if chemostratigraphic analysis is a viable method for correlating stratigraphic units along the riverine system.

CHAPTER TWO: METHODS

Sample Collection and Preparation

The recent (late Holocene) alluvial stratigraphy within the Big Harris Creek restoration project was examined at more than 20 sites. At each site, lithostratigraphic units were defined and characterized following the methods put forth by Kottlowski (1965) and Bridge (2006).[28,29] Four sites located along Upper Stick Elliott Creek (USE) were subsequently selected for this analysis because (1) thick sequences of legacy and pre-settlement deposits were exposed along the channel within the channel banks, (2) the legacy sediments were continuous and could be physically traced along the lower 2.5 km of the channel, and (3) the Upper Stick Elliott basin was found to be a prominent source of sediment to the modern channel. Sediment samples were collected at the four sites at approximately 5 cm increments from the ground surface to the base of the banks. Samples were not, however, allowed to cross the boundary of a defined lithostratigraphic unit. In addition, sample intervals within the lower pre-settlement deposits where variations in sediment character were minimal increased to 10 m; thus, while most samples were collected over a 5 cm interval, some samples varied from 2-10 cm in depth. All samples were placed in plastic sampling bags and returned to the laboratory for analysis.

In the laboratory, samples were removed from the bags and allowed to dry for at least 72 h before they were subdivided into subsamples using a Humboldt macro splitter. The macro splitter was used to create a homogenous non-biased subsample for analysis in the experiments. Samples were labeled with the creek abbreviation (USE), the site number, and the sampling depth range in cm. For example, USE 4 60-65 was acquired between 60 and 65 cm from the top of the channel bank at site #4 along Upper Stick Elliot Creek. This sample naming scheme was used throughout.

Physical Characterization

The subsample designated for particle size distribution analysis (PSDA) was combined with deionized water and dispersant and left to sit for 24-48 h. The samples were then analyzed using a Mastersizer 2000-particle size analyzer (PSA). Each sample was stirred and put into the instrument using a plastic pipette. Enough sample was added for the laser obscurity to be >10%, and the sample was analyzed in triplicate. The mean percentages of sand (2mm – 63 µm), silt (0.2 to 63 µm) and clay (<2 µm) within the sample were then calculated and used in the analysis.

Metal Signature Determination

Energy dispersive-x-ray fluorescence (ED-XRF) was used to determine the concentration of metals in sediment samples.[30] ED-XRF is designed to analyze groups of elements simultaneously. This method is commonly used for chemical analysis of sediment and has been since it was developed.[31] A piece of mylar was laid flat on the rim of the 30 mm plastic sample cup, and the ring was pushed smoothly on top of the cup, ensuring there were no wrinkles in the film. The cup was inverted and put on top of the film to prevent contamination. A small portion of the sediment sample was ground into a fine powder using a clean, dry mortar and pestle. The sample was transferred to a filter paper and slowly added to the cup. The cup was filled with leveled layers of sediment. A cotton ball was placed on top of the sediment to compress and secure it while the lid was placed on top and labeled with the site and depth. Ten samples were measured simultaneously along with 2 external standards, OREAS 930 and USGS SGR-1b. The values of the standards are found in Appendix A. A METEK Spectro Xepos spectrometer was used for ED-XRF measurements. Measurements were acquired using three channels. The X-ray generator settings were 40, 49.5 and 17.5 kV and the corresponding detector voltages were 25 keV (Zr target), 50 keV (Cs target) and 12.5 keV (HOPG target), respectively.

The ED-XRF analyses possess limitations in that it determines relative concentration instead of the absolute concentration. The ED-XRF is used to tell what the concentrations are of the elements present within a sample. However, matrix effects, where the composition of the samples may not match the composition of the standards, and overlap of spectral features, may limit the accuracy of the measurement.

CHAPTER THREE: DATA ANALYSIS

Chemical Composition

The METEK Spectro Xepos ED-XRF spectrometer uses a previously stored calibration to provide analyte concentrations. These concentrations were converted to relative concentrations using a two-point calibration curve based on analyte concentrations of standards measured at the time of each analysis: OREAS 930 and USGS SGR-1b. These standards were chosen because they contain metals of interest in a concentration range that was expected to be present in the samples. The composition of the standards is provided in Table A1. These standards were also used to validate the method, as described below.

Since we used a two-point calibration, it limits our calibration in a few ways. The check standards are the same standards that were used to calculate the concentrations of the samples. The two-point calibration limited the accuracy and only validated how well the standards used could be measured. The measurements do not account for matrix effects or inhomogeneity. Nonetheless, the results represent a valid "fingerprint" because the relative response reflects the composition of the sample.

Validation

The known concentrations of the elements in the standards OREAS 930 and USGS SGR-1b were compared to the measured concentrations of the elements. The relative difference between the known and measured standard concentrations were calculated to provide the accuracy of the instrument on each day. The relative standard deviation was used as the precision of the instrument. The concentrations were also used to find the limit of detection (LOD)

$$LOD = \frac{3\sigma c}{\mu} \tag{1}$$

and the limit of quantification (LOQ)

$$LOQ = \frac{10\sigma c}{\mu} \tag{2}$$

where σ is standard deviation of the concentrations, c is the known concentration of the element, and μ is the mean of the standard concentrations.

Determination of Fingerprinting Elements and Outliers

Fingerprinting elements are those that are determined to be most useful in separating sediments or strata with a similar geochemical composition within the pre-settlement and legacy deposits. A previous study from this research group (not published) identified a unique geochemical fingerprint for sediment sources that were likely to have contributed sediment to the modern channel of Upper Stick Elliott Creek. These sources included the primary types of upland soils (Appling soils, Cecil soils, and Pacolet soils), upland gullies, the pre-settlement deposits, and the legacy deposits. During the process of defining a fingerprint, a Kruskal Wallis H-test was applied to all analyzed elements to determine which ones were capable of differentiating between the sources at the 95 % level. Then, the elements which pass the Kruskal Wallis H-test were entered into a stepwise discriminate analysis which determined the elements that were most effective at defining (distinguishing between) the source materials. The analysis was evaluated by determining the number of samples from each source that were correctly classified. The discriminate analysis found that the best geochemical fingerprinting elements consisted of Al, Si, P, K, Ti, Cr, Fe, Co, Ni, Cu, Zn, and W. Since this previous analysis was successful in capturing the variation throughout the source materials that provided sediments to legacy and channel bed deposits, these same elements were subsequently used in the multivariate statistical methods used to define chemostratigraphic units.

Two samples from USE were considered outliers: USE 4 60-65 and 130-137. USE 4 60-65 possessed significantly lower concentrations of all the trace metals within the sediment and some metals were undetectable. USE 130-137 exhibited concentrations that were both significantly higher and lower than the rest of the samples, depending on the element. Most were found to be higher concentrations than the rest of the samples. While no statistical analysis was used to determine if these samples were outliers, they were removed from the data set. Two samples from USE 3 were accidentally omitted from the data set during data processing and were left out of the analysis: USE 3 5-10 and USE 3 135-140.

Normalization

One approach to assess spatial variations in elemental concentrations in alluvial sediments, particular within contaminated rivers, is the normalization of metal concentrations by a conservative element (also called a reference element). Conservative elements are thought to: (1) reflect the concentration of the element in geogenic (Earth) materials that underlie the basin, (2) have no anthropogenic source in the basin, and (3) exhibit no post-depositional migration within the alluvial sediments. The process of normalization is often intended to address differences in the grain size and particle mineralogy that may influence element concentrations within the samples collected for analysis. In other words, sedimentologic influences on concentrations are removed, allowing for an improved assessment of elemental sources. For example, the most widely used conservative element, Al, is an important component of aluminosilicate minerals, including fine-grained (<~2 µm) clay minerals. Its occurrence is therefore an indicator of the presence of grain size (fine-grained) sediments and clay minerals. Other commonly used conservative elements include Fe, Li, Rb, Si, Ti, and, more recently, Co. Here, three conservative elements that are naturally found within the bedrock were analyzed: titanium (Ti), iron (Fe), and aluminum (Al). The elements selected for analysis were then correlated to the conservative elements. If a correlation coefficient between an element and Ti, Fe, or Al was higher than 0.6, then that element's concentration was divided by the conservative metal concentration as a means of normalization, producing a ratio. A ratio greater than one means that the sample is enriched in that particular element relative to the mean geogenic concentrations in the basin. Enrichment could be produced by the introduction of a metal from a contaminant source, such as fertilizer, or through the sorption of dissolved elements on chemically reactive sediments (e.g., clay minerals, organic matter, or Mn oxides and hydroxides). A concentration ratio less than one indicates that the element is depleted, potentially being leeched out of the sediment possibly into the groundwater.

Principle Component Analysis

Principle component analysis (PCA) is often used for large data sets with many dimensions or large variability. It is a multivariate method that takes multiple features and combines them to make a fewer number of new components that more effectively describe the variations in selected variables (or elements) that are being analyzed.[32,33] In this study, the method allows variation in concentrations of all the fingerprinting elements (many dimensions) to be captured by just a few dimensions (principle components). PCA was performed on the relative element concentration data and the normalized concentration data. The metal concentrations determined by XRF were normalized using aluminum, titanium, and irononcentrations. Plots of principle component scores between the first two components were created and subsequently used to identify samples that were geochemically similar to each other.

Hierarchical Cluster Analysis

Hierarchical cluster analysis is another statistical method used to identify clusters or groups of samples (data) that are similar, and to assess how different one cluster is from another.[34] Cluster analysis was also used herein as a method to determine samples within the legacy and pre-settlement deposits that cluster together. The normalized Euclidean distance between the chemical composition of each sample was used to determine if samples belong to the same cluster.[34] The Euclidean distance (d) is defined as

$$d = \sqrt{(q_1 - p_1)^2 + (q_2 - p_2)^2} \quad (3)$$

where p_i and q_i are the coordinates of the ith data points.[35] These distances were calculated using an open source software program, Orange. The distances were used to produce a dendrogram that displayed the samples into clusters based on complete linkage in which the longest distance between the points in each cluster is considered the distance between the cluster.[36] This gives an overall inter-cluster distance. The dendrogram was then converted into a table which was entered into MS Excel to create vertical plots, which show sample clusters as a function of depth; the clusters were color-coded by their cluster group. The cluster analysis was performed separately for each USE site, and for all samples collected from all four USE sites.

CHAPTER FOUR: RESULTS AND DISCUSSION

Physical Stratigraphic Analysis

One of the goals of this research was to determine if the chemical composition of alluvial floodplain deposits could be used to define chemostratigraphic units that provide insights into the depositional processes and history of a river basin. In geochemical studies, silt and clay components are often grouped together as fine-grain material because of their chemically reactive nature.[37,38] The percent silt-clay within the deposits was also used to define lithostratigraphic units in field. In Figure 4, the percent silt-clay for USE 2 is plotted against depth. The stratigraphic units observed in the field can be seen in the photograph, where the organic-rich dark-colored pre-settlement sediments are overlain by the legacy deposits. Figure 4 shows the variations in grain-size that typically occur with both the pre-settlement and legacy deposits. The legacy deposits contained sand-dominated units (low percent silt-clay), particularly within the middle of the sediment package, and fine-grained sediments near the top of the legacy deposits. These trends in grain-size are consistent with the earlier studies that suggested that legacy sediments were deposited during three time periods: (1) the onset of upland erosion and gully formation during the beginning of channel and floodplain aggradation. During this period, the surface of the pre-settlement deposits (i.e., the floodplain surface) was locally eroded and incorporated into the base of the legacy deposits. The abrupt, linear boundary between the legacy and pre-settlement deposits at USE 2 (Figure 4) is an indicator of erosion during or prior to the deposition of the legacy deposits; (2) a period of overbank deposition in the form of distributary channels, splays, and vertical accretion as channel filling progressed and overbank flooding increased. This period is associated with an increase in coarse-sand deposition within the middle of the legacy deposits; and (3) the deposition of finer-grained sediments near the top of the legacy deposits by vertical accretion processes following the implementation of erosion control measures and land use change. The pre-settlement deposits were often characterized by organic-rich, fine-grained units near their interface between the legacy and pre-settlement boundary (0.1-62.5 µm), and coarse sediments at depth. Deposition of the pre-settlement deposits appears to be associated with lateral accretion processes at depth (the coarse sediment), and the vertical accretion processes of the fine sediment near the surface, forming a fining upward sequence typical of floodplain environments. Locally, the fine, organic sediment were observed to fill paleochannels cut in the floodplain deposits (e.g., at USE 1).

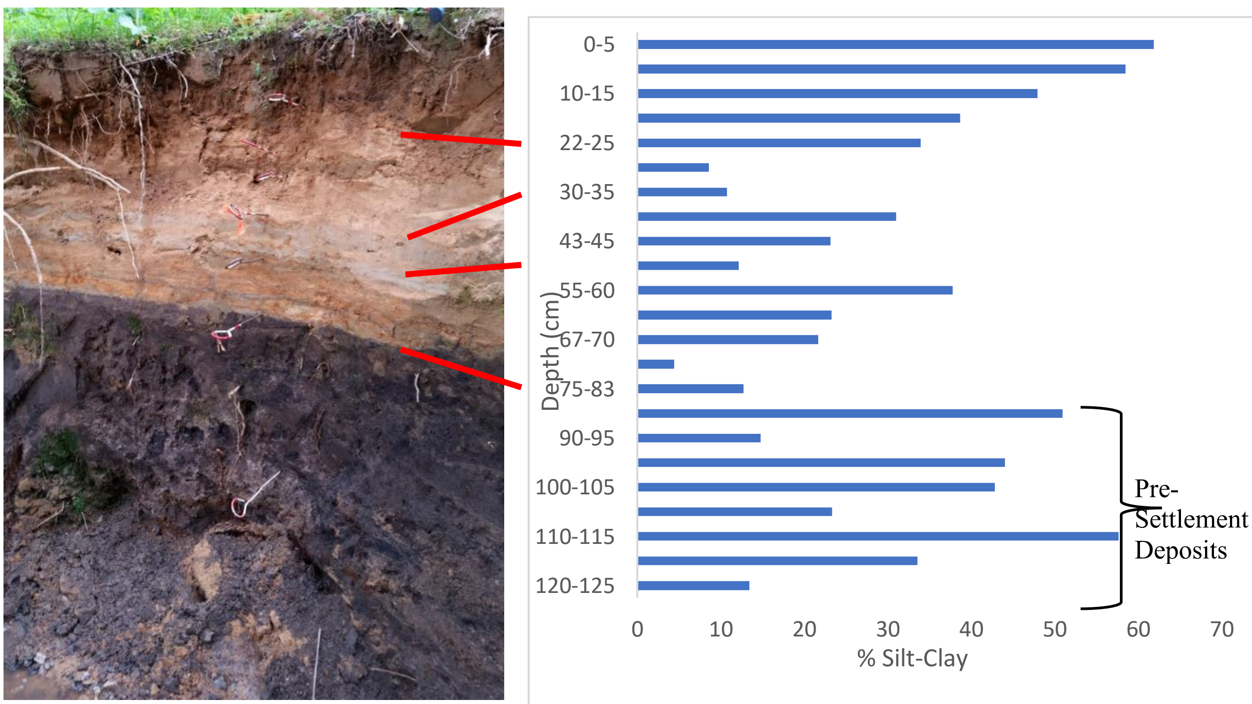

Figure 4. Photograph (left) and percentage of silt and clay-sized sediment (right) at USE 2.

Correlations Between Particle Size and Element Concentration

The particle size distributions were compared to the elemental concentrations (unnormalized) to determine if concentrations correlate with the percent silt-clay (and therefore grain size) in the deposits. Positive correlations between metal concentrations and percent silt-clay are common because of the chemically reactive nature of fine-grained particles.[37] For example, phosphorus has been found to sorb to silt and clay, which would result in an increase in phosphorus concentration when percent silt-clay is high. This relationship can be explored graphically for USE. In **Error! Reference source not found.**, the relative element concentrations for P is p lotted with the percent silt-clay within the deposits at USE 2. Phosphorus concentrations exhibit a similar profile to the percent silt-clay profile. Samples near the surface have high concentrations of P and high percent silt-clay. The P concentration spiked around 30-35 cm and then again at the pre-settlement boundary (83 cm). These high concentrations coincide with the high percent silt-clay. The similarity in profiles suggests that some elements, such as phosphorus, may be correlated with particle size. However, despite the graphical appearance of the correlation, the correlation coefficient for comparing phosphorus and percent silt-clay was only 0.13, so the correlation is not significant. In fact, the correlation coefficients for all element concentrations and percent silt-clay (see Appendix E) were all below 0.5, suggesting that grain size does not play a dominant role in controlling elemental concentrations.

Despite a lack of statistical correlation between element concentration and percent silt-clay, grain size effects may still play a role in sample composition. Normalizing concentration data by conservative element concentrations has been shown to reduce grain size effects.[39] Use of the concentration ratio derived from normalization would allow one to distinguish changes in composition due to grain size and mineralogy from changes due to different source materials. The effects of normalization will be explored with further analyses below.

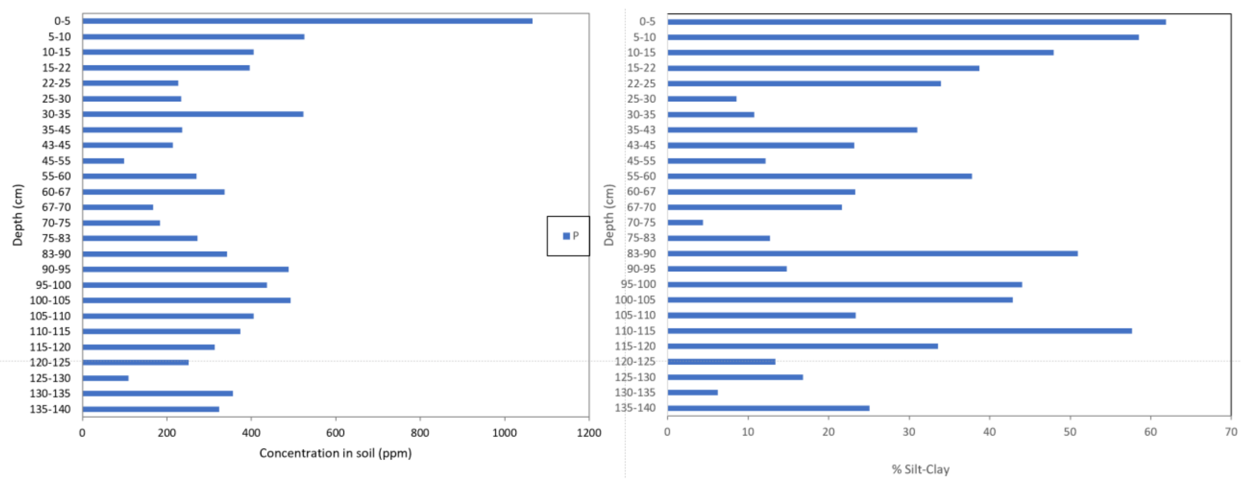

Figure 5. Phosphorous and manganese concentrations as a function of depth for USE 2 versus % silt and clay composition of USE 2.

Variation of Element Concentration Within a Single Site

Sediments within a channel and floodplain represent a mixture of sediment from all of the upland sources that exist in the basin, including sediments associated with different soil types and that were derived from upland gullies. If the geochemistry of the sediments in these sources differs, then the chemistry of the sediments found within the floodplain will vary through time and depth as a function of the relative amount of sediment that each source contributed to a specific deposit or package of floodplain material. Collaborative studies have shown that the potential sources of sediment within USE Creek do, in fact, differ in their geochemical characteristics. Thus, chemostratigraphic analysis may be well suited to this site.

Chemostratigraphy relies on not only variation of composition as a function of depth, but also on correlation between sample concentrations. Element concentration was plotted as a function of depth for certain elements to observe the degree of variation among stratigraphic units. For example, Figure 6 shows that the concentrations of cobalt and zinc are higher in the legacy sediment than in the pre-settlement sediment. There is also quite a bit of variation in the concentrations of these elements within these two stratigraphic units suggesting chemostratigraphic analysis will provide additional insight into geology of the site. Also, the spatial (vertical) profiles in Co and Zn concentrations at USE 1 are similar throughout the site. Within the upper section of the legacy sediments (0-80 cm), the concentration of both metals is high. As depth increases towards the pre-settlement deposits (80-113 cm), the concentrations of both metals decrease. One exception is immediately above the boundary between legacy and pre-settlement contact (110-113 cm) where Co concentration increases and Zn concentration decreases. This spike in Co concentration could be due to the presence of an additional source of Co when this stratigraphic unit was deposited. Finally, in the pre-settlement deposits, both elements have concentrations less than 20 ppm.

Since similarity in concentration profiles suggests the element concentrations are correlated. Indeed, the Zn and Co concentrations have a 0.734 correlation coefficient. The fact that the element concentrations correlate suggests that the chemical characteristics of the source materials is preserved as the elements are transported from the source to the channel. The concentrations were slightly more correlated in the pre-settlement samples (R^2 = 0.775) than in the legacy sediment (R^2 = 0.624). Although this difference is relatively small, the smaller correlation coefficient may mean that there are multiple sources of the legacy deposits.

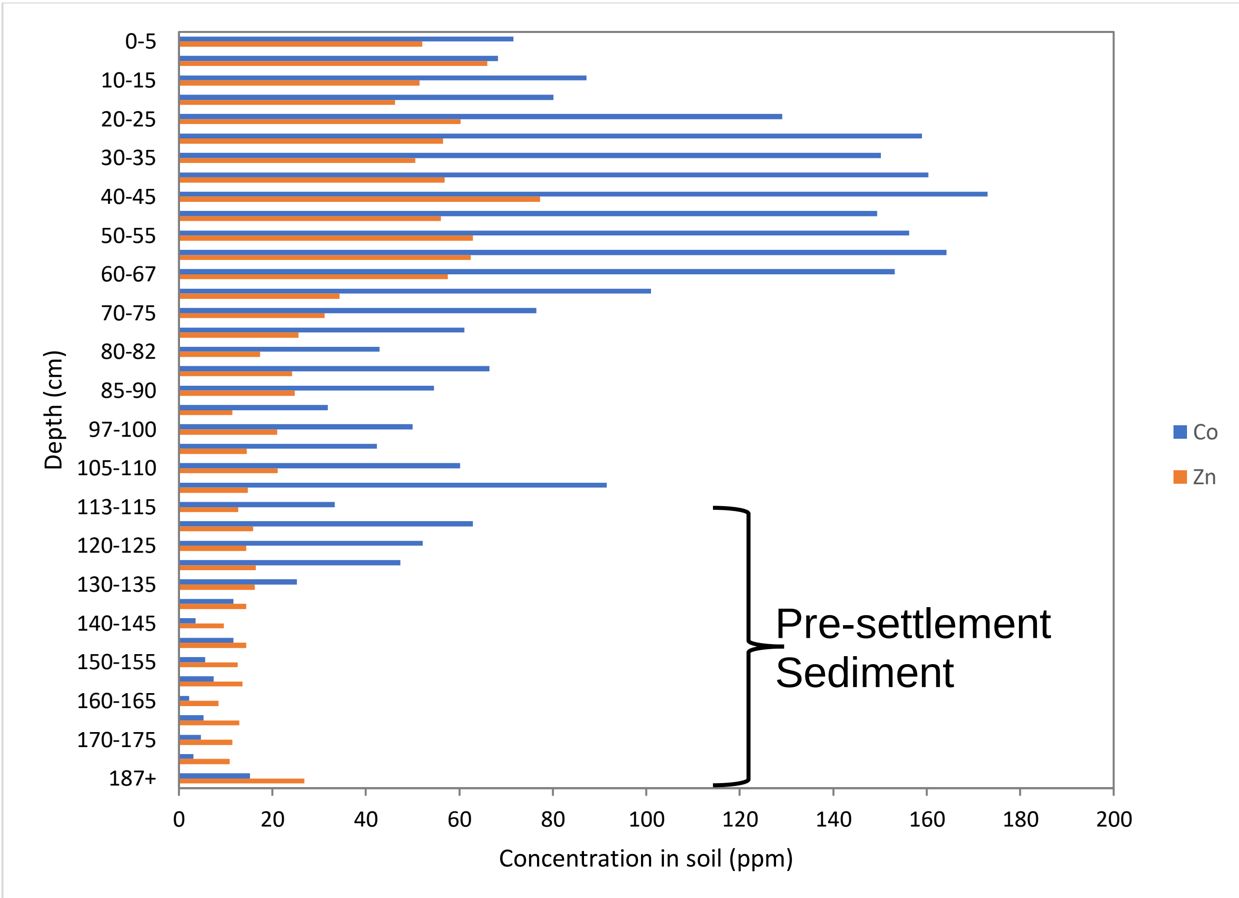

Figure 6. Elemental concentrations of cobalt and zinc as a function of depth at USE 1.

While some element concentrations correlate well with depth, others do not. The spatial relationship between iron, aluminum, and silicon concentrations within USE 1 are shown in Figure 7. All three elements show variability in concentration within the sediment. However, as Fe and Al concentrations increase with depth, Si concentration decreases and visa versa. For example, in the middle legacy sediments (67-110 cm), Si concentration increases while Fe and Al concentrations decrease at the same rate and depth. These opposing profiles are also indicated by the negative correlation coefficients, -0.35 for Si and Al and -0.497 for Si and Fe. This contrasting behavior could mean that Fe and Al are coming from the same source while Si is being deposited from a different source.

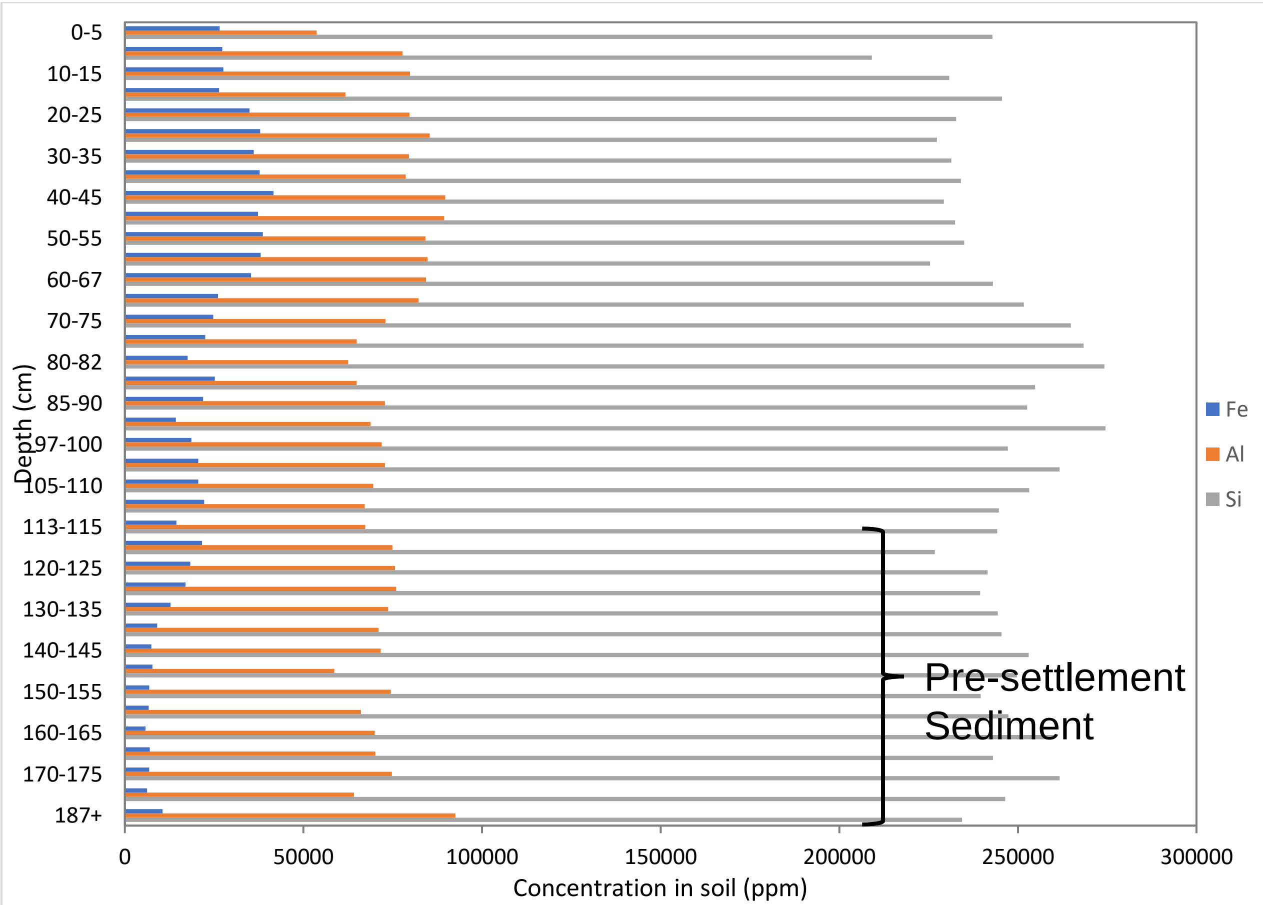

Figure 7. Relative element concentrations of iron, silicon, and aluminum in USE 1 as a function of depth.

While Fe and Al concentrations are generally correlated, with the top layer of the pre-settlement sediment, the iron concentration drops rapidly with depth, and the Al concentration stays about the the same. The correlation coefficient for Fe and Al concentrations is 0.425 correlation, but correlation of the legacy deposits alone yields a value of 0.617, indicating they are better correlated in the legacy deposits. One explanation for the weaker correlation between

Fe and Al in the pre-settlement deposits is the potential leaching of iron from the soil. As shown in Figure 3, the pre-settlement sediment layer is rich in organic material, giving rise to the black color. This organic content provides a chemically reducing environment, which prevents the Fe from attaching to the silt and clay and allows it to be dissolved by the groundwater. The fact that not all elements are correlated, but exhibit different trends may enhance the ability to define chemostratigraphic units. Concentrations of elements within USE 1 vary with depth, which means they can be used in identifying chemostratigraphic units. In fact, it is clear that concentrations differ significantly between pre-settlement and legacy deposits. (This could be proved statistically using a t-test or non-parametric method, which was not done.) Therefore, these differences in concentration profiles can be an indicator of different sources. Differences here were not unexpected. The legacy deposits are likely from gullies and heavily eroded soils, including subsoils; the pre-settlement deposits are likely from the topsoils of upland areas covered by forests. An important assumption inherent in defining these units is that there is only limited post-depositional migration of the elements within the floodplain deposits. Migration of the metals with downward infiltrating groundwaters would disturb the geochemical patterns in the sediments.

Effects of Normalization on Element Concentration

Although variation in chemical composition of the sediment can be due to different sediment sources, grain size effects can also play a role. Some elements can attach themselves to clay sized particles but not to sand (which is relatively inert) so the composition of the sediment depends on grain size. Finer grained material typically has higher metal concentrations than sand due to this effect even if it is from the same source as larger grained material. These materials can be separated from one another as source material moves from the upland source areas to the channel. The finer grained material (silt-clay) moves farther downstream than the sand-sized particles. Thus, the source sediments may be deposited in different areas of the floodplain. While their apparent concentrations may be different due to the different grain sizes, their relative concentrations should be the same if they are from the same source.

Normalization can be used to effectively define strata of similar chemical composition by reducing the influence of the variations in grain size and mineral composition between samples on elemental concentrations. Normalizing, then, may more effectively differentiate between lithostratigraphic units (defined on the basis of grain size, color, etc.) and chemostratigraphic units, defined solely on the basis of sediment chemistry. Unnormalized Cr and Zn concentrations have a similar profile throughout the channel bed, as shown in Figure 8. The high concentrations of Cr and Zn are parallel throughout the upper legacy sediment section (5-67 cm). Then, at greater depths (90-175 cm) going into the pre-settlement sediment, the concentration of Cr is lower, below 20 ppm. However, Zn concentrations continued to vary with depth within the pre-settlement deposits. Zinc and Cr have a high overall correlation of 0.677 showing that the concentrations of the two elements are related and the elements could be being deposited by the same source.

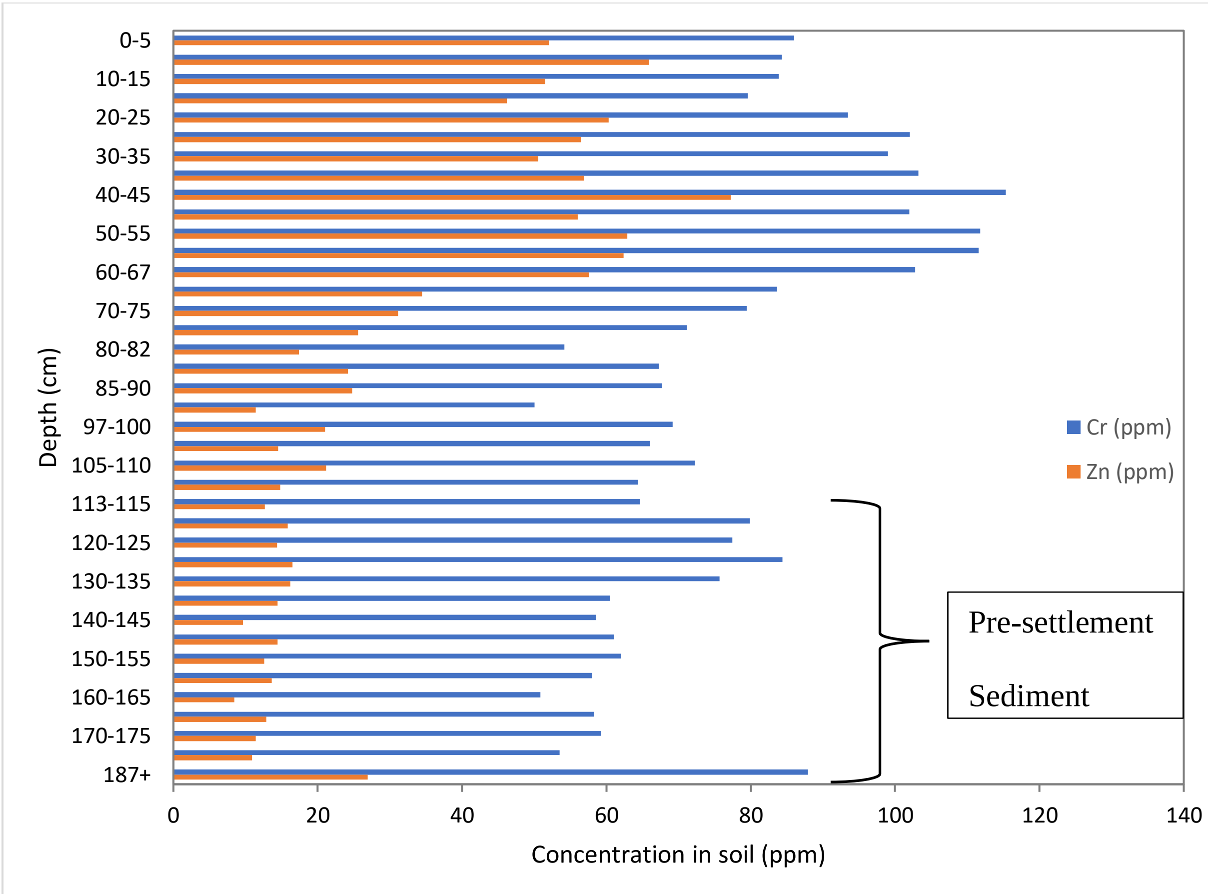

Figure 8. Elemental concentrations of chromium and zinc at USE 1 as a function of depth.

The effects of normalization were explored for Cr and Zn, and the result is shown in Figure 9. Here, Cr and Zn concentrations were both normalized by Fe concentration to calculate the concentration ratios. The Cr and Zn concentration ratios don't appear to be as correlated as the unnormalized element concentrations (Figure 8). For instance, while both elements' concentration ratios decreased from 67-85 cm, the rate of decrease was much higher for Zn than for Cr. Also, in the unnormalized concentration profile, the difference between the Cr and Zn concentrations was relatively constant, while in the normalized concentration ratios, the difference increased as a function of depth. This enrichment in Cr could not be explained. The overall correlation decreased to 0.463 using the normalized concentration ratios. Within the legacy sediment alone, there is a negative correlation of -0.011. These changes in correlation upon normalization suggest that previously observed correlation with unnormalized concentration may have been due to grain size and mineralogy effects rather than common sourcing. Normalization ratios seem to emphasize differences among chemostratigraphic units due to sources, which may assist with stratigraphic classification within a site.

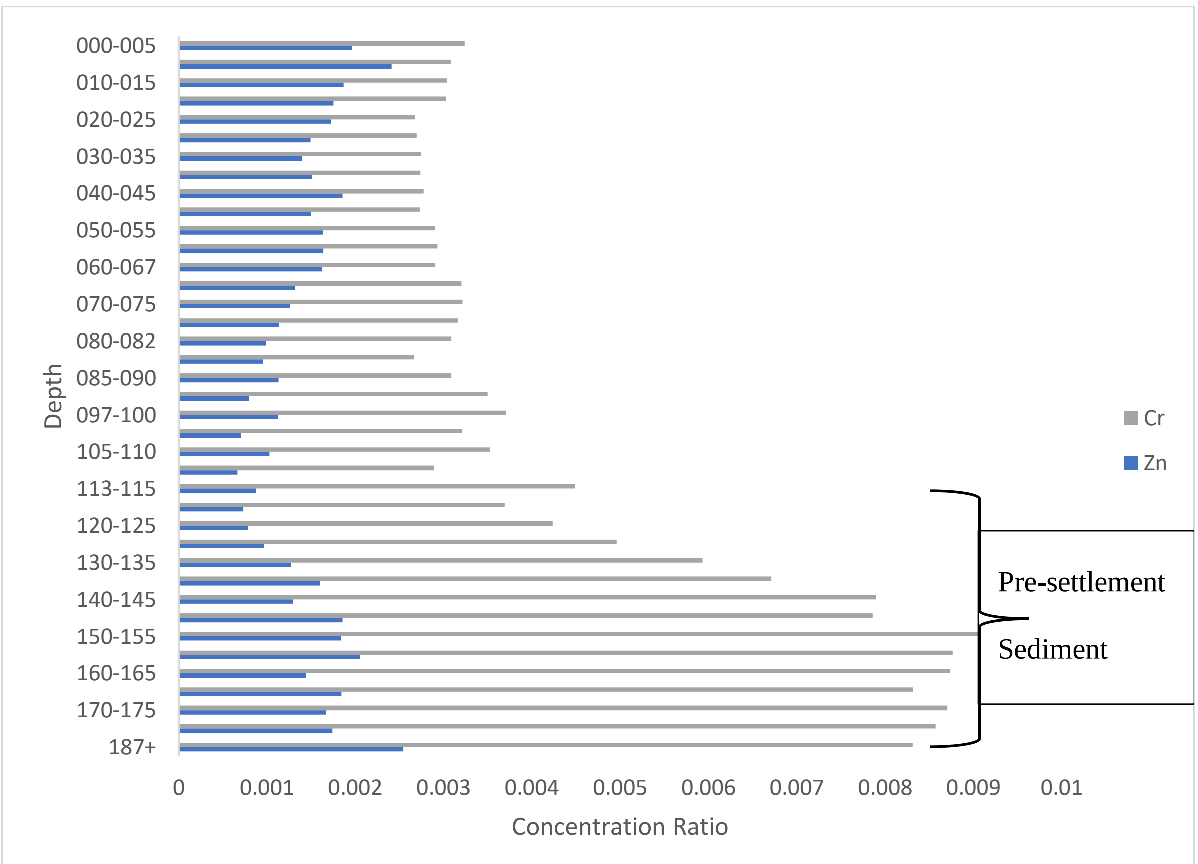

Figure 9. Normalized concentrations of chromium and zinc of USE 1 as a function of depth

Variation of Element Concentration Between Sites

After the comparison of multiple elements within a single site, the next step was to see if one element could be used to define and correlate chemostratigraphic units between multiple sites. Elemental concentration profiles for sites USE 3 and USE 2 were compared using iron as an example. (See

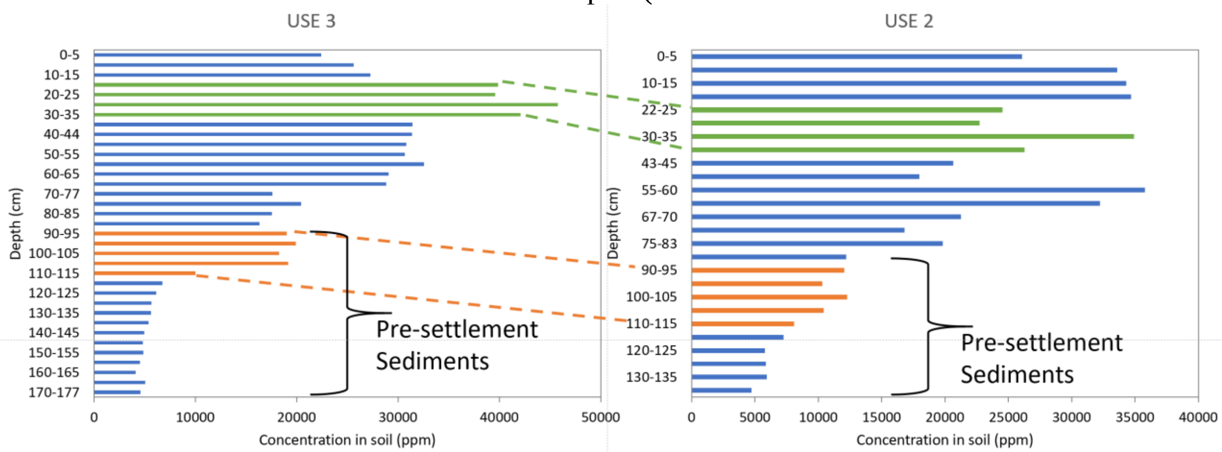

Figure 10.) USE 3 is located upstream from USE 2. There are packets of sediment that show similar Fe concentrations between sites and the metal can be correlated between the units. USE 3 shows an increase in Fe concentration from 10 cm to 15 cm. USE 2 has the same increase after 5 cm. After these depths, the profiles are similar leading up to a decrease in concentration around 35 cm for USE 3 and 22 cm for USE 2. These similarities in concentration suggest that the stratigraphic section of 15-30 cm at USE 3 correlates to the sediments between 5-22 cm at USE 2. Another possible correlation is between sediments within the interval from 95-115 cm at site USE 3 and sediments ranging from 90-115 cm at USE 2. The correlations between USE 3 and USE 2 suggest that not only do chemostratigraphic units exist at a single site, but that it may be possible to correlate these units between multiple sites. The normalized data for a single element (Fe in this case) yielded similar results.

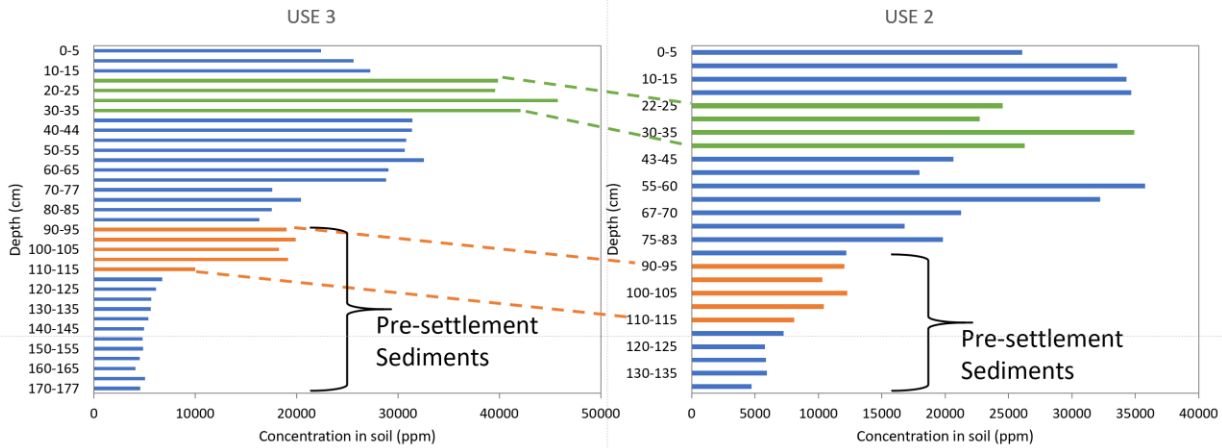

Figure 10. Correlation of Fe concentrations within USE 3 (left) and USE 2 (right).

While some units possess distinct Fe concentrations and can be correlated between sites, the vertical profiles are not identical and show variations within the concentration profile. The identification of chemostratigraphic units may benefit from a multivariate approach that uses the variations in concentrations of multiple elements to define the chemostratigraphic units. Multiple elements could show variation and resolution between the legacy and pre-settlement deposits.

Cluster Analysis Using Elemental and Normalized Concentration Data

A commonly used exploratory, multivariate method used to define group of similar samples is cluster analysis. It was utilized here to examine its potential to define chemostratigraphic units using multiple elements at one time. It was applied both to an individual site, and across multiple sites (using all of the geochemical samples). The advantage of analyzing multiple elements is that the influence of random variations in concentrations of elements can be removed, thereby identifying packages of sediment with unique, multi-elemental geochemical signatures.

Cluster Analysis Using Elemental Concentrations

All the elements (Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Y, Zr, Nb, Mo, Cd, W) that were not missing sample data were used for the cluster analysis. One of the simplest questions to determine if the cluster analysis could define chemostratigraphic units was to determine if it distinguished between legacy and pre-settlement sediments. All the lithostratigraphic units within USE (1-4) were loaded into the hierarchical cluster analysis and separated into two clusters. Figure 11 shows how each individual sample was classified by this two clusters approach. Generally, the samples were classified by being subdivided into two groups that corresponded to the known pre-settlement and legacy deposits; there were a few misclassifications. The upper most sediments within each unit was clustered with the pre-settlement sediment (a few orange markers near the top) which could be due to the samples having similar grain size and mineralogy. In USE 2, there are also some samples within the legacy sediment that are chemically similar to the pre-settlement sediment (orange markers around 40 cm). Lastly, there are some samples just below the pre-settlement line that have similar chemical composition as the legacy sediment seen in USE 1 and 3 (blue markers below the dashed lines), and in USE 4 there were no pre-settlement samples below the pre-settlement line (no orange markers below the dashed lines).

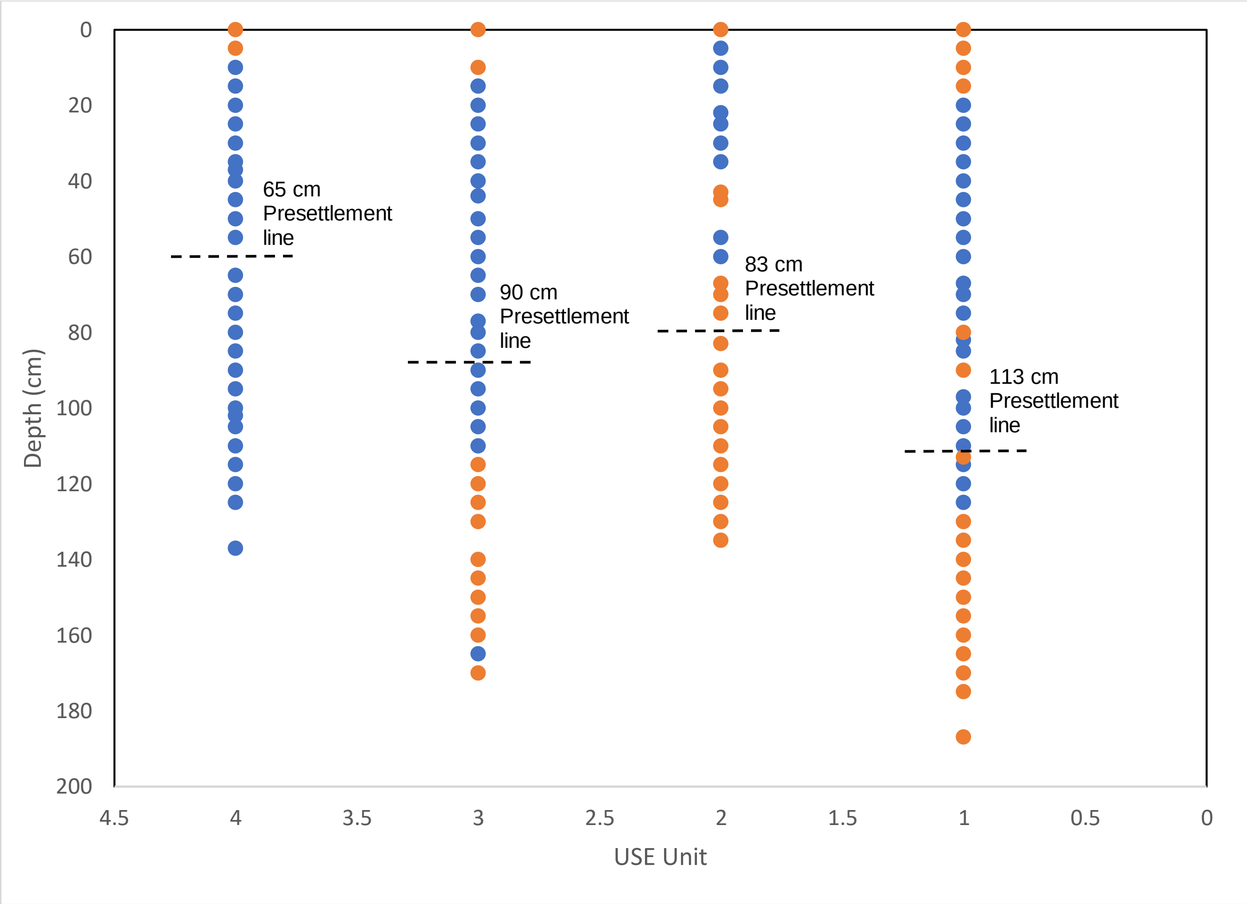

Figure 11. Lithostratigraphic units USE 1-4 divided into 2 clusters as a function by depth.

The upper most sediments may have clustered with the pre-settlement deposits because the grain size between the two is similar. One possible reason for this cluster is the organic matter content is high within the pre-settlement and upper legacy sediments. USE 4 was found to not have any chemical differences between the pre-settlement sediment and legacy sediment. The presence of samples within the legacy section that cluster with the top of the pre-settlement layer at sites 1 and 3 and the pre-settlement deposits with some legacy sediment at USE 2 suggest that there may be mixing between the two stratigraphic sections of legacy and pre-settlement that was not detectable by the lithostratigraphic units. Another possible explanation is that the trace metals are moving vertically within a site through the sediment through groundwater. Chemostratigraphy is based on the assumption that metals do not migrate following deposition, but these results suggest that the metals may be moving with groundwater. However, this migration is unlikely as the metals are not able to move far vertically within the sediment.

Cluster Analysis Using Normalized Concentrations

The next step was to see if the normalized ratios provide a more effective means of defining chemostratigraphic units than the elemental concentration data and to determine if improved correlations of the defined units between sites. Although a complete chemical profile was used to do the previously described cluster analysis, only the elements used in the fingerprinting source analysis study (Al, Si, P, K, Ti, Cr, Fe, Co, Ni, Cu, Zn, W) were used in the cluster analysis based on normalized concentrations.

Samples from all four USE sites were normalized using either by Fe, Ti, and Al, loaded into the cluster analysis and divided into two groups. The normalized data were generally able to divide the samples into legacy and pre-settlement deposits but with less resolution (Figure 12). For sites 1-3, the cluster containing the legacy sediments extends to around 22-25 cm in depth, past the pre-settlement boundary. Similar to the results generated by the concentration data, the legacy and pre-settlement sediments at USE 4 were not separated into chemically different units.

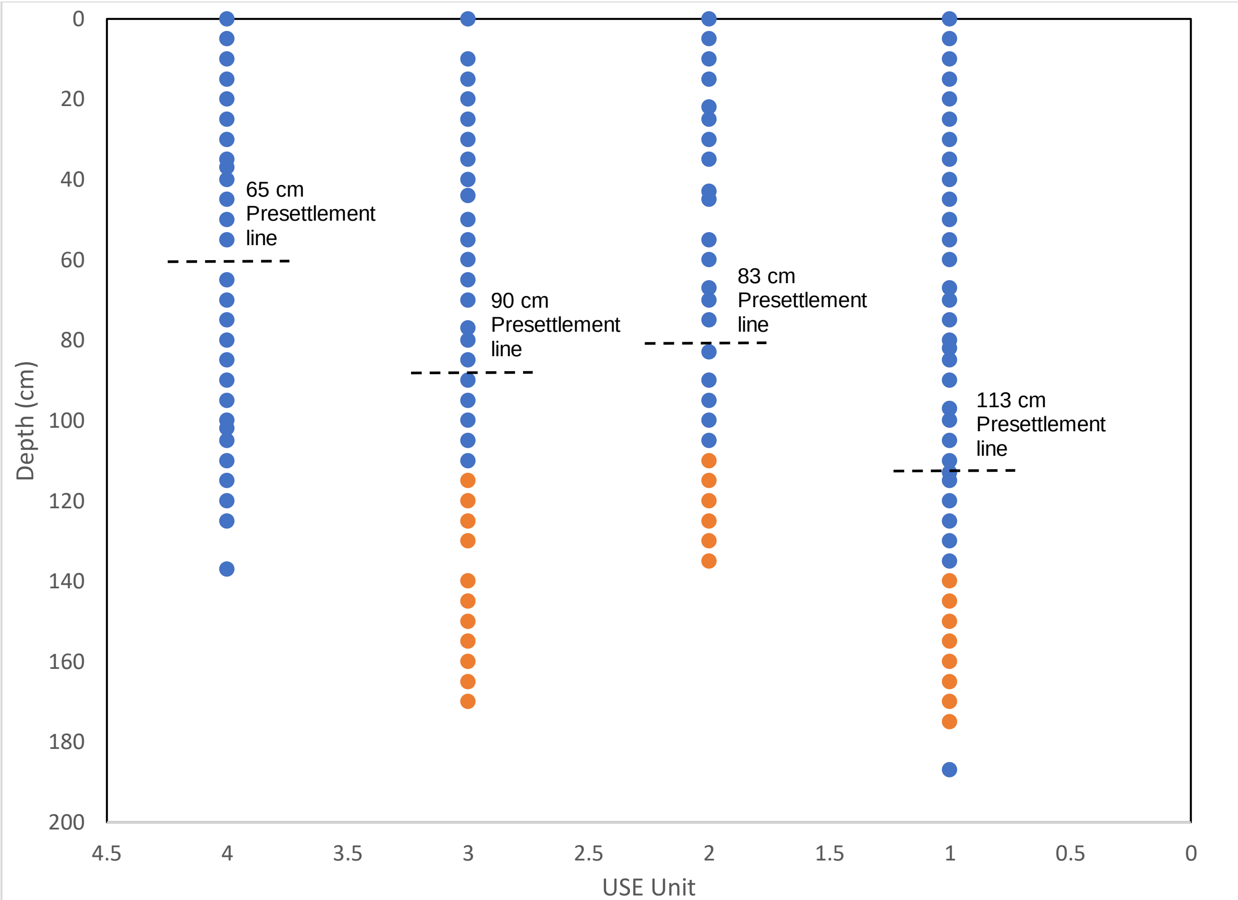

Figure 12. Lithostratigraphic units for USE 1-4 divided into two clusters as a function of depth using the normalized concentrations of fingerprinting elements

As was the case using the concentration data, these results could mean that metals in the sediment directly below the pre-settlement boundary were moving downward with the groundwater. The grain size within the legacy sediment is more coarse grained that the pre-settlement deposits.

The chemostratigraphic units defined by the hierarchical cluster analysis using the normalized data were compared to the lithostratigraphic units defined in the field to see if they were similar. Field observations subdivided USE 1 into eight lithostratigraphic units. Figure 13 shows the hierarchical clustering as colored markers overlaid with the descriptions of the lithostratigraphic units. When the hierarchical cluster analysis was used, imposing eight clusters resulted in similar chemostratigraphic sections to the physical stratigraphic sections already defined. However, there were some units that were not observed in the field. The upper-most legacy sediments (0-20 cm) seem to have its own chemical signature. In contrast, the next two physical lithostratigraphic units had a similar chemical composition. Another important difference is that some samples within a unit were defined as a separate cluster. The last difference is that the pre-settlement sediment had more variable elemental concentrations than the legacy sediment.

These results suggest that hierarchical analysis based on chemical composition can provide a different perspective of the sediment. The cluster analysis shows possible chemostratigraphic units that could have been deposited by the same source. In contrast, lithostratigraphic units show packages of sediment that were deposited under similar environmental conditions. The physical descriptions may not be able to capture slight differences that could be created by mixing of deposits that cause the differences in chemical composition. The chemostratigraphic clusters suggest that there is more variability in the pre-settlement sediment than could be discerned by physical characterization.

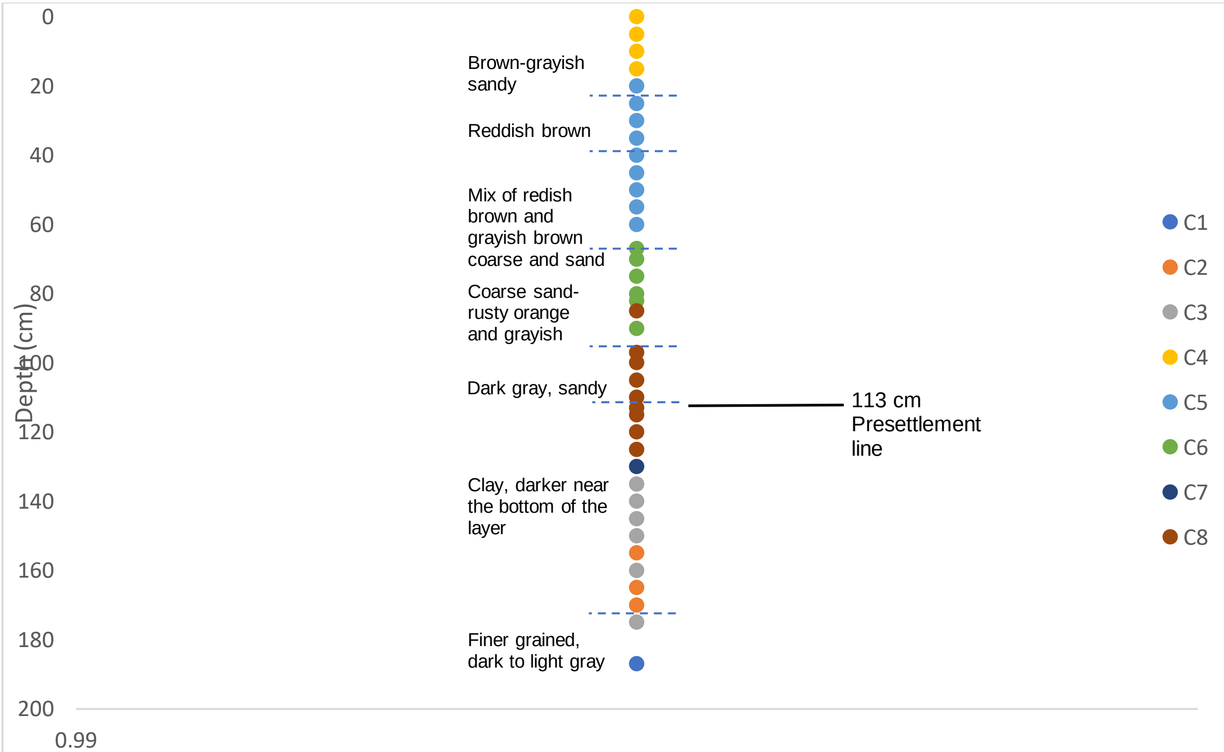

Figure 13. Cluster analysis of USE 1 with eight clusters as a function of depth. The stratigraphic descriptions acquired in the field are shown with the lines marking the lithostratigraphic sections.

Figure 13 demonstrates that there are differences between the lithostratigraphic and chemostratigraphic analyses. As previously discussed in the introduction, the lithostratigraphic units depend in large part on the site's environment of deposition as described by its flow condition (flow depth and velocity), sediment supply (amount and size of sediment), and the depositional process (lateral accretion, vertical accretion, channel fill or lag, etc.). These factors combine to control the size and density of the sediments found with the unit, primary stratigraphic features (laminations, layers, cross-bedding, etc.), and its other physical characteristics. Chemostratigraphic deposits also depend on the above factors but are much more dependent on the source of the sediments, and the chemistry of its source materials. Some chemostratigraphic units correlate rather well with lithostratigraphic units, but others do not. Some lithostratigraphic units are comprised of multiple chemostratigraphic units, and chemostratigraphic units are composed of more than one lithostratigraphic unit. This is true whether chemostratigraphic units are defined by cluster analysis or PCA. It appears that sediment sources and site-specific depositional processes were not perfectly correlated with each other.

The next cluster analysis performed was to determine if the chemostratigraphic clusters could be used to correlate the lithostratigraphic units across sites. The chemical composition for all four units were loaded into the hierarchical analysis and constrained to seven clusters using the normalized concentration and fingerprinting elements. The results are shown in Figure 14. The pre-settlement sections found at sites USE 1 and USE 2 are similar with two primary chemostratigraphic sections (orange and yellow markers below the pre-settlement boundary). There is also a cluster that is found throughout the legacy sediment shown by the navy-blue markers. USE 3 (15-65 cm) and USE 1 (20-60 cm) have the largest chemostratigraphic sections for this cluster, but the cluster is present at all four sites within the legacy sediment. Dashed lines are provided in Figure 14 to emphasize the correlation between chemostratigraphic units.

These defined chemostratigraphic clusters show that they are related to the lithostratigraphic units. The clusters can also be compared to the sources that are depositing them. The water flows from USE 4 (upstream) to USE 1 (downstream) meaning that the sediments deposited within a certain unit upstream may or may not be eroded at the next downstream site. This could account for the differences within the USE 3 pre-settlement sediments relative to the other sites. The clusters also show a mixing within the legacy sediment above the pre-settlement boundary of USE 1, 2, and 4 within the same chemostratigraphic cluster. These clusters could suggest correlation among the three sites at those depths caused by sediment being deposited from the same source.

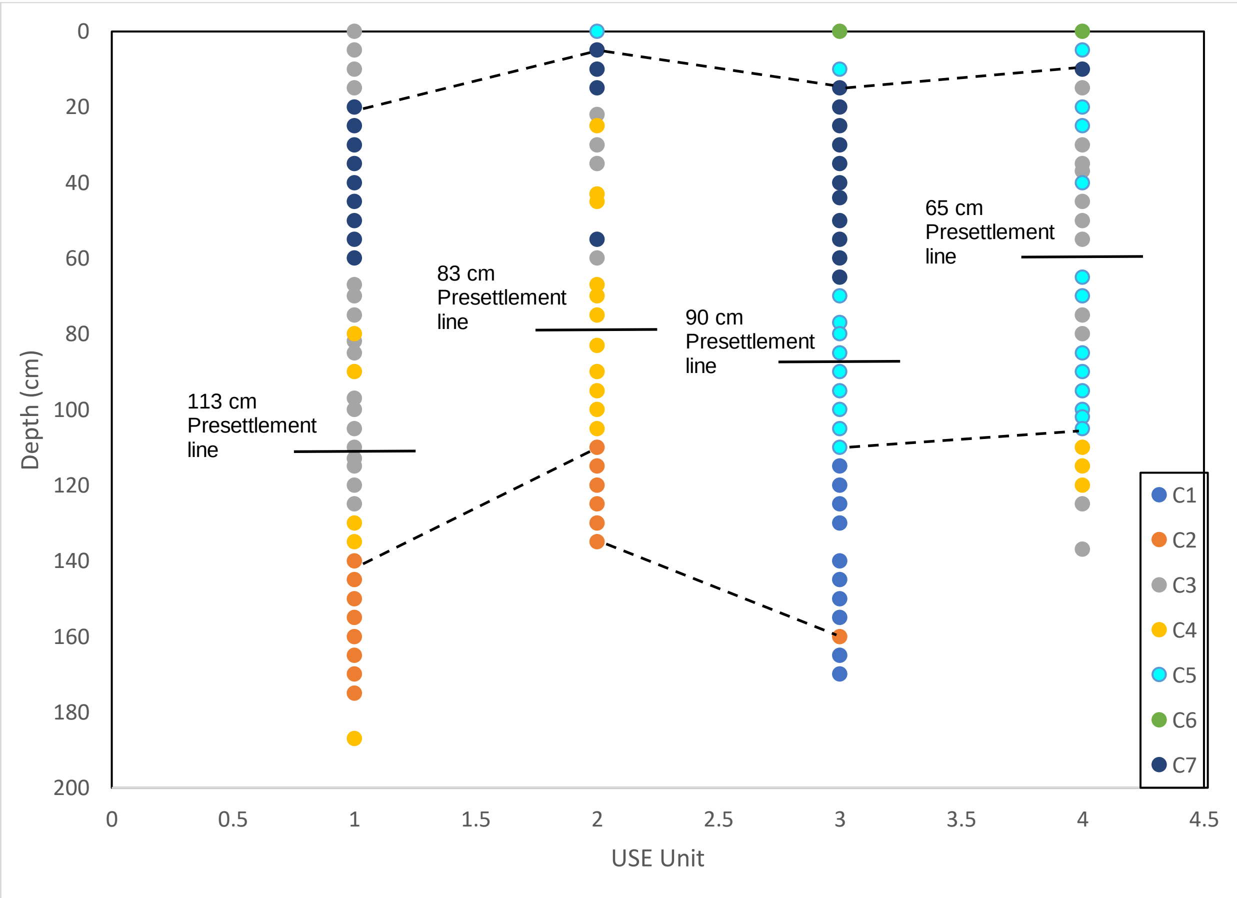

Figure 14. Lithostratigraphic units of sites USE 1-4 classified into seven clusters using normalized data as a function of depth. Dashed lines show correlation across sites for certain clusters.

Principle Component Analysis

Principle Component Analysis Using Elemental Concentrations

Principle component analysis (PCA) was another method used to find chemostratigraphic units within and between sites. There were 10 elements used in the analysis. The loading vectors that comprise the first two principal components (PCs) are shown in Table 1. The two components explained 66% of the variance within the element concentrations.

Table 1. Loading vectors for the unnormalized relative concentrations of the fingerprinting elements used for PCA.

	Component 1	Component2
Al	0.506	0.327
Si	-0.38	0.596
P	0.259	-0.727
K	0.689	0.202
Ti	0.813	0.331
Cr	0.822	0.322
Fe	0.898	-0.111
W	0.772	0.133
Zn	0.881	-0.184
Cu	0.876	-0.302

A score plot, which is a plot of the weights of the PCs against one another for each sample, is shown in Figure 15. The points are colored according to whether the samples were collected from legacy (blue) or pre-settlement (orange) deposits as determined in the field. The number next to each point represents the sample number from the ground surface to the base of the channel bank. The score plot shows clustering of data points. These clusters were subjectively defined by ellipses that encompass group members. Generally, all four sites show clustering of legacy and pre-settlement sediment samples. That is, clusters (groups) are comprised of either orange or blue markers. However, each site also contains a cluster that could not separate into solely legacy or pre-settlement deposits. The samples that comprise these clusters lie immediately above and below the contact between the legacy and pre-settlement deposits and may be related to (1) the erosion and incorporation of pre-settlement sediments into the legacy deposits in the form of a mixing layer, and/or the downward movement of particulates (translocation), or dissolved elements from the legacy sediments into the pre-settlement deposits (leeching).

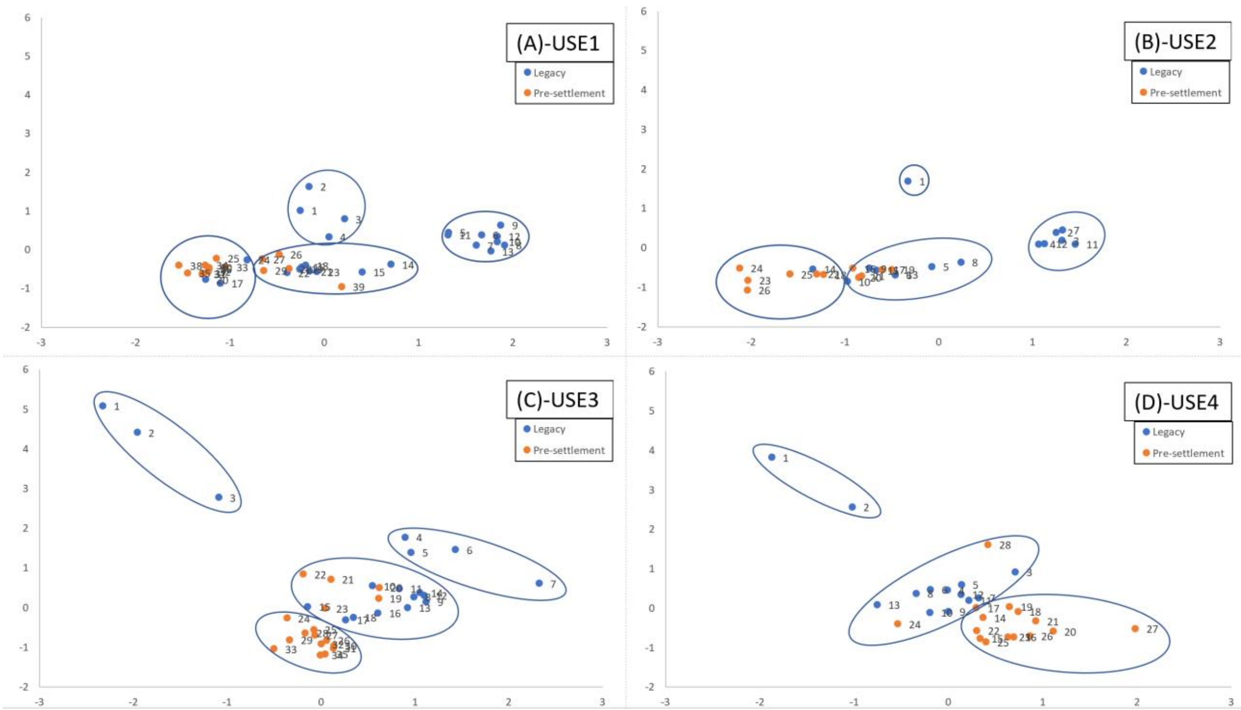

Figure 15. Score plots of the USE units using the element concentrations. (A)-USE1, (B)-USE2, (C)-USE3, (D)-USE4. The x-axis is the weight of principle component 1 and y-axis is the weight of principle component 2.

For USE 1, five clusters were determined. The top layer (0-20 cm, samples 1-4) is in its own cluster. The next layer was designated as the middle legacy sediments (20-67 cm, samples 5-13) and are clustered together. The third cluster includes samples from the bottom of the legacy sediments (67-80, 82-90, 97-100, 105-110 cm, samples 14-16, 18-19, 21, 23). There are some samples from the bottom layer of the legacy sediment (samples 17, 20, 22, 24) that were clustered with the two remaining pre-settlement sediment clusters (samples 26-29 and 25, 30-

38). The last (deepest) sample within USE 1 (sample 39) did not belong to any of the five clusters.

A closer inspection of the elemental loadings on the principal components (Table 1) provide insights on the origins of the clustering. The PC1 and PC2 values for each sample within each site are shown graphically as a function of depth in Figure 16. The sites are arranged from left to right in the direction of water flow, i.e. USE 4 is on the left and USE 1 is on the right. This cluster of sediment was presumably deposited after the implementation of erosion conservation measures, including conversion of cotton fields to pastures. Sedimentation appears to have occurred by vertical accretion processes that were much slower than the processes involved with the deposition of deeper sediments. Most of these upper-most sediments were presumably derived from the slow erosion of upland soils. The sediment in this cluster are also finer grained.

The sediments in the middle of the legacy deposits are characterized by here quantities of sand-sized sediment and differs from the top layer. These sediments are thought to have been deposited during the phase of channel and valley floor aggradation during which the floodplain was dominated by lateral accretion processes associated with distributary channels, splays, and, to a lesser degree, vertical accretion processes. In addition, these sediments were likely derived from gullies and subsoils that were being eroded at the time. The pre-settlement and bottom legacy sediments were not able to be fully separated by the principal components.

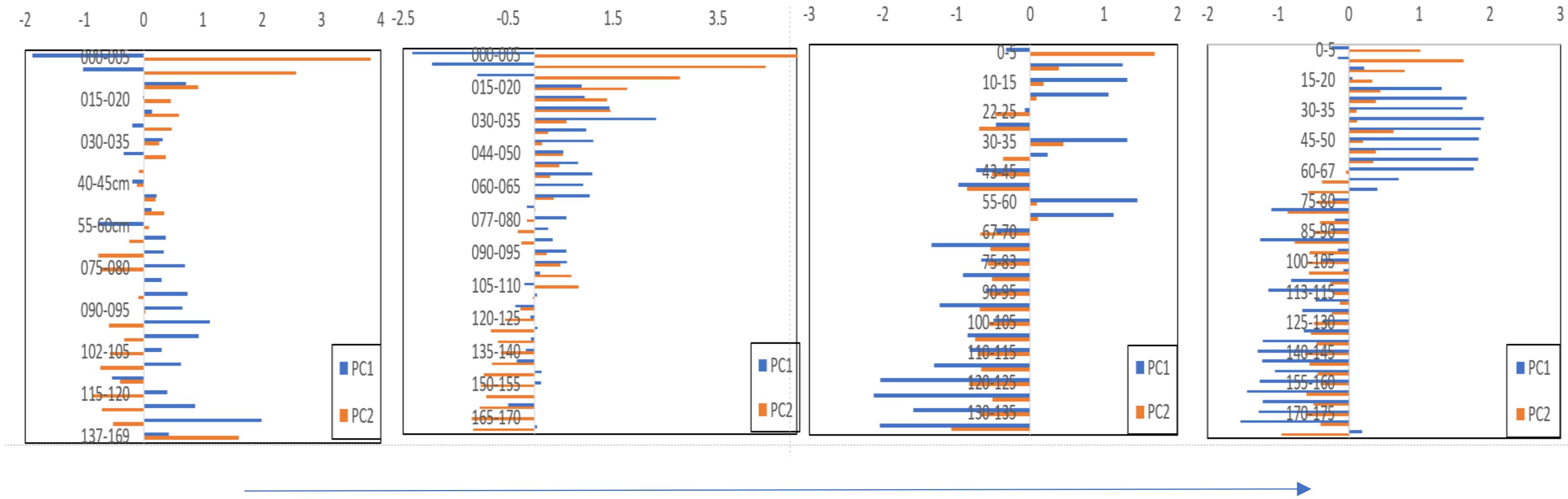

Figure 16. PC1 and PC2 values derived from unnormalized elemental concentrations plotted as a function of depth at each site. The arrow indicates the direction of water flow within the stream from USE 4 (left) to USE 1 (right).

Principle Component Analysis Using Normalized Concentrations

The element concentrations were normalized by a conservative element and analyzed using PCA. The fingerprinting elements for the concentration ratios were found to be different than those of the elemental concentrations. The first two principle components explained 87% of the variance within the dataset. The loading vectors are shown in Table 2.

Table 2: Loading vectors for the normalized concentrations of the fingerprinting elements used for PCA.

Element	Component 1	Component 2
V	0.846	0.432
Cr	0.956	0.116
Fe	-0.924	0.179
Co	-0.85	0.292
Cu	-0.291	0.815
Zn	0.492	0.693
W	0.933	0.101

Score plots of PC1 vs. PC2, Figure 17, show that the sample’s cluster into more discrete groups than they did for the PCA that used the elemental concentration data. Generally, the mixing layer was divided into two clusters that distinguished between the legacy and pre-settlement samples. There was still some mixing between the legacy and pre-settlement sediments at some sites, but this was expected given the field observations that showed that pre-settlement deposits had been eroded and incorporated into the legacy sediments.

At USE 1, the legacy sediments clustered into approximately three clusters with better separation and resolution than the unnormalized PCA. As seen with the unnormalized elemental concentrations, there is a cluster of samples from the top and the middle of the legacy sediments. There is also a cluster of samples from the bottom of the legacy sediments (samples 14-16, 18-

19, 24) that is now separated from the mixing layer. This is in contrast to the results of the unnormalized PCA in which samples from the bottom of the legacy sediments and the mixing layer were combined in a single cluster. The next cluster contains some bottom legacy samples (80-82 and 90-110 cm, samples 17, 20-23) and the top of the pre-settlement sediments (115-135 cm, samples 25-29). The remaining cluster contains the rest of the samples from the pre-settlement deposits beginning at a depth of 135 cm (sample 30), including the lowest depth sample (sample 39), which did not belong to a cluster when the data was not normalized. These results show that below 135 cm, the sediments had a similar chemical composition. The clusters have been color coded to show the similarities between the sites and scores.

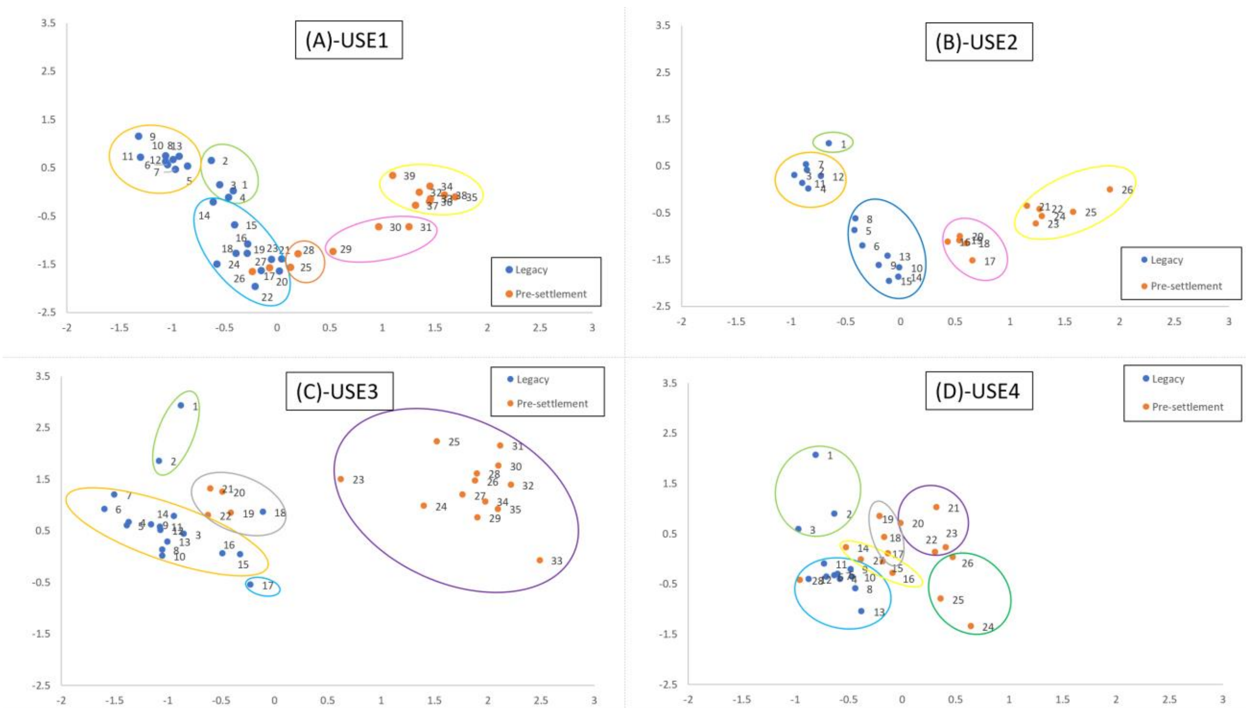

Figure 17. Score plots of the USE units using normalized concentrations. (A)-USE1, (B)-USE2, (C)-USE3, (D)-USE4 the x-axis is principle component 1 and y-axis is principle component 2.

These score plots show that the normalized data group samples into more distinguishable chemostratigraphic units. That is, the groups of samples are spread out on the plot, allowing them to be more easily defined. The colors of the clusters demonstrate the similar scores of the principle components between the sites and how the chemostratigraphic units possibly correlate based on the scores.

The PC1 and PC2 scores for each sample within each site are shown graphically as a function of depth in Figure 18. The sites are arranged from left to right in the direction of the water flow, i.e. USE 4 is on the left and USE 1 is on the right.

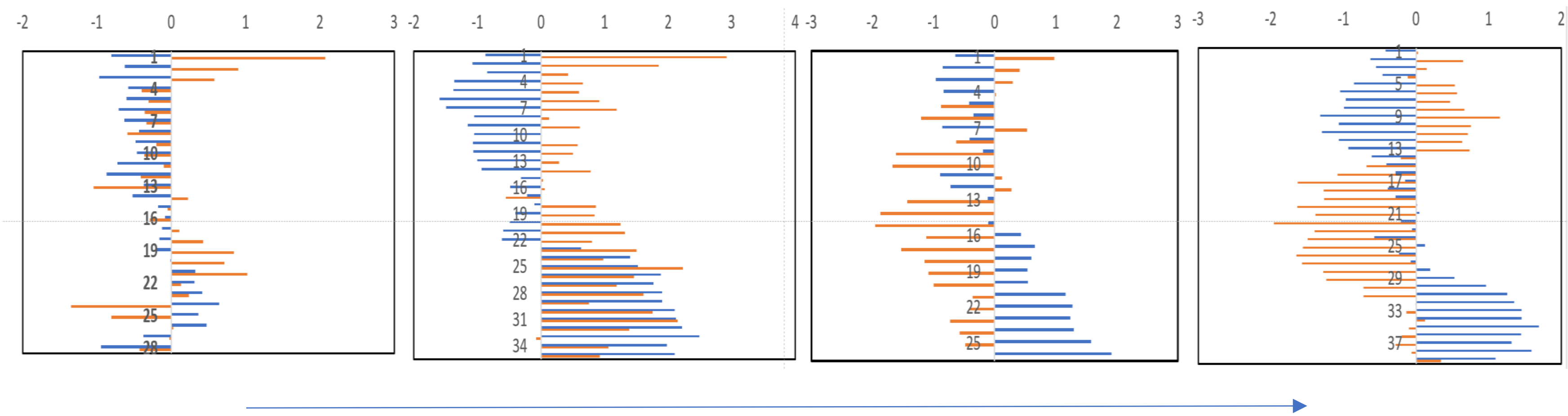

Figure 18. Vertical plots of normalized concentration data graphing principal components as a function of depth. The arrow displays at which the water flows within the stream. The far left is USE 4 going to the far right is USE 1.

Method Comparison

The two methods, hierarchical cluster analysis and PCA, were used to identify chemostratigraphic units that could be correlate between measured stratigraphic sections (sites). A comparison of the chemostratigraphic units (sampling groupings) at USE 1 defined by cluster analysis and PCA using element concentrations is shown in Figure 19. The cluster analysis defined five distinct clusters (chemostratigraphic units), which matched the number of clusters observed in the PCA. The samples contained within the units (clusters) defined by both methods were similar, as indicated by the colored circles in the score plot and the colored markers in the cluster analysis. However, the score plot shows that samples of the pre-settlement sediments (orange markers) were divided by the PCA into two clusters, while all the pre-settlement clusters were placed in a single cluster by the hierarchical cluster analysis. The unclustered samples (187+ cm, sample 39) in the score plot were included in a cluster with two other legacy sediment samples in the cluster analysis (80-85 and 90-95 cm). Conversely, these two samples from the pre-settlement deposits were clustered with the sediments in the PCA score plot.

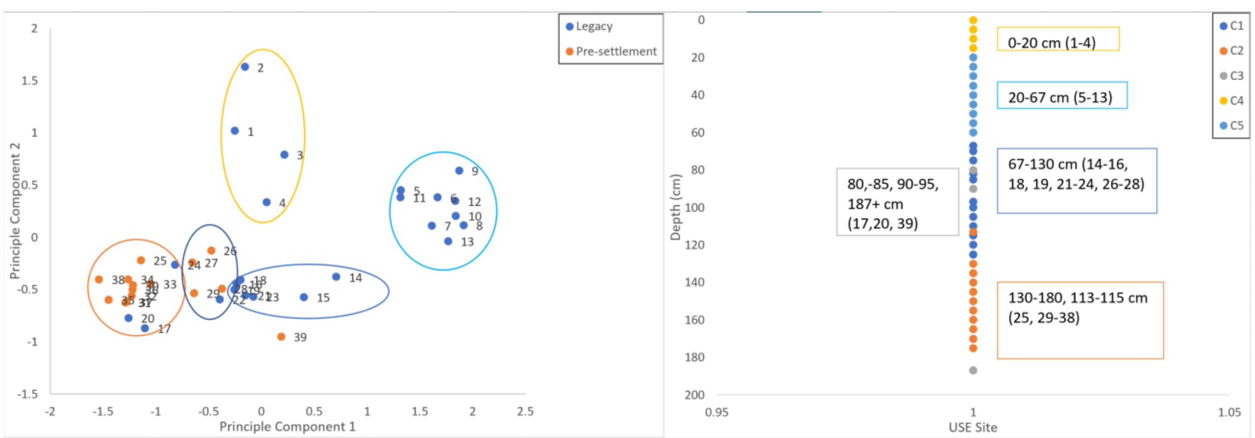

Figure 19. Score plot on right based on PCA using element concentration data from USE 1; axes represent principle components. Left plot shows chemostratigraphic units defined by the hierarchical cluster analysis of concentration data collected at USE 1 as a function of depth.

The methods give similar results, but the principle component analysis used fewer elements, which could explain the slight differences. Turning to the objectives, hierarchical cluster analysis and principle component analysis were able to identify chemostratigraphic units within the legacy and pre-settlement when using the normalized concentration data. However, the hierarchical cluster analysis showed difficulty with finding distinct chemostratigraphic units for USE 4. In contrast, PCA, when considering all four units, defined more chemostratigraphic units than the cluster analysis. PCA also did a better job at separating legacy from pre-settlement deposits.

Correlation of Chemostratigraphic Units Defined By PCA

The principal components were not only used to define the chemostratigraphic units at individual USE sites, but also used to correlate the units between stratigraphic sections. The normalized data were used to correlate the chemostratigraphic units between sites. The vertical plots show the principal component scores by depth and displays the correlations within the sites by color (**Error! Reference source not found.**).

There is a package of sediment within the upper most sediments (light green) that is found throughout the floodplain. These upper units represent the most recent period of deposition of fine-grained sediment on the floodplain following the erosion control measures. The correlation of the mid-lower legacy sediments was more difficult. This is not surprising given the potential nature of the depositional processes. The sediment was found to mostly be coarse grained sediments deposited by vertical accretion processes as well as by lateral accretion associated with overbank floodplain channels and splays. These processes created more variation in grain size and composition. There were two main legacy units that were able to be correlated throughout the 4 sites (orange and light blue). In the pre-settlement, the chemostratigraphic units were harder to correlate between the four sites. The units could only be correlated with the site next to them. There were four chemostratigraphic units found within USE 4, however, only two of them were also found in USE 3. The other two units pinched out before continuing downstream. USE 2 had two chemostratigraphic units unique to the site as well that were correlated downstream with USE 1.

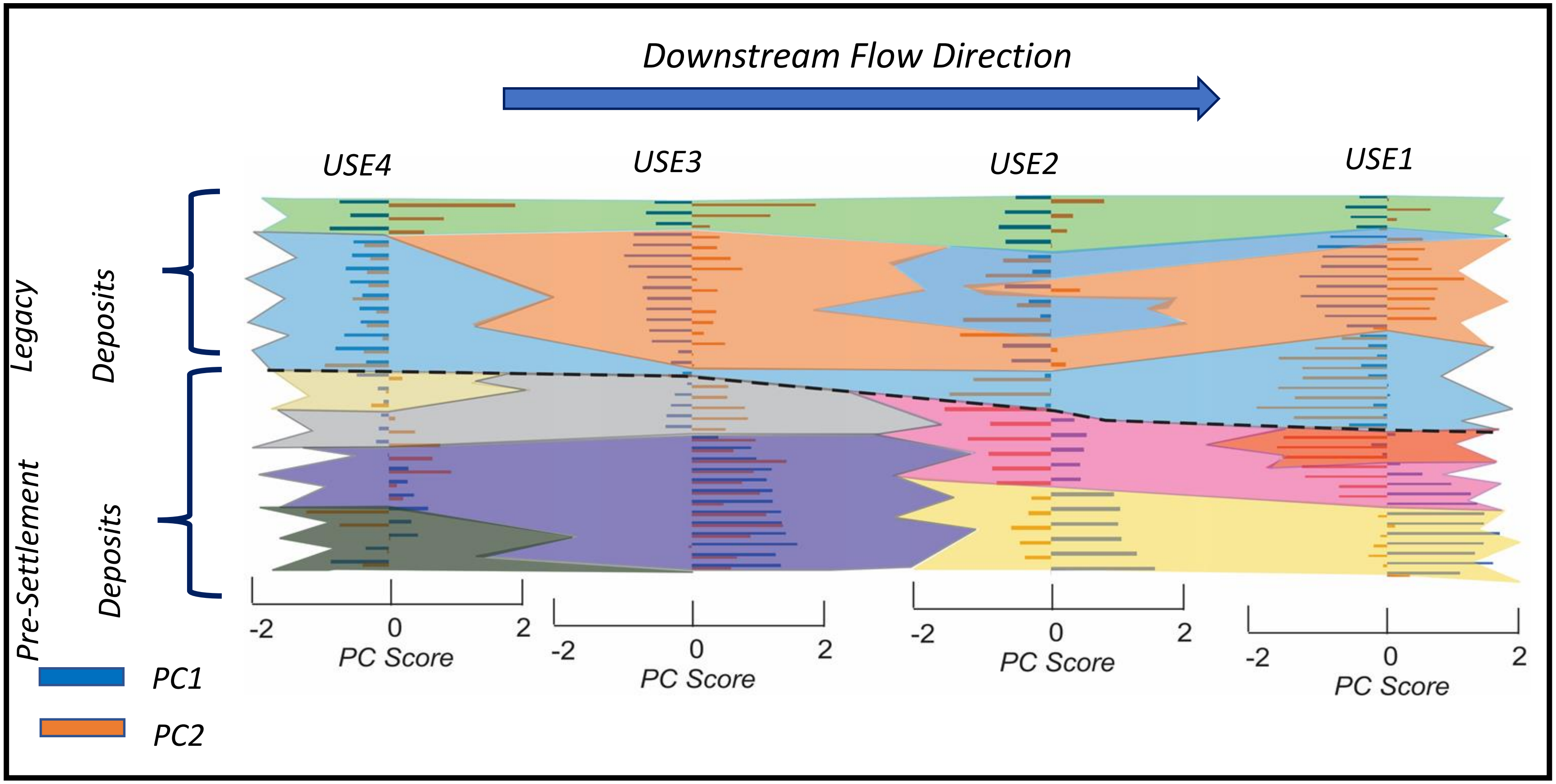

Figure 20. Vertical plots of lithostratigraphic units with correlations of chemostratigraphic units shown by color and patterns. The dotted lines represent less confidence while the solid lines present higher confidence in the correlation.

The legacy sediment in USE 4 (light blue) was found throughout the floodplain but was shown to be thinner at USE 3, possibly because it was partly eroded following deposition. This chemostratigraphic unit in USE 2 was layered with another chemostratigraphic unit (orange). The legacy sediment that was deposited onto this chemostratigraphic unit was found from USE 3 downstream to USE 1. These legacy units are most likely related to the overbank flooding and lateral accretions. The two units are coming from two separate upland sources since they are discovered to have to separate chemical compositions. The pre-settlement deposit correlations could be explained by depositional rates and processes that differ from the legacy sediments. Principle component analysis provided a good correlation method for all four sites. The method showed the ability to identify chemostratigraphic units and correlate them along the valley.

CHAPTER FIVE: CONCLUSIONS AND FUTURE DIRECTIONS

For this research, there were four main objectives related to the identification of chemostratigraphic units. Two methods, hierarchical cluster analysis and principle component analysis, were used to statistically define chemostratigraphic units using multiple elements. Observed variations in elemental concentrations, both at a site and between sites showed that chemostratigraphic units could be defined with the Upper Stick Elliott floodplain. More specifically, PCA demonstrated that legacy and pre-settlement deposits were found to differ in their chemical composition at all four sites. Hierarchical cluster analysis was also able to identify chemostratigraphic units within both legacy and pre-settlement deposits. However, when using cluster analysis, chemical differences at USE 4 between the legacy and pre-settlement deposits could not be defined. For both methods, the normalized data were found to subdivide legacy and pre-settlement sediments into chemostratigraphic units with a higher spatial resolution.

Chemostratigraphic units were exhibited some correlations with lithostratigraphic units, as expected. However, some chemostratigraphic units were comprised of one or more lithostratigraphic units showing that there are differences within the source materials that were deposited within a specific depositional environment. The ability to identify and correlate the chemostratigraphic units throughout the four USE sites using both methods suggests that chemostratigraphy is a viable method for correlating alluvial stratigraphic units. One way to incorporate even more chemical information about each sample is to use the XRF spectrum directly, rather than performing a calibration to convert the spectrum to a concentration profile. The spectrum is information rich, capturing potentially subtle differences in the sample that may be missed when analyzing only the maximum intensity of individual peaks. Providing more information in the chemical fingerprint could help develop better resolution of the chemostratigraphic units. Also, a multi-linear regression could be performed which would elucidate the impact that the elements have on the chemical composition and the chemostratigraphic units.

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APPENDIX A: EXTERNAL STANDARDS

Table 3. Concentrations (ppm) of elements in external standards.

Element	OREAS 930 (ppm)	USGS SGR-1b (ppm)
Ag	9	0.161
Al	63500	34507.1455
As	20	67
Ba	284	290
Ba	284	298
Bi	136	0.689
Ca	4330	59891.08625
Cd	0.75	0.89
Co	62	12
Cr	63	30
Cu	25200	66
Fe	94700	21192.59282
Hf		1.4
K	22300	13780.4531
Mg	15600	26775.01247
Mn	950	267
Mo	2	35
Mo	2	35
Nb	11.6	5.2
Ni	31.1	29
P	560	1431.459791
Pb	141	38
Pb	141	38
S	28800	15300
Sb	1.51	2.38
Se	73	3.5
Si	275700	131815.3978
Sn	31.1	1.9
Sr	34.8	420
Th	13.5	4.8
Ti	3100	1516.337531
U	2.56	5.4
V	79	130
W	14.5	2.6
Y	17.5	13
Zn	492	74
Zr	89	53
Zr	89	53

APPENDIX B: RELATIVE CONCENTRATIONS

The following pages contain tables of the relative concentrations of elements in each sample given in ppm. Data is separated by site and has been grouped by lithostratigraphic classification of legacy and pre-settlement sediment.

Table 4. Percent silt-clay and relative concentrations (ppm) of elements in legacy sediment of USE 1.

Depth (cm)	Silt + Clay (%)	Al	As	Br	Ce	Co	Cr	Cu	Fe	Hf	K	La	Mn	Mo	Nb	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
000-005	32	53676	17	3	148	72	86	13	26535	5	16291	41	271	78	9	27	913	242840	35	5234	77	6	16	52	83
005-010	34	77677	16	2	137	68	84	18	27328	1	17204	39	316	100	8	29	820	209114	36	4972	67	3	16	66	75
010-015	34	79899	16	3	184	87	84	14	27598	4	15272	82	292	97	8	27	717	230823	35	5094	73	7	16	52	77
015-020	42	61795	19	3	158	80	80	12	26316	4	14884	50	248	78	10	27	586	245598	32	5250	69	7	17	46	82
020-025	52	79691	27	4	210	129	93	21	34931	5	14435	56	245	113	13	27	523	232714	38	7290	99	9	18	60	81
025-030	45	85351	29	5	221	159	102	24	37851	6	13348	80	258	75	14	26	475	227316	35	7462	96	10	19	56	82
030-035	43	79514	28	6	220	150	99	23	36111	6	13211	92	288	77	14	26	404	231335	37	7472	92	10	18	51	82
035-040	43	78684	30	7	239	160	103	24	37706	5	14207	84	306	61	15	26	403	234054	38	7609	104	11	18	57	84
040-045	32	89677	25	6	221	173	115	31	41616	1	16565	78	364	78	14	31	340	229326	33	7219	108	5	19	77	83
045-050	46	89380	28	7	247	149	102	27	37305	7	14352	101	336	77	15	27	385	232360	36	7417	89	9	20	56	83
050-055	43	84195	28	7	248	156	112	26	38558	6	14435		326	80	15	27	345	234921	38	7711	94	3	21	63	83
055-060	36	84758	24			164	112	24	38033	7	15150		344	66	13	27	428	225386	33	7006	94	9	18	62	82
060-067	60	84314	26	7	249	153	103	23	35353	11	13302	139	286	43	16	27	397	242958	42	7853	110	9	21	58	84
067-070	31	82299	26	6	189	101	84	12	26149	10	11789	111	220	64	13	27	458	251745	37	7183	65	8	18	34	78
070-075	26	72965	24	5	197	76	79	9	24714	10	11827	110	188	75	13	27	479	264865	41	7427	73	6	17	31	82
075-080	27	64847	22	5	185	61	71	7	22493	8	10951	105	171	85	11	27	530	268411	38	6549	62	6	17	26	81
080-082	5	62536	19	3	21	43	54	4	17541	3	9681	92	144	98	8	26	165	274242	32	3924	37	5	15	17	77
082-085	28	64847	21	5	172	66	67	7	25216	8	10502	74	168	97	11	27	420	254857	35	6442	66	7	16	24	77
085-090	43	72788	22	4	172	55	68	6	21925	9	10724	94	144	97	11	27	361	252611	36	6194	54	5	17	25	76
090-097	7	68788	19			32	50	4	14278	7	9491		144	108	8	26	299	274557	28	4288	37	4	14	11	73
097-100	41	71928	27	9	176	50	69	4	18662	11	10363	127	144	83	11	27	432	247174	41	6584	55	7	17	21	74
100-105	47	72758	23			42	66	4	20585	7	11578		144	98	8	27	500	261673	44	6112	37	5	15	15	75
105-110	55	69588	28	11	170	60	72	4	20527	9	10194	94	144	92	12	27	485	253242	44	6787	64	7	17	21	75
110-113	59	67158	27	16	180	92	64	4	22238	5	9245	41	144	76	10	26	425	244653	34	5300	59	5	17	15	74

Table 5. Percent silt-clay and relative concentrations (ppm) of elements in pre-settlement sediment of USE 1.

Depth (cm)	Silt + Clay (%)	Al	As	Br	Ce	Co	Cr	Cu	Fe	Hf	K	La	Mn	Mo	Nb	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
113-115	61	67365	24	15	72	33	65	4	14410	9	9287	148	144	89	9	27	464	244219	36	4671	37	5	17	13	71
115-120	55	74921	28	12	122	63	80	4	21641	8	10355	129	144	80	10	26	461	226765	41	5000	60	6	17	16	73
120-125	55	75602	27	9	120	52	77	4	18284	6	9910	160	144	75	9	26	513	241579	35	4893	52	5	16	14	73
125-130	56	75928	27	7	101	47	84	4	17017	8	9836	142	144	82	10	27	393	239373	36	5095	69	6	19	16	72
130-135	48	73736	25	6	98	25	76	4	12756	10	10025	168	144	114	10	28	376	244416	50	4822	37	5	15	16	70
135-140	33	71039	23	5	104	12	61	4	9016	10	9322	169	144	111	8	28	311	245401	41	4140	37	4	15	14	71
140-145	22	71691	21			4	59	4	7413	9	10237		144	110	7	27	304	252966	42	3993	37	4	15	10	70
145-150	25	58565	23			12	61	4	7771	12	10261		144	93	8	28	300	249696	43	4509	52	4	15	14	74
150-155	38	74417	23			6	62	4	6832	11	11345		144	113	8	28	376	239609	42	4617	37	4	16	13	69
155-160	58	66151	24			7	58	4	6614	12	11080		144	109	8	28	406	247332	43	4533	37	4	15	14	69
160-165	42	70032	21			2	51	4	5817	11	10987		144	102	8	27	364	260019	36	3827	37	4	16	8	70
165-170	74	70091	22	6	66	5	58	4	7006	9	10766	114	144	97	8	28	293	242958	35	4001	37	4	16	13	68
170-175	57	74743	23	7	49	5	59	4	6810	10	11082	112	144	93	7	27	382	261634	50	3978	37	3	15	11	70
175-180	35	64225	21	6	90	3	54	4	6245	10	10061	113	144	104	7	27	331	246504	36	3838	37	4	15	11	68
187+	14	92551	18	2	79	15	88	5	10572	11	12024	175	144	100	9	29	119	234409	32	5309	57	4	16	27	71

Table 6. Percent silt-clay and relative concentrations (ppm) of elements in legacy sediment of USE 2.

Depth (cm)	Silt + Clay (%)	Al	As	Br	Ce	Co	Cr	Cu	Fe	Hf	K	La	Mn	Mo	Nb	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
000-005	62	68906	22	3	182	88	78	20	26098	7	13964	96	273	81	10	27	1066	229089	36	5374	61	7	16	55	78
005-010	59	81025	20	3	197	129	100	20	33606	5	14854	74	312	82	11	27	525	230981	39	6595	83	8	17	56	80
010-015	48	77943	26	4	238	138	98	20	34305	7	14603	79	293	70	13	26	406	229011	35	6732	69	9	18	51	82
015-022	39	78240	26	4	206	119	92	18	34683	8	13492	87	279	79	13	27	396	235709	37	6792	97	8	18	48	82
022-025	34	76847	24	3	178	70	67	8	24488	7	12009	95	196	91	10	27	227	245953	31	5345	72	6	17	29	78
025-030	9	58891	21	3	145	71	68	5	22719	6	11510	34	187	70	10	26	234	261910	33	4867	67	6	16	24	82
030-035	11	79691	27			129	93	21	34931	5	14435		245	113	13	27	523	232714	38	7290	99	9	18	60	81
035-043	31	72314	22	3	148	77	82	10	26280	6	12861	65	219	96	10	26	236	240161	30	5085	78	7	16	35	77
043-045	23	69558	21	2	132	43	54	4	20665	5	12648	76	187	100	8	26	214	250247	30	4282	51	5	14	23	75
045-055	12	56550	18	2	87	29	58	4	17985	3	12192	22	174	99	7	26	119	265417	30	3975	52	4	14	19	77
055-060	38	84136	20	4	228	129	98	19	35769	4	15386	91	294	86	11	27	270	219909	31	6422	88	8	18	54	81
060-067	23	73321	18	4	161	108	99	18	32222	3	15013	99	263	84	10	27	337	233148	29	5970	75	8	17	56	79
067-070	22	67632	18	3	135	49	66	4	21240	5	11994	79	181	107	7	26	168	253084	24	4351	60	6	15	27	75
070-075	4	65676	17	2	23	24	55	4	16798	3	10005	107	144	107	6	26	184	255172	28	3282	37	4	14	15	72
075-083	13	77025	17	2	163	27	57	4	19835	6	11155	90	144	112	8	26	272	250287	26	4893	37	5	15	18	74

Table 7. Percent silt-clay and relative concentrations (ppm) of elements in pre-settlement sediment of USE 2.

Depth (cm)	Silt + Clay (%)	Al	As	Br	Ce	Co	Cr	Cu	Fe	Hf	K	La	Mn	Mo	Nb	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
083-090	51	71869	23	4	102	25	59	4	12181	9	9649	134	144	108	9	27	342	249381	34	5027	37	5	15	17	72
090-095	15	71514	22	6	1021	14	91	4	12035	10	12161	636	144	116	13	27	488	249972	35	4466	37	4	30	11	72
095-100	44	62151	22	4	80	18	55	4	10302	9	10005	135	144	100	9	27	437	274360	34	4892	37	5	16	11	74
100-105	43	68995	25	5	146	25	64	4	12269	11	11275	116	144	110	10	28	493	252690	40	6336	37	6	16	18	71
105-110	23	66832	24	4	73	22	62	4	10448	10	11079	121	144	98	9	28	405	264313	37	5524	37	4	15	13	75
110-115	58	73795	23	4	108	11	58	4	8097	12	11284	151	144	117	10	28	374	257064	38	5270	37	5	15	15	70
115-120	34	58980	23	4	60	8	59	4	7275	10	9968	126	144	107	9	28	313	257615	35	4589	37	4	15	11	73
120-125	13	52817	19	3	101	2	43	4	5789	7	9529	120	144	111	7	27	251	279798	35	3273	37	3	14	3	73
125-130	17	50423	20	4	28	2	43	4	5859	8	8909	53	144	126	6	27	119	246189	31	2898	37	3	14	5	68
130-135	6	63751	20	5	110	2	51	4	5920	7	10965	140	144	127	6	27	356	266559	35	3549	37	4	14	5	69
135-140	25	41898	18	4	980	2	58	4	4734	11	8538	631	144	100	9	26	324	304344	32	3245	37	3	25	3	77

Table 8. Percent silt-clay and relative concentrations (ppm) of elements in legacy sediment of USE 3.

Depth (cm)	Silt + Clay (%)	Al	As	Br	Ce	Co	Cr	Cu	Fe	Hf	K	La	Mn	Mo	Nb	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
000-005	25	57173	19	6	105	88	51	30	25457	0	10633	36	462	127	8	27	1665	140636	41	4316	89	4	15	81	64
005-010	60	68373	20	0	0	102	61	29	28821	0	11842	0	395	114	9	28	1666	167310	38	4662	85	3	16	67	72
010-015	68	68788	23	4	163	97	64	20	30518	1	12473	69	317	111	8	26	1258	188980	42	5133	86	6	15	50	73
015-020	64	96106	28	4	164	161	87	33	43641	0	13561		144	76	10	25	643	187089	37	6112	102	8	16	51	81
020-025	67	98506	27	4	109	161	83	33	43349	0	12777	70	144	90	10	25	406	184607	34	5960	99	8	15	46	78
025-030	27	101232	32	6	178	214	87	40	49809	0	12306		144	79	11	25	313	179997	40	6072	143	10	16	46	81
030-035	86	75691	33	7	223	221	128	39	45949	0	15074		144	56	14	25	293	205765	43	7300	129	10	17	49	87
035-040	81	96462	25	4	90	136	83	22	34851	0	14055	99	144	82	9	25	216	201549	31	5833	97	8	15	34	79
040-044	39	93736	30	6	129	155	69	25	34785	0	15911	134	144	70	11	25	267	225898	39	6204	105	8	18	39	82
044-050	35	98862	29	5	64	132	74	20	34196	0	12777	45	144	84	10	25	241	191974	33	5206	94	7	15	32	79
050-055	52	81440	28	6	244	149	74	24	34064	5	12952	78	144	85	13	25	300	207853	37	6600	104	9	19	40	78
055-060	64	86477	29	7	242	146	81	25	36053	4	12838	37	144	86	14	26	296	215851	38	7041	120	8	19	39	80
060-065	78	88284	34	8	130	134	76	21	32411	5	13796	136	144	79	14	26	352	235000	39	6803	92	8	18	36	81
065-070	39	86003	35	10	165	129	75	24	32164	1	15409		144	96	13	26	334	215221	41	6803	110	8	18	44	77
070-077	75	73825	26	7	78	65	60	11	20468	3	14565	97	144	105	10	26	267	216087	34	5273	77	6	17	29	72
077-080	100	90269	26	6	114	76	69	13	23410	3	16770	136	144	100	11	26	325	222943	40	6112	76	6	17	34	74
080-085	55	88403	23	5	81	55	62	9	20439	4	16032	88	144	110	8	26	352	230547	33	5864	64	6	15	28	73
085-090	24	82714	26	5	108	64	62	11	19121	5	16344	144	144	98	11	26	303	245047	41	5651	77	6	17	51	74

Table 9. Percent silt-clay and relative concentrations (ppm) of pre-settlement sediment of USE 3.

Depth (cm)	Silt + Clay (%)	Al	As	Br	Ce	Co	Cr	Cu	Fe	Hf	K	La	Mn	Mo	Nb	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
090-095	77	79958	35	15	103	78	73	16	21961	6	15591	161	144	101	12	27	429	213684	40	6595	75	7	19	39	72
095-100	45	81440	36	22	129	90	73	19	22879	5	14816	178	144	98	12	27	343	190871	40	6569	98	7	21	39	74
100-105	86	84877	22	30	201	78	70	18	21146	0	15203	139	144	107	12	29	569	210296	45	6787	90	4	20	40	71
105-110	78	71780	22	41	133	84	69	16	22092	0	14565	143	144	113	12	29	600	206553	36	6432	84	4	20	37	70
110-115	83	76551	33	19	127	40	69	9	12567	8	14595	169	144	114	12	28	374	209508	38	6133	86	6	20	32	67
115-120	79	72580	27	13	126	20	64	4	9179	8	14063	181	144	118	10	28	341	218136	38	5666	76	5	17	27	66
120-125	41	78002	29	13	108	22	71	6	8509	9	14816	169	144	115	11	28	262	227829	41	5585	85	5	19	28	68
125-130	62	82003	26	11	113	17	68	3	8013	8	14633	182	144	118	12	28	208	229444	36	6163	88	5	17	26	68
130-135	52	76521	26	11	125	16	73	4	8011	8	14747	163	144	112	9	28	258	227356	32	5549	69	5	17	24	68
135-140	26	69351	26	0	0	12	77	4	7755	8	14078	0	144	106	10	28	144	220067	36	5400	65	4	17	30	72
140-145	50	73588	25	11	116	13	68	2	7319	8	14390	144	144	117	10	28	202	233896	37	5402	71	4	16	23	68
145-150	44	82743	26	10	111	15	72	3	7165	8	14679	164	144	118	9	28	148	230468	37	5910	73	5	16	26	68
150-155	64	77825	26	10	113	16	70	4	7203	9	15120	170	144	111	10	28	124	234960	40	5788	78	5	17	26	69
155-160	55	81084	25	9	82	6	70	4	6881	8	15257	153	144	120	9	28	206	236063	38	5630	63	5	16	24	70
160-165	25	79128	23	8	90	-12	69	3	6407	5	13059	138	144	125	8	28	82	239452	39	4643	57	3	15	17	71
165-170	11	64728	24	8	87	10	73	3	7412	7	15690	189	144	104	10	28	137	249538	37	5747	64	5	16	23	75
170-177	40	83751	25	9	72	9	67	2	6931	7	15143	153	144	123	10	28	105	243865	39	5404	53	5	15	26	71

Table 10. Percent silt-clay and relative concentrations (ppm) of elements in legacy sediment of USE 4.

Depth (cm)	Silt + Clay (%)	Al	As	Br	Ce	Co	Cr	Cu	Fe	Hf	K	La	Mn	Mo	Nb	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
000-005	61	70951	19	5	160	75	55	26	23957	1	12397	52	317	113	9	27	1729	196033	39	5051	81	4	15	58	69
005-010	37	74091	24	4	159	86	63	20	26149	4	12777	53	259	94	9	26	1511	220934	33	5444	92	7	16	46	73
010-015	85	81588	26	5	192	128	80	25	34698	3	13834	37	154	70	13	25	720	227868	35	6899	111	8	18	43	80
015-020	34	84195	23	3	221	80	65	14	26615	4	12374	98	144	85	12	26	730	235866	27	6498	81	7	18	27	76
020-025	61	86210	24	4	207	82	67	15	27489	5	13196	89	159	85	12	26	805	231375	30	6808	87	7	18	26	75
025-030	70	83721	23	4	225	80	61	15	25755	5	12093	110	144	82	12	26	716	239885	32	6356	53	7	16	26	76
030-035	46	85054	25	4	230	91	70	14	26491	5	13036	114	158	76	13	26	722	238309	31	6955	71	8	18	26	77
035-037	17	84106	22	3	218	58	59	11	22449	4	13416	119	144	87	10	26	741	240043	33	6128	64	6	16	23	74
037-040	35	76699	25	4	229	89	67	11	22580	8	12998	88	153	65	13	26	622	254463	32	6386	79	7	18	27	77
040-045	73	78121	24	4	231	80	63	10	21408	6	12321	118	144	62	11	25	593	253872	30	6386	71	6	17	25	75
045-050	16	77973	24	3	216	116	74	14	28646	1	12998	94	187	68	10	25	680	254897	28	6082	93	8	17	34	76
050-055	9	74536	28	3	173	130	93	13	30350	2	13416	79	148	63	10	25	814	255606	28	5559	80	7	16	31	77
055-060	29	79040	19	3	140	68	53	6	19747	3	11485	80	144	79	10	25	632	244219	23	5666	61	5	17	19	73

Table 11. Percent silt-clay and relative concentrations (ppm) of elements in pre-settlement sediment of USE 4.

Depth (cm)	Silt + Clay (%)	Al	As	Br	Ce	Co	Cr	Cu	Fe	Hf	K	La	Mn	Mo	Nb	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
065-070	63	71425	26	6	224	100	63	11	22624	5	14785	117	144	64	13	26	367	240476	44	6929	78	7	18	40	75
070-075	90	72047	25	6	78	80	63	7	19063	5	15135	136	144	75	12	26	206	248829	44	6310	78	7	17	36	74
075-080	20	81943	26	7	37	60	67	7	20599	6	14922	126	144	102	11	27	172	237561	43	7127	75	6	17	41	77
080-085	10	46713	31	9	238	59	63	12	22325	2	14420	108	144	21	11	26	395	231926	44	6960	59	9	17	43	75
085-090	64	62180	32	10	205	69	72	14	23622	3	13675	62	144	13	13	26	304	222470	43	7158	85	10	17	43	75
090-095	68	51247	35	13	265	77	74	17	23986	1	12602	129	144	10	14	27	293	221919	43	7427	98	10	18	45	75
095-100	40	67010	34	12	97	71	98	13	21714	6	12466	214	144	68	14	29	119	219830	42	7924	113	7	18	43	81
100-102	45	66002	32	10	268	50	81	13	18881	5	12960	145	144	13	13	29	226	216284	43	7422	89	10	17	42	73
102-105	74	79840	30	9	80	43	81	7	15502	5	11541	180	144	93	12	29	119	215418	43	6402	67	6	16	33	76
105-110	22	76077	28	8	67	44	88	7	16762	8	13987	153	144	85	10	29	119	225346	39	6173	86	6	18	37	78
110-115	24	43069	23	5	143	12	62	4	13791	2	16633	82	144	16	8	27	119	211399	50	4308	37	6	14	22	75
115-120	10	72136	21	5	81	38	79	4	17606	3	16527	117	144	94	9	27	119	233384	39	5394	78	6	17	33	77
120-125	8	68847	19	5	546	37	75	4	17839	2	18078	343	144	84	10	26	119	231414	42	6955	74	5	20	60	79
125-130	16	60432	22	5	358	86	101	12	30045	2	21044	178	144	63	15	26	119	218570	43	7437	83	8	34	63	86
137-169	17	42565	34	5	308	97	83	22	43160	1	16367		144	-6	9	25	695	194063	34	5223	68	11	19	51	79

APPENDIX C: METHOD VALIDATION

The following tables give the percent error in the measured concentration for each element relative to the known concentration (in ppm) for two standards, USGS SGR-1b and OREAS 930. From the multiple measurements of the samples, the standard deviation and relative standard deviation of the measured concentration was calculated. Also, the limit of detection and limit of quantification were calculated. These values are also provided.

Table 12. Percent error of element concentrations measured for external standard USGS SGR-1b.

Measurement Date	Al	As	Ba	Ca	Co	Cr	Cu	Fe	Hf	K	Mg	Mn	Mo	Nb	Ni	P	Pb	S	Se	Si	Sr	Ti	V	W	Y	Zn	Zr
2/26/19	2	1	0	2928	1	9	4	2	21	0	6	1	62	4	1	4	1	1	19	1	6	1	5	10	0	1	23
3/6/19	2	1	0	2971	7	11	2	1	36	1	1	0	20	12	1	6	6	1	0	1	7	3	5	17	1	1	23
3/7/19	4	1	0	2980	4	7	4	1	29	2	3	0	18	16	1	5	3	0	19	1	7	4	6	0	1	0	24
3/20/19	1	2	0	2926	9	6	3	1	29	1	7	0	10	13	1	1	17	0	0	1	6	1	2	0	0	0	23
3/27/19	4	1	1	2895	4	7	3	1	86	0	5	0	24	11	1	8	5	6	0	0	6	4	6	31	3	0	22
3/27/19	1	1	0	2928	6	11	4	2	157	1	8	1	34	12	1	3	9	4	0	0	6	4	3	29	2	1	23
4/8/19	0	0	0	2906	5	12	2	1	129	0	6	0	37	17	1	5	1	3	19	0	6	4	0	36	1	1	22
4/24/19	6	3	0	2935	8	3	5	1	7	1	0	0	37	24	1	3	8	3	0	0	6	2	13	26	1	1	23
4/29/19	0	0	1	2946	5	6	4	1	36	1	1	0	26	15	0	3	1	2	19	0	5	1	1	48	2	1	23
6/3/19	12	1	0	2875	3	4	2	1	43	1	4	0	91	13	1	3	12	4	19	1	4	2	8	31	1	1	22
6/5/19	9	0	0	2898	10	12	3	1	79	1	2	0	104	17	1	1	2	2	19	0	4	1	3	12	2	0	22
6/10/19	6	0	0	2858	3	5	2	1	86	1	8	0	109	11	0	3	2	2	0	0	4	2	10	43	2	1	21
9/6/19	13	13	0	2911	1	8	6	1	7	1	7	2	16	19	0	5	96	0	57	0	4	2	1	0	3	4	23
9/18/19	7	3	1	2945	10	5	0	0	14	1	0	3	2	9	0	9	17	1	38	0	3	1	3	41	1	5	23
9/19/19	6	0	0	2949	9	0	1	1	121	1	3	1	15	19	0	12	1	1	19	0	5	2	3	22	2	3	23
10/24/19	1	1	0	2922	24	12	1	1	7	0	8	3	4	4	0	11	13	0	0	1	5	1	2	26	2	2	23
10/29/19	4	1	1	2900	17	8	0	1	57	0	3	2	20	3	1	14	2	0	0	0	6	1	2	14	0	0	22
11/6/19	7	2	1	2888	22	2	1	1	71	0	5	0	20	8	0	14	8	1	0	1	6	0	3	31	1	1	23
11/18/19	16	1	0	3023	20	3	0	1	79	1	5	0	21	11	1	6	3	1	0	0	6	1	3	34	1	1	23
Known Conc (ppm)	34507	67	290	59891	12	30	66	21193	1	13780	26775	267	35	5	29	1431	38	15300	4	131815	420	1516	130	3	13	74	53
Average Measured Conc (ppm)	35301	67	290	1811978	13	28	67	21414	2	13833	27291	265	31	6	29	1347	41	15053	3	132061	442	1536	135	3	13	73	65
St. Dev. Of Measured Conc. (ppm)	2337	2	1	23391	1	1	2	92	1	104	1249	3	17	0	0	62	9	277	1	870	5	29	5	0	0	1	0
Relative Standard Deviation	7%	3%	0%	1%	9%	5%	2%	0%	30%	1%	5%	1%	53%	5%	0%	5%	21%	2%	20%	1%	1%	2%	4%	12%	1%	2%	0%
Limit of Detection (ppm)	6852	7	3	2319	3	4	5	273	1	309	3676	9	55	1	0	199	24	846	2	2604	14	85	14	1	1	4	1
Limit of Quantification (ppm)	22840	23	11	7731	10	14	16	911	4	1031	12255	30	185	3	1	664	82	2818	7	8680	46	282	48	3	2	12	3

Table 13. Percent error of element concentrations measured in external standard OREAS 930.

Measurement Date	Al	As	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Nb	Ni	P	Pb	S	Se	Si	Sr	Ti	V	W	Y	Zn	Zr
2/26/19	10	4	75	6	3	4	3	2	1	3	22	6	2	12	6	1	5	11	7	2	7	3	1	3	13
3/6/19	6	7	52	13	12	0	0	0	17	0	1120	2	0	21	4	2	2	10	10	1	15	11	6	1	19
3/7/19	4	5	20	12	10	0	0	1	13	0	624	1	0	5	3	2	1	10	10	1	24	1	0	1	19
3/20/19	0	5	53	11	4	1	0	1	11	0	470	4	1	16	1	3	3	9	13	2	7	3	3	1	19
3/27/19	3	2	28	6	10	0	0	0	7	0	1351	9	0	8	2	3	3	10	12	1	1	10	4	1	17
3/27/19	2	5	28	1	7	1	1	0	3	1	1325	3	0	9	1	3	1	10	13	3	3	13	4	2	18
4/8/19	4	7	0	5	4	1	1	0	7	0	1624	6	1	12	5	3	1	10	10	0	9	2	2	0	16
4/24/19	5	1	2	5	6	3	2	1	2	1	2069	0	1	5	5	1	2	10	8	0	6	3	1	2	15
4/29/19	7	6	36	1	10	3	2	0	2	3	1470	1	2	6	6	1	5	10	8	0	0	8	1	2	15
6/3/19	7	3	42	5	6	0	0	2	13	1	2279	13	1	2	3	2	2	11	7	2	5	11	1	1	17
6/5/19	4	0	35	4	5	2	2	2	6	1	2365	14	1	16	3	2	2	10	15	0	7	1	4	3	14
6/10/19	3	0	72	2	9	2	1	1	14	1	1766	8	0	0	2	4	3	9	3	2	2	1	3	0	15
9/6/19	6	0	98	5	2	5	3	2	5	3	1128	5	2	12	5	2	6	10	7	2	10	12	2	4	13
9/18/19	1	1	34	17	3	0	0	0	8	1	487	8	1	3	2	3	3	10	2	1	16	12	3	1	17
9/19/19	5	2	97	17	7	0	0	0	1	1	710	16	1	4	1	3	2	10	6	1	20	14	0	2	18
10/24/19	6	5	68	13	8	3	2	1	0	3	487	13	3	8	7	2	3	10	0	1	5	11	2	2	15
10/29/19	6	1	83	9	4	4	3	1	5	3	829	9	2	8	4	2	5	10	2	1	15	11	0	3	13
11/6/19	1	2	173	21	1	3	2	1	3	1	1151	14	1	2	1	3	5	10	5	3	3	16	2	4	20
11/18/19	4	3	71	1	2	5	4	2	2	4	1111	12	2	0	7	2	6	9	2	0	11	8	1	4	12
Known Conc. (ppm)	63500	20	4330	62	63	25200	94700	22300	15600	950	2	10	31	560	141	28800	73	275700	35	3100	79	27	18	492	89
Average Measured Conc. (ppm)	66272	21	4676	66	66	24838	93608	22176	14940	940	26	9	31	556	136	29424	72	248404	37	3119	80	29	18	490	103
St. Dev, of Measured Conc. (ppm)	1580	1	3027	5	3	568	1473	243	1088	14	13	1	0	56	4	337	2	1498	2	45	9	1	0	11	2
Relative Standard Deviation	2%	3%	65%	7%	4%	2%	2%	1%	7%	2%	51%	9%	1%	10%	3%	1%	3%	1%	4%	1%	11%	5%	2%	2%	2%
Limit of Detection (ppm)	4541	2	8410	13	8	1729	4469	732	3410	44	3	3	1	168	11	989	8	4989	5	135	26	4	1	35	6
Limit of Quantification (ppm)	15135	6	28033	45	26	5762	14898	2442	11366	146	10	9	3	559	37	3297	25	16630	15	451	86	13	4	115	19

APPENDIX D: NORMALIZED CONCENTRATION RATIOS

Relative element concentrations from Appendix B were divided by the relative element concentrations of Fe, Al or Ti (conservative metals) if they were highly correlated (correlation coefficient of 0.6 or higher). If correlation was high for all three metals, the conservative metal with the highest correlation was used. The resulting normalized concentration ratios are provided below for elements that were included in the classification analyses. Data is organized by site and lithostratigraphic classification of legacy and pre-settlement sediment samples.

Table 14. Normalized concentration ratios for elements in legacy sediment of USE 1.

Depth (cm)	Al	As	Ce	Fe	K	La	Mn	Mo	Ni	P	Si	Sr	Ti	Y
000-005	53676	17	148	26535	16291	41	271	78	27	913	242840	35	5234	16
005-010	77677	16	137	27328	17204	39	316	100	29	820	209114	36	4972	16
010-015	79899	16	184	27598	15272	82	292	97	27	717	230823	35	5094	16
015-020	61795	19	158	26316	14884	50	248	78	27	586	245598	32	5250	17
020-025	79691	27	210	34931	14435	56	245	113	27	523	232714	38	7290	18
025-030	85351	29	221	37851	13348	80	258	75	26	475	227316	35	7462	19
030-035	79514	28	220	36111	13211	92	288	77	26	404	231335	37	7472	18
035-040	78684	30	239	37706	14207	84	306	61	26	403	234054	38	7609	18
040-045	89677	25	221	41616	16565	78	364	78	31	340	229326	33	7219	19
045-050	89380	28	247	37305	14352	101	336	77	27	385	232360	36	7417	20
050-055	84195	28	248	38558	14435		326	80	27	345	234921	38	7711	21
055-060	84758	24	0	38033	15150	0	344	66	27	428	225386	33	7006	18
060-067	84314	26	249	35353	13302	139	286	43	27	397	242958	42	7853	21
067-070	82299	26	189	26149	11789	111	220	64	27	458	251745	37	7183	18
070-075	72965	24	197	24714	11827	110	188	75	27	479	264865	41	7427	17
075-080	64847	22	185	22493	10951	105	171	85	27	530	268411	38	6549	17
080-082	62536	19	21	17541	9681	92	144	98	26	165	274242	32	3924	15
082-085	64847	21	172	25216	10502	74	168	97	27	420	254857	35	6442	16
085-090	72788	22	172	21925	10724	94	144	97	27	361	252611	36	6194	17
090-097	68788	19	0	14278	9491	0	144	108	26	299	274557	28	4288	14
097-100	71928	27	176	18662	10363	127	144	83	27	432	247174	41	6584	17
100-105	72758	23	0	20585	11578	0	144	98	27	500	261673	44	6112	15
105-110	69588	28	170	20527	10194	94	144	92	27	485	253242	44	6787	17
110-113	67158	27	180	22238	9245	41	144	76	26	425	244653	34	5300	17

Table 15. Normalized concentration ratios for elements in pre-settlement sediment of USE 1.

Depth (cm)	Al	As	Ce	Fe	K	La	Mn	Mo	Ni	P	Si	Sr	Ti	Y
113-115	67365	24	72	14410	9287	148	144	89	27	464	244219	36	4671	17
115-120	74921	28	122	21641	10355	129	144	80	26	461	226765	41	5000	17
120-125	75602	27	120	18284	9910	160	144	75	26	513	241579	35	4893	16
125-130	75928	27	101	17017	9836	142	144	82	27	393	239373	36	5095	19
130-135	73736	25	98	12756	10025	168	144	114	28	376	244416	50	4822	15
135-140	71039	23	104	9016	9322	169	144	111	28	311	245401	41	4140	15
140-145	71691	21	0	7413	10237	0	144	110	27	304	252966	42	3993	15
145-150	58565	23	0	7771	10261	0	144	93	28	300	249696	43	4509	15
150-155	74417	23	0	6832	11345	0	144	113	28	376	239609	42	4617	16
155-160	66151	24	0	6614	11080	0	144	109	28	406	247332	43	4533	15
160-165	70032	21	0	5817	10987	0	144	102	27	364	260019	36	3827	16
165-170	70091	22	66	7006	10766	114	144	97	28	293	242958	35	4001	16
170-175	74743	23	49	6810	11082	112	144	93	27	382	261634	50	3978	15
175-180	64225	21	90	6245	10061	113	144	104	27	331	246504	36	3838	15
187+	92551	18	79	10572	12024	175	144	100	29	119	234409	32	5309	16

Table 16. Normalized concentration ratios for elements in legacy sediment of USE 2.

Depth (cm)	Al	As	Ce	Fe	K	La	Mn	Mo	Ni	P	Si	Sr	Ti	Y
000-005	68906	22	182	26098	13964	96	273	81	27	1066	229089	36	5374	16
005-010	81025	20	197	33606	14854	74	312	82	27	525	230981	39	6595	17
010-015	77943	26	238	34305	14603	79	293	70	26	406	229011	35	6732	18
015-022	78240	26	206	34683	13492	87	279	79	27	396	235709	37	6792	18
022-025	76847	24	178	24488	12009	95	196	91	27	227	245953	31	5345	17
025-030	58891	21	145	22719	11510	34	187	70	26	234	261910	33	4867	16
030-035	79691	27	0	34931	14435	0	245	113	27	523	232714	38	7290	18
035-043	72314	22	148	26280	12861	65	219	96	26	236	240161	30	5085	16
043-045	69558	21	132	20665	12648	76	187	100	26	214	250247	30	4282	14
045-055	56550	18	87	17985	12192	22	174	99	26	119	265417	30	3975	14
055-060	84136	20	228	35769	15386	91	294	86	27	270	219909	31	6422	18
060-067	73321	18	161	32222	15013	99	263	84	27	337	233148	29	5970	17
067-070	67632	18	135	21240	11994	79	181	107	26	168	253084	24	4351	15
070-075	65676	17	23	16798	10005	107	144	107	26	184	255172	28	3282	14
075-083	77025	17	163	19835	11155	90	144	112	26	272	250287	26	4893	15

Table 17. Normalized concentration ratios for elements in pre-settlement sediment of USE 2.

Depth (cm)	Al	As	Ce	Fe	K	La	Mn	Mo	Ni	P	Si	Sr	Ti	Y
083-090	71869	23	102	12181	9649	134	144	108	27	342	249381	34	5027	15
090-095	71514	22	1021	12035	12161	636	144	116	27	488	249972	35	4466	30
095-100	62151	22	80	10302	10005	135	144	100	27	437	274360	34	4892	16
100-105	68995	25	146	12269	11275	116	144	110	28	493	252690	40	6336	16
105-110	66832	24	73	10448	11079	121	144	98	28	405	264313	37	5524	15
110-115	73795	23	108	8097	11284	151	144	117	28	374	257064	38	5270	15
115-120	58980	23	60	7275	9968	126	144	107	28	313	257615	35	4589	15
120-125	52817	19	101	5789	9529	120	144	111	27	251	279798	35	3273	14
125-130	50423	20	28	5859	8909	53	144	126	27	119	246189	31	2898	14
130-135	63751	20	110	5920	10965	140	144	127	27	356	266559	35	3549	14
135-140	41898	18	980	4734	8538	631	144	100	26	324	304344	32	3245	25

Table 18. Normalized concentration ratios for elements in legacy sediment of USE 3.

Depth (cm)	Al	As	Ce	Fe	K	La	Mn	Mo	Ni	P	Si	Sr	Ti	Y
000-005	57173	19	105	25457	10633	36	462	127	27	1665	140636	41	4316	15
005-010	68373	20	0	28821	11842	0	395	114	28	1666	167310	38	4662	16
010-015	68788	23	163	30518	12473	69	317	111	26	1258	188980	42	5133	15
015-020	96106	28	164	43641	13561		144	76	25	643	187089	37	6112	16
020-025	98506	27	109	43349	12777	70	144	90	25	406	184607	34	5960	15
025-030	101232	32	178	49809	12306		144	79	25	313	179997	40	6072	16
030-035	75691	33	223	45949	15074		144	56	25	293	205765	43	7300	17
035-040	96462	25	90	34851	14055	99	144	82	25	216	201549	31	5833	15
040-044	93736	30	129	34785	15911	134	144	70	25	267	225898	39	6204	18
044-050	98862	29	64	34196	12777	45	144	84	25	241	191974	33	5206	15
050-055	81440	28	244	34064	12952	78	144	85	25	300	207853	37	6600	19
055-060	86477	29	242	36053	12838	37	144	86	26	296	215851	38	7041	19
060-065	88284	34	130	32411	13796	136	144	79	26	352	235000	39	6803	18
065-070	86003	35	165	32164	15409		144	96	26	334	215221	41	6803	18
070-077	73825	26	78	20468	14565	97	144	105	26	267	216087	34	5273	17
077-080	90269	26	114	23410	16770	136	144	100	26	325	222943	40	6112	17
080-085	88403	23	81	20439	16032	88	144	110	26	352	230547	33	5864	15
085-090	82714	26	108	19121	16344	144	144	98	26	303	245047	41	5651	17

Table 19. Normalized concentration ratios for elements in pre-settlement sediment of USE 3.

Depth (cm)	Al	As	Ce	Fe	K	La	Mn	Mo	Ni	P	Si	Sr	Ti	Y
090-095	79958	35	103	21961	15591	161	144	101	27	429	213684	40	6595	19
095-100	81440	36	129	22879	14816	178	144	98	27	343	190871	40	6569	21
100-105	84877	22	201	21146	15203	139	144	107	29	569	210296	45	6787	20
105-110	71780	22	133	22092	14565	143	144	113	29	600	206553	36	6432	20
110-115	76551	33	127	12567	14595	169	144	114	28	374	209508	38	6133	20
115-120	72580	27	126	9179	14063	181	144	118	28	341	218136	38	5666	17
120-125	78002	29	108	8509	14816	169	144	115	28	262	227829	41	5585	19
125-130	82003	26	113	8013	14633	182	144	118	28	208	229444	36	6163	17
130-135	76521	26	125	8011	14747	163	144	112	28	258	227356	32	5549	17
135-140	69351	26	0	7755	14078	0	144	106	28	144	220067	36	5400	17
140-145	73588	25	116	7319	14390	144	144	117	28	202	233896	37	5402	16
145-150	82743	26	111	7165	14679	164	144	118	28	148	230468	37	5910	16
150-155	77825	26	113	7203	15120	170	144	111	28	124	234960	40	5788	17
155-160	81084	25	82	6881	15257	153	144	120	28	206	236063	38	5630	16
160-165	79128	23	90	6407	13059	138	144	125	28	82	239452	39	4643	15
165-170	64728	24	87	7412	15690	189	144	104	28	137	249538	37	5747	16
170-177	83751	25	72	6931	15143	153	144	123	28	105	243865	39	5404	15

Table 20. Normalized concentration ratios for elements in legacy sediment of USE 4.

Depth (cm)	Al	As	Ce	Fe	K	La	Mn	Mo	Ni	P	Si	Sr	Ti	Y
000-005	70951	19	160	23957	12397	52	317	113	27	1729	196033	39	5051	15
005-010	74091	24	159	26149	12777	53	259	94	26	1511	220934	33	5444	16
010-015	81588	26	192	34698	13834	37	154	70	25	720	227868	35	6899	18
015-020	84195	23	221	26615	12374	98	144	85	26	730	235866	27	6498	18
020-025	86210	24	207	27489	13196	89	159	85	26	805	231375	30	6808	18
025-030	83721	23	225	25755	12093	110	144	82	26	716	239885	32	6356	16
030-035	85054	25	230	26491	13036	114	158	76	26	722	238309	31	6955	18
035-037	84106	22	218	22449	13416	119	144	87	26	741	240043	33	6128	16
037-040	76699	25	229	22580	12998	88	153	65	26	622	254463	32	6386	18
040-045	78121	24	231	21408	12321	118	144	62	25	593	253872	30	6386	17
045-050	77973	24	216	28646	12998	94	187	68	25	680	254897	28	6082	17
050-055	74536	28	173	30350	13416	79	148	63	25	814	255606	28	5559	16
055-060	79040	19	140	19747	11485	80	144	79	25	632	244219	23	5666	17

Table 21. Normalized concentration ratios for elements in pre-settlement sediment of USE 4.

Depth (cm)	Al	As	Ce	Fe	K	La	Mn	Mo	Ni	P	Si	Sr	Ti	Y
065-070	71425	26	224	22624	14785	117	144	64	26	367	240476	44	6929	18
070-075	72047	25	78	19063	15135	136	144	75	26	206	248829	44	6310	17
075-080	81943	26	37	20599	14922	126	144	102	27	172	237561	43	7127	17
080-085	46713	31	238	22325	14420	108	144	21	26	395	231926	44	6960	17
085-090	62180	32	205	23622	13675	62	144	13	26	304	222470	43	7158	17
090-095	51247	35	265	23986	12602	129	144	10	27	293	221919	43	7427	18
095-100	67010	34	97	21714	12466	214	144	68	29	119	219830	42	7924	18
100-102	66002	32	268	18881	12960	145	144	13	29	226	216284	43	7422	17
102-105	79840	30	80	15502	11541	180	144	93	29	119	215418	43	6402	16
105-110	76077	28	67	16762	13987	153	144	85	29	119	225346	39	6173	18
110-115	43069	23	143	13791	16633	82	144	16	27	119	211399	50	4308	14
115-120	72136	21	81	17606	16527	117	144	94	27	119	233384	39	5394	17
120-125	68847	19	546	17839	18078	343	144	84	26	119	231414	42	6955	20
125-130	60432	22	358	30045	21044	178	144	63	26	119	218570	43	7437	34
137-169	42565	34	308	43160	16367		144	-6	25	695	194063	34	5223	19

APPENDIX E: CORRELATION TABLES

Correlation tables give the R^2 value for elements and percent silt-clay when compared pairwise. High values indicate strong correlation. Analysis was done for all samples across all sites as well as samples separated by lithographic unit classification (legacy and pre-settlement sediments). Analysis was also done using normalized concentration ratios from Appendix D.

Table 22. Correlation values from all element concentrations.

	Al	As	Co	Cr	Cu	Fe	K	Mn	Mo	Nb
As	0.263									
Co	0.504	0.406								
Cr	0.382	0.354	0.702							
Cu	0.452	0.392	0.906	0.609						
Fe	0.425	0.323	0.962	0.682	0.882					
K	0.268	0.22	0.362	0.477	0.385	0.378				
Mn	0.086	-0.189	0.469	0.465	0.523	0.486	0.21			
Mo	0.158	-0.408	-0.452	-0.389	-0.352	-0.499	-0.232	-0.052		
Nb	0.375	0.602	0.668	0.68	0.564	0.593	0.39	0.234	-0.453	
Ni	-0.094	-0.087	-0.464	0.042	-0.32	-0.496	0.001	0.105	0.353	-0.064
P	-0.019	-0.153	0.241	-0.055	0.381	0.283	-0.061	0.499	-0.012	-0.007
Si	-0.35	-0.422	-0.484	-0.324	-0.668	-0.497	-0.449	-0.276	0.153	-0.265
Sr	-0.104	0.4	-0.066	0.082	0.03	-0.114	0.172	-0.093	-0.134	0.214
Ti	0.433	0.576	0.648	0.646	0.538	0.606	0.5	0.21	-0.462	0.904
V	0.512	0.551	0.816	0.638	0.81	0.756	0.538	0.321	-0.341	0.703
W	0.245	0.579	0.739	0.592	0.631	0.745	0.37	0.194	-0.686	0.672
Y	0.04	0.229	0.239	0.45	0.198	0.22	0.394	0.034	-0.211	0.602
Zn	0.283	0.236	0.734	0.677	0.788	0.755	0.659	0.707	-0.347	0.573
Zr	0.209	0.179	0.758	0.712	0.589	0.793	0.344	0.356	-0.538	0.58
Percent Silt+Clay	0.344	0.401	0.225	0.102	0.262	0.13	0.123	-0.06	-0.036	0.337

	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
P	-0.186									
Si	0.048	-0.3								
Sr	0.288	-0.095	-0.233							
Ti	-0.055	0.022	-0.32	0.231						
V	-0.21	0.135	-0.639	0.082	0.714					
W	-0.455	0.044	-0.371	0.073	0.704	0.664				
Y	-0.012	-0.059	-0.102	0.126	0.428	0.301	0.269			
Zn	-0.05	0.335	-0.625	0.125	0.627	0.747	0.562	0.302		
Zr	-0.375	-0.045	-0.063	-0.087	0.57	0.547	0.648	0.319	0.567	
Percent Silt+Clay	0.027	0.13	-0.357	0.271	0.315	0.302	0.17	0.063	0.113	-0.096

Table 23. Correlation values from element concentrations compared within legacy sediment.

	Al	As	Co	Cr	Cu	Fe	K	Mn	Mo	Nb
As	0.579									
Co	0.614	0.691								
Cr	0.343	0.407	0.793							
Cu	0.564	0.531	0.887	0.626						
Fe	0.617	0.586	0.962	0.803	0.903					
K	0.408	0.182	0.435	0.537	0.478	0.459				
Mn	-0.156	-0.209	0.267	0.461	0.397	0.313	0.323			
Mo	-0.272	-0.409	-0.536	-0.533	-0.256	-0.427	-0.16	0.037		
Nb	0.44	0.693	0.684	0.671	0.508	0.607	0.271	0.182	-0.602	
Ni	-0.247	-0.316	-0.13	0.262	-0.026	-0.057	0.226	0.634	0.223	0.08
P	-0.216	-0.216	-0.078	-0.195	0.215	-0.063	-0.019	0.421	0.172	-0.148
Si	-0.424	-0.284	-0.533	-0.191	-0.774	-0.581	-0.303	-0.33	-0.163	-0.06
Sr	0.106	0.494	0.338	0.279	0.401	0.311	0.162	0.19	-0.031	0.417
Ti	0.501	0.647	0.633	0.659	0.459	0.585	0.311	0.135	-0.55	0.93
V	0.568	0.664	0.887	0.608	0.869	0.866	0.47	0.213	-0.368	0.613
W	0.458	0.61	0.703	0.587	0.506	0.655	0.265	0.021	-0.542	0.647
Y	0.371	0.55	0.579	0.612	0.397	0.492	0.364	0.217	-0.577	0.919
Zn	0.215	0.156	0.624	0.66	0.766	0.664	0.62	0.811	-0.07	0.396
Zr	0.295	0.414	0.672	0.809	0.436	0.689	0.398	0.147	-0.652	0.648
Percent Silt+Clay	0.391	0.427	0.354	0.198	0.399	0.327	0.29	-0.072	-0.199	0.345

	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
P	0.104									
Si	0.069	-0.385								
Sr	0.197	0.145	-0.324							
Ti	0.079	-0.09	-0.053	0.432						
V	-0.142	0.053	-0.623	0.376	0.562					
W	-0.332	-0.188	-0.19	0.244	0.656	0.63				
Y	0.131	-0.13	0.01	0.284	0.85	0.533	0.533			
Zn	0.453	0.337	-0.597	0.379	0.352	0.62	0.277	0.397		
Zr	0.051	-0.43	0.075	0.202	0.599	0.509	0.61	0.571	0.347	
Percent Silt+Clay	-0.164	0.119	-0.413	0.391	0.393	0.376	0.296	0.286	0.165	0.128

Table 24. Correlation values from element concentrations compared within pre-settlement sediment.

	Al	As	Co	Cr	Cu	Fe	K	Mn	Mo	Nb
As	0.053									
Co	-0.01	0.601								
Cr	0.281	0.423	0.511							
Cu	-0.129	0.64	0.834	0.38						
Fe	-0.172	0.558	0.926	0.576	0.809					
K	0.143	0.278	0.457	0.474	0.416	0.468				
Mn	0.47	0.255	-0.023	0.079	0.122	-0.159	0.458			
Mo	0.531	-0.48	-0.577	-0.324	-0.571	-0.713	-0.256	0.397		
Nb	0.167	0.601	0.757	0.649	0.647	0.634	0.51	0.18	-0.38	
Ni	0.529	-0.002	-0.331	0.166	-0.161	-0.427	-0.102	0.369	0.425	0.052
P	-0.145	0.111	0.285	-0.131	0.316	0.299	-0.298	-0.12	-0.103	0.003
Si	-0.229	-0.658	-0.624	-0.567	-0.668	-0.636	-0.618	-0.386	0.381	-0.55
Sr	0.011	0.258	0.297	0.15	0.223	0.271	0.3	-0.127	-0.369	0.274
Ti	0.246	0.627	0.731	0.605	0.622	0.631	0.642	0.233	-0.411	0.877
V	0.267	0.645	0.679	0.605	0.639	0.554	0.646	0.44	-0.312	0.782
W	-0.253	0.753	0.749	0.504	0.72	0.821	0.467	-0.117	-0.84	0.651
Y	-0.054	0.067	0.412	0.575	0.364	0.421	0.433	0.062	-0.135	0.586
Zn	0.07	0.534	0.775	0.621	0.714	0.775	0.803	0.169	-0.538	0.753
Zr	-0.355	0.161	0.539	0.524	0.393	0.646	0.352	-0.411	-0.568	0.433
Percent Silt+Clay	0.373	0.371	0.302	-0.018	0.233	0.082	-0.004	0.346	0.048	0.368

	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
P	-0.26									
Si	-0.108	-0.004								
Sr	-0.056	-0.103	-0.283							
Ti	0.127	-0.121	-0.626	0.371						
V	0.158	-0.223	-0.71	0.214	0.823					
W	-0.329	0.067	-0.606	0.33	0.697	0.574				
Y	-0.198	0.098	-0.214	-0.012	0.333	0.334	0.263			
Zn	-0.11	-0.154	-0.727	0.373	0.877	0.804	0.759	0.441		
Zr	-0.33	-0.161	-0.132	0.232	0.449	0.313	0.521	0.463	0.567	
Percent Silt+Clay	0.215	0.287	-0.299	0.155	0.282	0.304	0.083	-0.051	0.106	-0.366

Table 25. Correlation values from normalized concentration ratios for all samples.

	Al	As	Co	Cr	Cu	Fe	K	Mn	Mo	Nb
As	0.263									
Co	0.469	0.447								
Cr	-0.243	-0.173	-0.787							
Cu	0.245	0.313	0.35	-0.126						
Fe	0.425	0.323	0.816	-0.823	0.378					
K	0.268	0.22	0.368	-0.216	0.281	0.378				
Mn	0.086	-0.189	0.373	-0.349	0.402	0.486	0.21			
Mo	0.158	-0.408	-0.431	0.472	-0.066	-0.499	-0.232	-0.052		
Nb	-0.187	0.039	-0.051	0.179	0.141	-0.067	-0.274	0.011	0.027	
Ni	-0.094	-0.087	-0.385	0.551	0.027	-0.496	0.001	0.105	0.353	-0.028
P	-0.019	-0.153	0.28	-0.374	0.416	0.283	-0.061	0.499	-0.012	-0.079
Si	-0.35	-0.422	-0.443	0.364	-0.602	-0.497	-0.449	-0.276	0.153	0.178
Sr	-0.104	0.4	-0.041	0.16	0.162	-0.114	0.172	-0.093	-0.134	-0.042
Ti	0.433	0.576	0.718	-0.486	0.261	0.606	0.5	0.21	-0.462	-0.22
V	-0.085	0.045	-0.523	0.851	0.066	-0.676	0.034	-0.314	0.43	0.059
W	-0.306	-0.012	-0.713	0.913	-0.129	-0.816	-0.205	-0.451	0.308	0.095
Y	0.04	0.229	0.265	-0.062	0.163	0.22	0.394	0.034	-0.211	0.45
Zn	0.041	0.068	-0.17	0.463	0.207	-0.324	0.486	0.116	0.236	-0.242
Zr	-0.362	-0.27	-0.845	0.952	-0.13	-0.856	-0.348	-0.386	0.485	0.212
Percent Silt+Clay	0.344	0.401	0.338	-0.092	0.327	0.13	0.123	-0.06	-0.036	0.009

	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
P	-0.186									
Si	0.048	-0.3								
Sr	0.288	-0.095	-0.233							
Ti	-0.055	0.022	-0.32	0.231						
V	0.507	-0.325	0.098	0.165	-0.242					
W	0.438	-0.398	0.345	0.208	-0.386	0.83				
Y	-0.012	-0.059	-0.102	0.126	0.428	-0.04	-0.126			
Zn	0.572	-0.08	-0.282	0.319	0.115	0.677	0.45	0.049		
Zr	0.431	-0.332	0.462	0.099	-0.617	0.775	0.899	-0.167	0.295	
Percent Silt+Clay	0.027	0.13	-0.357	0.271	0.315	0.067	-0.028	0.063	0.095	-0.147

Table 26. Correlation values from normalized concentration ratios compared within legacy sediment.

	Al	As	Co	Cr	Cu	Fe	K	Mn	Mo	Nb
As	0.579									
Co	0.533	0.718								
Cr	-0.529	-0.39	-0.441							
Cu	0.423	0.37	0.625	-0.65						
Fe	0.617	0.586	0.758	-0.578	0.658					
K	0.408	0.182	0.39	-0.114	0.492	0.459				
Mn	-0.156	-0.209	0.221	-0.025	0.484	0.313	0.323			
Mo	-0.272	-0.409	-0.62	0.002	-0.084	-0.427	-0.16	0.037		
Nb	0	0.366	0.406	-0.099	0.234	0.253	-0.023	0.146	-0.341	
Ni	-0.247	-0.316	-0.19	0.401	0.037	-0.057	0.226	0.634	0.223	0.018
P	-0.216	-0.216	0.029	-0.271	0.497	-0.063	-0.019	0.421	0.172	-0.198
Si	-0.424	-0.284	-0.424	0.731	-0.812	-0.581	-0.303	-0.33	-0.163	-0.012
Sr	0.106	0.494	0.323	-0.099	0.396	0.311	0.162	0.19	-0.031	0.123
Ti	0.501	0.647	0.653	-0.132	0.323	0.585	0.311	0.135	-0.55	0.179
V	0.004	0.218	0.21	-0.141	0.26	-0.142	0.146	-0.113	0.055	0.165
W	-0.166	0.05	-0.146	0.431	-0.491	-0.465	-0.289	-0.444	-0.131	-0.053
Y	0.371	0.55	0.677	-0.066	0.319	0.492	0.364	0.217	-0.577	0.484
Zn	-0.162	-0.213	0.13	-0.011	0.585	0.098	0.476	0.751	0.253	0.092
Zr	-0.596	-0.542	-0.773	0.657	-0.743	-0.941	-0.504	-0.4	0.359	-0.175
Percent Silt+Clay	0.391	0.427	0.399	-0.314	0.415	0.327	0.29	-0.072	-0.199	-0.005

	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
P	0.104									
Si	0.069	-0.385								
Sr	0.197	0.145	-0.324							
Ti	0.079	-0.09	-0.053	0.432						
V	-0.144	0.235	-0.18	0.153	0.041					
W	-0.304	-0.224	0.532	-0.08	0.08	0.201				
Y	0.131	-0.13	0.01	0.284	0.85	0.159	0.039			
Zn	0.539	0.529	-0.416	0.299	-0.031	0.279	-0.341	0.097		
Zr	0.031	-0.141	0.672	-0.31	-0.586	0.04	0.486	-0.508	-0.23	
Percent Silt+Clay	-0.164	0.119	-0.413	0.391	0.393	0.166	-0.057	0.286	0.006	-0.394

Table 27. Correlation values from normalized concentration ratios compared within pre-settlement sediment.

	Al	As	Co	Cr	Cu	Fe	K	Mn	Mo	Nb
As	0.053									
Co	0.204	0.599								
Cr	0.14	-0.476	-0.755							
Cu	-0.079	0.279	0.11	0.063						
Fe	-0.172	0.558	0.694	-0.869	0.034					
K	0.143	0.278	0.402	-0.281	0.063	0.468				
Mn	0.47	0.255	0.115	0.289	0.331	-0.159	0.458			
Mo	0.531	-0.48	-0.365	0.623	-0.032	-0.713	-0.256	0.397		
Nb	-0.267	-0.22	-0.156	0.172	0.108	-0.14	-0.395	-0.185	0.141	
Ni	0.529	-0.002	-0.078	0.387	0.212	-0.427	-0.102	0.369	0.425	-0.204
P	-0.145	0.111	0.22	-0.329	0.115	0.299	-0.298	-0.12	-0.103	0.223
Si	-0.229	-0.658	-0.566	0.534	-0.203	-0.636	-0.618	-0.386	0.381	0.342
Sr	0.011	0.258	0.273	-0.351	-0.028	0.271	0.3	-0.127	-0.369	-0.302
Ti	0.246	0.627	0.77	-0.584	0.136	0.631	0.642	0.233	-0.411	-0.44
V	0.284	-0.097	-0.349	0.776	0.245	-0.631	0.111	0.664	0.507	-0.05
W	-0.022	-0.247	-0.638	0.86	0.159	-0.8	-0.211	0.267	0.402	0.021
Y	-0.054	0.067	0.313	-0.217	0.121	0.421	0.433	0.062	-0.135	0.435
Zn	0.47	0.177	0.067	0.327	0.071	-0.18	0.613	0.681	0.181	-0.488
Zr	-0.1	-0.576	-0.817	0.923	0.134	-0.874	-0.429	0.104	0.579	0.245
Percent Silt+Clay	0.373	0.371	0.481	-0.182	0.224	0.082	-0.004	0.346	0.048	0.014

	Ni	P	Si	Sr	Ti	V	W	Y	Zn	Zr
P	-0.26									
Si	-0.108	-0.004								
Sr	-0.056	-0.103	-0.283							
Ti	0.127	-0.121	-0.626	0.371						
V	0.46	-0.475	0.125	-0.263	-0.145					
W	0.298	-0.348	0.439	-0.259	-0.45	0.754				
Y	-0.198	0.098	-0.214	-0.012	0.333	-0.168	-0.368			
Zn	0.452	-0.54	-0.352	0.108	0.427	0.676	0.392	-0.019		
Zr	0.199	-0.24	0.695	-0.371	-0.731	0.646	0.843	-0.31	0.079	
Percent Silt+Clay	0.215	0.287	-0.299	0.155	0.282	0.055	-0.093	-0.051	0.148	-0.239