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Process recognition in multi-element soil and stream-sediment geochemical data

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Abstract

Stream-sediment and soil geochemical data from the Upper and Lower Coastal Plains of South Carolina (USA) were studied to determine relationships between soils and stream sediments. From multi-element associations, characteristic compositions were determined for both media. Primary associations of elements reflect mineralogy, including heavy minerals, carbonates and clays, and the effects of groundwater. The effects of groundwater on element concentrations are more evident in soils than stream sediments. A "winnowing index" was created using ratios of Th to Al that revealed differing erosional and depositional environments. Both soils and stream sediments from the Upper and Lower Coastal Plains show derivation from similar materials and subsequent similar multi-element relationships, but have some distinct differences. In the Lower Coastal Plain, soils have high values of elements concentrated in heavy minerals (Ce, Y, Th) that grade into high values of elements concentrated into finer-grain-size, lower-density materials, primarily comprised of carbonates and feldspar minerals (Mg, Ca, Na, K, Al.). These gradational trends in mineralogy and geochemistry are inferred to reflect reworking of materials during marine transgressions and regressions. Upper Coastal Plain stream-sediment geochemistry shows a higher winnowing index relative to soil geochemistry. A comparison of the 4 media (Upper Coastal Plain soils and stream sediments and Lower Coastal Plain soils and stream sediments) shows that Upper Coastal Plain stream sediments have a higher winnowing index and a higher concentration of elements contained within heavy minerals, whereas Lower Coastal Plain stream sediments show a strong correlation between elements typically contained within clays. It is not possible to calculate a functional relationship between steam sediment-soil compositions for all elements due to the complex history of weathering, deposition, re-working and re-deposition. However, depending on the spatial separation of the stream-sediment and soil samples, some elements are more highly correlated than others.

1. Introduction

Geochemical surveys are an important part of geoscience investigations in both mineral exploration and environmental studies. Geochemical samples are commonly analyzed for as many as 50 elements. A soil or lake-sediment survey can consist of several thousand samples. Analyzing and interpreting these large arrays of data can be a challenge. Data can be both categorical (discrete numeric or non-numeric) or continuous in nature. To extract the maximum amount of information from these large arrays of data, there are a wide range of multivariate data analysis techniques available. In many cases, these techniques reduce large arrays of data into a few simple diagrams that can outline important geochemical trends and assist with interpretation. Often the trends that are identified include variations associated with underlying lithologies, zones of alteration, and in special cases, zones of potentially economic mineralization. From an environmental perspective, trends may also represent natural background elemental behavior as well as distinctive multi-element geochemical signatures resulting from anthropogenic activity.

The extent of interpretation that can be inferred from geochemical survey data is subject to a number of factors (Grunsky, 2009) including:

1) spatial sampling density (i.e., the scale of the survey),
2) knowledge of the local and regional geology,
3) knowledge of the mineralogy,
4) knowledge of analytical protocols including sample media, methods of digestion and analytical instrumentation,
5) knowledge of human activities (i.e., industry, agriculture, etc.) in the study area.

The spatial sampling density, or scale, of a geochemical survey determines the resolution of the geochemical features delineated from the resulting data. Continental-scale geochemical surveys (1 sample site per a few thousand km^2) are most likely to reveal patterns related to processes acting at these broad scales, such as weathering of parent materials of varying composition. Detailed geochemical surveys (1 sample site per tens to hundreds of km^2) will reveal more detailed features related to processes such as mineralization or, in some cases, anthropogenic activities.

Geochemical data can be collected from a variety of sample media (Darnley et al., 1995). Depending on the sample media, multi-element geochemical data can be evaluated to detect or infer geochemical processes that have occurred with the resulting geochemical response. Evaluation and interpretation of geochemical data rely on a sound understanding of sample material. Different materials require different methods and techniques for an interpretation of results. In the case of till, lake sediments and stream sediments, different size fractions of specimens may reflect different geological processes. The choice of size fraction can have a profound influence on how the geochemistry of an area may be interpreted. In any geochemical survey, the collected material should be carefully sampled and classified to provide clues about underlying geochemical processes. A summary paper on the concept of "landscape geochemistry" by Fortescue (1992) gives a perspective on the processes that modify geochemical signatures.

The estimation of the geochemical composition of soils based on the geochemical composition of other media (till, stream sediments, bedrock, etc.) has been addressed by relatively few investigators. Estimation of soil composition has been carried out based on the ratios of mean values for elements (Cannon et al., 2004) and by geostatistical approaches (Rawlins et al., 2003; Appleton et al., 2008). This contribution analyzes the relationship between pairs of stream-sediment and soil samples collected from catchment basins in the Coastal Plains of South Carolina. Some elements are used as proxies for mineralogy, which can help interpret the environment of deposition and subsequent modifications of that depositional environment. The spatial relationship between the two sample media is examined in terms of defining their maximum correlation as a function of distance of separation. Principal component analysis is applied to determine the relationship between elements and their environments (e.g., soil versus stream sediment and Upper Coastal Plain versus Lower Coastal Plain). A discriminant analysis is applied to determine how well a particular environment of deposition can be predicted followed by a test of soil composition predictions based on paired stream-sediment compositions. Finally, the question 'can the composition of either a soil or stream sediment be effective in calculating the other?' is tested using methods of regression and non-linear methods.

2. Geology of depositional environments of South Carolina

South Carolina can be subdivided into two broad geographic regions, the Piedmont and the Coastal Plain (Fig. 1). A small portion of the Blue Ridge province cuts through the extreme NW part of the state. The Piedmont province and the Coastal Plain are separated by the Fall Zone, which is the western limit of Cretaceous and Cenozoic sediments in South Carolina (Gohn, 1988) (Fig. 1). West of the Fall Zone, crystalline rocks of the southern Appalachians comprise the Blue Ridge province and the Piedmont province. The Blue Ridge province is a multiply tectonized accretionary complex that ranges in age from Neoproterozoic to Lower Paleozoic (Hibbard et al., 2006). Rocks of the Piedmont province were juxtaposed against rocks of the Blue Ridge province along the Brevard fault zone during the Paleozoic. Between the Brevard fault zone and the Fall Zone, the Piedmont province can be subdivided into the western, central, and eastern Piedmont.

Western Piedmont rocks are Neoproterozoic to Cambrian amphibolite-facies mafic and felsic gneisses derived from metavolcanic and metaclastic rocks. The central Piedmont is comprised of the Carolina terrane, an assemblage of volcanic and clastic sediments at a lower metamorphic grade than rocks in the western Piedmont. The central Piedmont includes the Slate Belt, an area of known base metal mineralization. In the northern part of the central Piedmont is a Mesozoic graben called the Wadesboro sub-basin of the Deep River basin. The boundary between the eastern Piedmont and central Piedmont is the Modoc shear zone. Eastern Piedmont rocks are metamorphosed magmatic-arc/oceanic rocks that yield Neoproterozoic to Cambrian ages (Hibbard et al., 2006).

The Coastal Plain is underlain by Cretaceous and Cenozoic sediments derived from the Blue Ridge and Piedmont areas. It is divided into two topographic regions, the Upper Coastal Plain (UCP) and Lower Coastal Plain (LCP), separated by the Orangeburg Scarp, a marine erosional feature. (Fig.1). The UCP, located between the Fall Zone and the Orangeburg Scarp, is topographically higher and has greater relief than the LCP, which is located between the Orangeburg Scarp and the Atlantic Coast.

The geologic history of the Coastal Plain is complex, with variable thermal regimes, lithospheric cooling, and sedimentary loading from the weathering of the terrain west of the Fall Zone (Gohn, 1988). In terms of this study, soils and stream sediments of the Coastal Plain are largely derived from the weathering and transportation of materials sourced from the Piedmont province. Larsen (1993) describes a transition of depositional environments between the Piedmont province and the Coastal Plain at the Fall Zone (Fig. 1). The Fall Zone defines a boundary where river dynamics change, with a significant decrease in stream velocity south of the Fall Zone. As a result of this decrease in flow rates, coarse suspended particles are deposited at the Fall Zone while medium- and finer-grained materials are deposited in lower energy fluvial-deltaic environments further downstream. Southeast of the Orangeburg Scarp, in the LCP, stream sediments primarily derived from weathering of rocks of the Piedmont province and the UCP to the west were reworked in transgressive and regressive beach environments (Larsen, 1993). In the LCP, the reworking of these media is shown by a change in landscape texture in the digital elevation model across the Orangeburg Scarp (Fig. 2). Cocker (1998) describes the LCP environment as a series of major river systems forming deltaic complexes followed by shoreline processes that include longshore currents, beach processes, and eolian processes that extensively modified accumulating sediments.

3. Mineralogy of the Coastal Plain

Minerals found in soils and stream sediments of the Coastal Plain are mainly derived from the Piedmont province. Source rocks in the Piedmont represent a wide range of materials, from simple granitoid and volcanic assemblages to mixed metasedimentary rocks, including slates and shales that contain a wide range of elements derived from scavenging and earlier weathering events. Minerals reported from the Piedmont include microcline, orthoclase, plagioclase, beryl, quartz, biotite, muscovite, phlogopite, amphibole, pyroxene, tourmaline, allanite, fluorite, garnet, andalusite, apatite, sillimanite, epidote, zoisite, dumortierite, olivine, psilomelane, piedmontite and titanite. Minerals associated with the rare-earth suite of elements include monazite, zircon, rutile (anatase) and ilmenite (Larsen, 1993). The contrast of densities among these minerals plays an important role in the weathering process and their subsequent depositional environment. In the Coastal Plain, mineralogies include (1) heavy minerals, defined as those minerals with a specific gravity that exceeds quartz (Larsen, 1993; Overstreet, 1962), concentrated near the Fall Zone and in other zones of accumulation; (2) residual minerals resistant to reworking and weathering processes; and (3) minerals formed during chemical weathering.

Larsen (1993) describes the physics of particle transport and separation of heavy minerals as a function of specific gravity and shape. The type of fluid flow (laminar or turbulent) also plays a significant role in the transport dynamics and final deposition of mineral grains. These factors have had a significant influence on the sorting and location of heavy mineral occurrences. Quartz is highly resistant to chemical and physical weathering and has been transported throughout the Coastal Plain as the result of weathering of the eastern Appalachians. Resistance to communition and chemical weathering plays a critical role in development of residual mineralogy. Cocker (1998) describes the distribution of mineral suites throughout the UCP of Georgia where heavy minerals are preferentially concentrated by intensive pre-depositional weathering of placer deposits.

Chemical weathering has affected minerals such as ilmenite through the removal of Fe and the extensive development of kaolinite and bauxitization of kaolinite deposits. The mineralogy of the lighter fraction of fluvial and upland deposits in North Carolina has been described by Soller (1988). No such studies have been carried out in South Carolina, but it is assumed that observed mineralogies are similar between the two States. Non-opaque, heavy minerals observed in the fluvial deposits of the LCP of North Carolina are dominantly hornblende and epidote, while quartz and feldspar make up the dominant mineral species of the lighter fractions. Iron oxide coatings and aggregates have been noted. Layers of shells are also found throughout the fluvial sequences. The dominant clay mineral is kaolinite

Based on geological reports of the UCP and LCP areas from Georgia to North Carolina (Overstreet, 1962; Bell, 1976; Soller, 1988; Larsen, 1993; Cocker, 1998), specific mineralogies can be inferred from observed geochemical compositions of stream sediments and soils. Heavy minerals are represented by Y, La, Ce, Nd and Th; feldspars are represented by Sr, Na, K, Ba and Ca; clay minerals are represented by Al and Mg with contributions of Li and Ca. Elements including Fe, Cr, Zn, V, As, Cu, Pb and Mn tend to be part of the crystal structure of medium-density ferromagnesian minerals or adsorb onto the surface of clays and Fe-Mn oxy-hydroxides in lower energy depositional environments.

4. Geochemical surveys in South Carolina

The stream-sediment samples used in this study were collected during the U.S. Department of Energy's National Uranium Resource Evaluation Hydrogeochemical and Stream Sediment Reconnaissance (NURE HSSR) Program conducted during the late 1970s and early 1980s (Bolivar, 1980). This program included the systematic sampling of several hundred thousand samples of stream sediments, soils, lake sediments, and a few other solid sample media, and a comparable number of stream- and well-water samples across about 65 % of the USA (Smith, 1997). Unfortunately, the program used a variety of analytical protocols and a consistent data base was not established (Grossman, 1998). In the late 1990s, the U.S. Geological Survey (USGS) initiated a project, the National Geochemical Survey, to reanalyze a subset of the NURE HSSR stream-sediment samples by a standardized analytical protocol at a minimum density of 1 sediment sample per 289 km^2 and to collect new samples in those portions of the nation not covered by NURE HSSR (USGS, 2004). Stream sediments were collected at 6,191 sites in South Carolina during the NURE HSSR program and 1,291 of these samples were reanalyzed as part of the USGS effort. A set of 594 soil samples was collected in 1998-1999 as part of a joint U.S. Geological Survey – South Carolina Geological Survey project to characterize the upper 15 cm of residual soils of the coastal plain of South Carolina (USGS, 2004).

5. Sampling and analytical methods

At each stream-sediment site in the NURE HSSR program, samples were collected from 6 to 10 locations upstream and downstream of the site, sieved to a grain size of <2 mm, and composited into a single sample. This composite was further sieved to <150 µm prior to chemical analysis. Soil sampling protocols used in the South Carolina coastal plain involved collecting the top 15 cm from 3 sites about 10 m apart. Soil from these 3 sample sites was composited and sieved to <150 µm prior to analysis. In most soil studies throughout the world, samples are sieved to <2 mm prior to chemical analysis. The selection of the <150-µm size fraction for this study is considered “non-standard” for soils and was chosen to be consistent with the size fraction used for stream sediments in the NURE HSSR Program. According to national soil characterization data obtained from the Natural Resources Conservation Service (http://soils.usda.gov/survey/nscd/), the top 15 cm sampled in this study may have resulted in material derived: (1) entirely from the O horizon; (2) entirely from the A horizon; or (3) from some varying proportion of O and A horizons, with or without an E horizon. In addition to the complications introduced by the winnowing of minerals, co-precipitation of labile elements, sequestration by organic matter, and mineral weathering as identified by Garrett et al. (2005), the potential combinations of soil horizons will complicate the development of a method of estimating soil composition from stream-sediment data.

Both the soils and stream sediments were analyzed by the same analytical protocols. Aluminum, Ca, Fe, K, Mg Na, S, Ti, Ag, Au, Ba, Be, Bi, Cd, Ce, Co, Cr, Cu, Eu, Ga, Ho, La, Li, Mn, Mo, Nb, Nd, Ni, P, Pb, Sc, Sn, Sr, Ta, Th, U, V, Y, Yb and Zn were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES), following a near-total 4-acid (HCl, HNO_3, $HClO_4$ and HF) digestion (Briggs, 2002). The 4-acid digestion is effectively a total dissolution for most mineral constituents of soil and stream sediment. However, it does not fully dissolve some of the more refractory or resistant minerals such as barite (Ba), chromite (Cr), rutile (Ti), cassiterite (Sn), and monazite (rare earth elements). Arsenic was determined by hydride generation-atomic absorption spectrometry (HGAAS) following a sodium peroxide fusion at 750 ^{o}C (Hageman and Brown, 2002).

Accuracy of the data was determined by analysis of standard reference materials at the rate of 1 per each batch of 20 samples. The accuracy for elements determined by ICP-AES was considered acceptable if recovery was within the range of 85-115% at 5 times the lower detection limit (LLD). The accuracy for As by HGAAS was considered acceptable if recovery was within 80-120% at 5 times the LLD. Precision was determined by analysis of duplicate samples. The precision for elements determined by ICP-AES was considered acceptable if the relative standard deviation (RSD) of duplicate samples was no greater than 15%. The precision for As was acceptable if the RSD was no greater than 20%.

6. Multi-element statistical methods applied to stream sediments and soils

Drew et al. (2004) and Drew (2005) studied reanalyzed NURE HSSR stream-sediment samples and USGS soil data acquired for South Carolina and demonstrated broad links between stream-sediment and soil geochemistry for trace elements in the Coastal Plain heavy mineral suite. Garrett et al. (2005) examined stream-sediment data from the UCP of South Carolina to determine correlations between the geochemistry of stream sediments and soils. They concluded that any possible relation between the two media is difficult to decipher due to the winnowing of minerals, co-precipitation of labile elements (e.g., Pb, Zn and As with Fe-Mn oxy-hydroxides), sequestration of certain elements with organic matter, and mineral weathering. As will be shown, there are fundamental differences in the nature of correlations in geochemistry between soils and stream sediments within UCP and LCP environments. For this study, stream sediment-soil pairs were created by matching stream-sediment and soil samples within defined catchment areas. Within any catchment area, a stream sediment – soil pair was created by selecting the geographically closest pair of samples. Only one pair per catchment area was chosen. A total of 68 paired stream sediment – soil sites were selected from the UCP, NW of the Orangeburg Scarp, and a total of 168 paired sites were selected from the LCP, SEof the Orangeburg Scarp (Fig. 3).

6.1 Spatial variability of stream sediment – soil pairs

Experimental semi-variograms, testing the difference between an element's concentration in soil compared to stream sediment, were determined for elements at different lag intervals (the distance between the points used in the computation) for the stream sediments and soils of the Upper and Lower Coastal Plains. All of the computed semi-variograms show medium to high nugget effects for individual elements. The presence of a high nugget effect suggests limited spatial continuity at the sample density used in this study. Previous studies (Overstreet, 1962; Soller, 1988; Larsen 1993; Cocker, 1998) have shown that there are unique elemental/mineralogical associations for UCP stream sediments, UCP soils, LCP stream sediments and LCP soils. These associations are evident from the differences of experimental semi-variograms between the media types and areas (Figs 4 and 5). Aluminum, which can be considered a proxy for clay minerals, displays a greater nugget effect in stream sediments than in soils (Figs 4a, b).In addition, the overall variance of Al in soils is lower than that of stream sediments, indicating more spatial continuity of Al in soils. The sill value (a measure of the true population variance) of Al in soils occurs at a lag distance of 20,000 m, whereas the sill value of Al in stream sediments is reached within 10,000 m and appears to have a monotonically linear increase in variance. For the LCP (Figs 4c, d), the variance of Al is lowest in soils and about the same in stream sediments (cf. Fig. 4b). Both Figures 4c and 4d display a very short range (less than 20,000 m) that suggests that any spatial continuity is not evident at this sampling density.

Figures 5a-d show experimental semi-variograms for Th, which can be considered a proxy for heavy minerals in both soils and stream sediments. The range of variances of Th varies significantly between UCP stream sediments (Fig. 5a) and LCP soils (Fig. 5d). The variance between UCP soils and LCP stream sediments appears to be similar. From the 4 plots in Figure 5, an approximate estimate of the range of Th is about 20,000 m, which may also reflect a limitation on the sampling density for the area.

The variances displayed in the experimental semi-variograms of Figures 4 and 5 can be used to infer something about the energy of the environment of deposition. The variance of Al in LCP soils (Fig. 4d) is the lowest, suggesting that the Al compositions for all LCP soils are not very different and thus may represent a stable depositional environment. Figure 5a displays a very large variance in the semi-variogram for UCP stream sediments, which implies significant differences in Th compositions from site to site. This can be interpreted as varied depositional environments that include sites with higher concentrations of Th and sites where Th concentrations are very low. A stream environment with varying degrees of winnowing would best account for this type of variability in the coastal plain setting of South Carolina.

6.2 Stream sediment – soil pair distances

Distances were computed between each stream sediment – soil pair. A histogram of the distances (Fig. 6) shows that the mode of distances between samples is approximately 3000 m. For subsequent analysis, only pairs with a distance of less than 7500 m were chosen. Because stream sediment – soil pairs are variably separated, a measure of the degree of correlation between each stream sediment – soil pair is a useful measure to test the potential of estimating the composition of one media type given the other. The UCP and LCP were separated into two groups and the stream sediment – soil pairs and correlations between elements were determined based on specified distances between pairs. Correlations were determined for all pairs that fell within the ranges of 600 to 10,000 m in 100-m increments. The results of these correlations are shown in Figures 7 and 8 for Al, K, Fe and Th.

Figure 7 shows the correlations between stream sediment – soil pairs for the UCP. For Al, there appears to be a moderate amount of correlation at pair distances of 2000 to about 3500 m (Fig. 7a). This correlation is less for distances of less than 2000 m and for distances greater than about 3500 m. This pattern is observed for many elements including Ce, Fe, Na, P, Ti, Cr, La, Li, Nb, Nd, Pb, Sr, Th, V, Y and As. Potassium (Fig. 7b), Sr and Ba have a significantly higher correlation for all pairs less than 3000 m and suggest that prediction of a soil composition given a stream sediment composition for these elements is possible. Patterns for Fe (Fig. 7c) and Th (Fig. 7d) have correlations much like those of Al.

Correlations between pairs of stream sediments and soils for the LCP are significantly different from those of the UCP. Figure 8 shows correlations as a function of distance for Al, K, Fe and Th. Correlations for Al (Fig. 8a) are higher and more consistent over distance relative to pairs in the UCP. Elements that display similar patterns are Li and Mn. Correlations for K (Fig. 8b) decrease in the range of 2000 m and level to a value of 0.4 for the remaining distances. This pattern is also observed for Mg, Na, Ba, Cu and Sr. Iron (Fig. 8c) and Ti show a high correlation between pairs (up to 0.9) in the range of 0 to 2500 m, and Th (Fig. 8d) displays high correlations at distances less than 2000 m with a significant decay at larger distances. This pattern is also observed for Y, Nd, Ce, and La.

From the correlations of stream sediment – soil pairs from the UCP and LCP, it is observed that the patterns are different between the two regions for several elements, indicating that the mineralogies are likely different between the two regions. In addition, these correlations provide evidence that any functional relationship between compositions will be governed by a significant degree of spatial correlation between the pairs themselves. Thus, it can be inferred that many of the element correlations between stream sediments and soils are complicated by the spatial separation of the pairs and the geological processes that have taken place to form these two sedimentary types.

6.3. The index of winnowing

The multi-element stream-sediment and soil geochemistry data were adjusted using a log-centered transformation (Aitchison, 1986). Subsequent to log-centering, an "index of winnowing" was created as described by Garrett et al. (2005). The calculation of such an index provides a distinction between stream sediments and soils and can be beneficial in understanding processes that have resulted in the existing geochemical compositions. The Th/Al ratio provides a measure of the "winnowing" of minerals as it acts as a proxy for the ratio of high-density minerals to low-density minerals, such as clay, thus separating out mineral fractions on the basis of density and energy of the erosional/depositional environment. The "winnowing index" (WI) is determined by the following method:

1. Log-centered Th/Al ratios standardized = Index:
   Index = (Th/Al – mean (Th/Al)) / std.dev. (Th/Al)

2. Offset Index to a minimum of zero and add 0.01 so there are no zero values:
   Index = Index –minimum (Index) + 0.01
3. Rescale Index between 0.01 and 3.0:
   Interval = 3.0/maximum (Index)
4. Calculate Winnowing Index (WI):
   WI = Index x Interval

A plot of Th versus Al, using log centered coordinates, for the soils and stream sediments in the UCP and LCP (Fig. 9a) reveals that UCP soils and stream sediments have higher concentrations of Th relative to Al and thus represent a greater degree of sorting (winnowing), which also implies a higher-energy depositional environment. Soils and stream sediments from the LCP have correspondingly higher amounts of Al and a subsequent lower WI, which indicates lower-energy environments with fewer detrital grains of high density and a greater amount of low-density clay minerals.

A quantile-quantile plot of the WI is shown in Figure 9b. Significant breaks in the plot occur at 0.75, 0.9, 1.3, 1.9, and 2.45. These breaks may represent degrees of sorting within the stream sediments and soils.

Figure 10 displays a map of WI values with different symbols based on media type and symbol sizes based on the intervals defined by the upper 4 breaks (0.9, 1.3, 1.9, 2.45) noted in Figure 9b. From Figure 10, it is clear that larger WI values for both stream sediments and soils are within catchments located between the Fall Zone and the Orangeburg Scarp in the UCP, and lower WI values for both media are SE of the Orangeburg Scarp in the LCP. Thus, the degree of winnowing is higher in the UPC and lower in the LCP.

To obtain a sense of the continuity of the WI in the entire Coastal Plain, WI for each media type was interpolated using a kriging method (surfaces not shown). The resulting surface for stream sediments was a continuous gradient from west to east showing a decrease in the value of the kriged WI. For soils, the kriged WI surface was not a continuous decreasing surface down slope. There are patches of higher WI values within the LCP and an area of lower values in the UPC. This gradient is consistent with the findings of Cocker (1998).

6.4. Principal component analysis of stream sediments and soils of the UCP and LCP

Another way of looking at the data is with the application of multivariate techniques such as a principal component analysis (PCA) (Zhou et al., 1983). Principal component analysis was applied to UCP and LCP stream sediments and soils using Al, Ca, Fe, K, Mg, Na, P, Ti, Ba, Ce, Cr, Cu, La, Li, Mn, Nb, Nd, Pb, Sc, Sr, Th, V, Y, Zn and As.

Figure 11 is a biplot of the first two principal components from combined UCP and LCP soils and stream sediments. The first two components account for 56.4% of variation of the data, while the first 5 principal components account for more than 75% of the overall variation. The different symbols distinguish the 4 classes of observations (LCP stream sediments, LCP soils, UCP stream sediments, UCP soils). Symbol size is proportional to the WI. From Figure 11, the pattern of winnowing and sorting of heavy minerals along the C1 axis is apparent. The larger symbols, reflecting larger WI values, are generally represented by UCP and LCP stream sediments, and the smaller symbols by UCP and LCP soils. LCP soils thus represent a lesser degree of sorting and UCP stream sediments a greater degree of sorting.

LCP soils lie in the same direction as clay minerals, represented by Mg and Al along the negative C1 axis. LCP stream sediments and soils lie in the direction of feldspars and carbonates and elements typical of these minerals (Ca, Mn, Na, K, Sr and Ba) to a greater extent than UCP stream sediments and soils. LCP soils also display a relative increase in a ferromagnesian component defined by the positive C2 and negative C1 axes.

A third component (not shown) represents the relative enrichment of Mn, Zn, Pb and Ti, likely indicative of adsorbed transition metals on oxy-hydroxide coatings resulting from groundwater interactions in soils. These coatings are likely to occur on minerals of large surface areas (e.g., clays) in low- to medium-energy environments, reflected in the symbol sizes shown in LCP soils of Figure 11. LCP soils show the greatest relative increase in these elements compared to other media, consistent with low-energy environments where groundwater effects are stable.

6.5. Linear discriminant analysis of stream sediments and soils of the UCP and LCP

Testing the 4 types of data for the uniqueness of their depositional environment was carried out using linear discriminant analysis (LDA) (Venables and Ripley, 2002). LDA is sensitive to differences in variances of the groups that are tested. The analysis of variance revealed that many elements show similar variances, whereas others do not. The quadratic discriminant analysis function (QDA) can be used to derive discriminant scores when the variances between the groups are not equal. Both the QDA and LDA methods were tested using the geochemical data. Results indicated that there was little difference between the two methods, so only the LDA analysis is reported here.

The 4 groups of data were evaluated for two scenarios; stream sediment – soil pairs that are less than 7500 m apart and stream sediment-soil pairs that are less than 2500 m apart. Table 1 shows the LDA results for pairs that are less than 7500 m apart and a plot of the scores for the first two discriminant functions is shown in Figure 12. The classification procedure was also subjected to a 10-fold cross validation (10 random selections of the 468 observations), the results of which are shown in Table 1. Figure 12 shows the discriminant scores coded for the source as shown in the legend. The WI is shown by the relative size of the symbols used for the scores. From Figure 12, it is apparent that UCP stream-sediment scores have the highest WI values and a large amount of dispersion relative to soils of both the UCP and LCP. LCP stream sediments also display a large amount of dispersion with some overlap with UCP stream sediments. Scores for soils from both the UCP and LCP have lower WI values and show much less dispersion relative to stream sediments. There is some overlap between the UCP and LCP soil scores, and this region of overlap also displays higher WI values suggesting a higher energy depositional environment for these samples. Both soil groups and stream-sediment groups overlap to some degree with each other, but the overlap between soils and stream sediments appears to be minimal and mostly due to the presence of outliers.

Table 1 shows the trace of the discriminant roots where the first discriminant function accounts for 69.7% of the separation of the groups. The second and third discriminant functions account for 24.1% and 6.2% of group separation, respectively. The overall accuracy of the classification is 86.54%, and the confusion matrix indicates that there is confusion between UCP and LCP soils and UCP and LCP stream sediments, but little confusion between all stream sediments and all soils. An analysis of variance was carried out on the 4 groups of data to determine which elements best distinguished the groups. The results of the analysis are shown in Figure 13, where the F-values determined from the analysis are plotted. From Figure 13, it appears that As is the best discriminator among the groups, while Fe shows the poorest discrimination among the groups. The lack of discriminating power for Fe, Pb, Mn, Nb and Sc is most probably due to these elements' ubiquitous nature as co-precipitates in oxy-hydroxide coatings on minerals due to groundwater interaction with stream sediments and soils. Thorium and rare earth elements associated with heavy minerals (La, Nd, Ce and Y) appear to be good discriminators, followed by elements associated with feldspars (Na, K, Sr and Ba). Aluminum, the most diagnostic element for clays, appears to have moderate discriminating ability.

Because stream sediment – soil pairs of less than 2500 m have higher correlations for several elements, an LDA was repeated on the subset of these pairs with distances of less than 2500 m (88 observations). Table 2 shows the numeric results of the analysis. Because there are only 12 observations for UCP stream sediments and soils, a reduced number of elements was used to carry out the LDA. The elements chosen (Al, Fe, Ce, Th, K and As) represent the major mineral groups and oxy-hydroxide coatings observed in the principal component analysis. The scores for the first two discriminant functions for pairs less than 2500 m apart are shown in Figure 14. In Figure 14, the data fall into 4 very clear groups. Stream sediments of the UCP and LCP overlap, as do soils of the UCP and LCP, but stream sediments are largely distinct from soils. There is an overall accuracy of prediction of 86.4% (Table 2). From the LDA, it can be concluded that there is sufficient distinction between the soils and stream sediments to consider looking at functional relationships or predicting the composition of a soil or stream sediment when given the other.

6.6. Estimation of soil composition based on stream-sediment composition

The composition of soils is of primary concern for many environmental issues. Given the fact that there exists extensive stream-sediment coverage across the United States, can the chemical composition of a local soil be estimated given the chemical composition of a stream sediment? In a study based on a sample size of 84 pairs of stream-sediment and soil compositions from the UCP, Garrett et al. (2005) concluded that stream-sediment compositions from South Carolina could not be used to estimate soil compositions. The attempted correlation technique in Garrett et al. (2005) was based on a least trimmed squares (LTS) approach to mean values of elements as a function of a WI calculated as described above using Th/Al ratios. They concluded that, due to the complexity and contrasts among the various stream-sediment depositional environments, it was not possible to estimate soil compositions. However, their analysis did not take into account the distance between stream sediment and soil pairs. As shown in Figures 7 and 8, some elements show a high correlation coefficient between the two sample media when the stream sediment-soil pair distance is less than 2500 m. Not all elements show the same level of correlation, and the correlation of elements between the two types of media of the UCP is generally lower than those of the LCP.

In order to test the ability to predict soil compositions, all stream sediment - soil pairs were selected from the LCP group where their separation distance is less than 2500 m. Although higher correlations were observed for pair distances of less than 2500 m (see Figs 7 and 8), the number of observations were significantly fewer and in some cases extreme values between low values and high values defined the linear trend, which could be interpreted as false correlations. A linear regression was carried out for the elements, Al, Ce, K, Th, Fe, P, As, Ca and Zn. These elements were chosen for the representative features in the study. Aluminum represents clay minerals, whereas Ce, P and Th represent the detrital heavy minerals. Potassium was chosen as a representative for feldspars and Ca was chosen as a representative of feldspars and carbonates. Iron and Zn represent the effects of groundwater and subsequent precipitation of oxy-hydroxide coatings, and As was chosen as an element of environmental concern. A summary of results from the linear regression is shown in Table 3 where the F-value, R^2, adjusted R^2, and p-values are shown as diagnostic measures of the regression.

In Figure15, plots of soil versus stream sediments for the selected elements include the calculated regression line and the 90 % confidence limits. The symbol size for each observation is based on the WI. It is apparent that the correlations are not strong, as many of the data values are outside the confidence intervals. Of the 9 elements, Ce, K and Th have the smallest number of observations outside of the confidence intervals. Table 3 indicates that Al, Ce, K, Fe and P have R^2 values > 0.2, which is slightly below the level of significance for 41 degrees of freedom at the 90% level of significance. These elements also have p-values of 0.00. The predictions for Zn are clearly the poorest among this group of elements. The Zn p-value is large with a near-zero R^2 value. From Figure 15, there appears to be a crude level of correlation between stream sediments and soils for Al, Ce, K, Th, Fe, P, Ca and As. Zinc shows no correlation between the two sample media. Examination of the correlations of Ce and Th shows a consistent increase of the WI with increasing concentrations for those elements. As would be expected, Al shows the inverse; WI increases with lower Al abundance. From this analysis of these selected elements and samples with pair distances less than 2500 m, the degree of correlation is weak, at best. This same group of elements was subjected to the same linear regression with sample pair distances less than 7500 m. The regression results were much less significant. It is also worth noting that for several of the elements, such as As, Ca, and Zn, observations that plot outside of the 90% confidence interval, in general, have a higher WI.

7. Summary and Conclusions

This evaluation of the stream sediment–soil pairs from the UCP and LCP of South Carolina has established a number of interesting observations:

1) The character of the stream sediments and soils in the Coastal Plain can be defined geochemically based on their affinity with specific elements, which reflect mineralogies in specific depositional environments as described in field studies. Major differences among depositional environments are spatially delineated by the Orangeburg Scarp, separating the UCP from the LCP.

2) There is a significant contrast in the character of UCP and LCP stream sediments and soils. Generally, LCP stream sediments and soils have a lower WI. LCP soils have the lowest WI and the UCP stream sediments have the highest WI.
3) LCP soils have a greater relative quantity of elements typically adsorbed to oxy-hydroxide coatings on clay and lighter residual ferromagnesian minerals, characteristics attributed to groundwater effects in a low-energy post-depositional environment. UCP and LCP stream sediments have correspondingly higher concentrations of rare earth elements because of the concentration of weathering-resistant minerals of higher density (e.g., monazite, zircon, ilmenite). Minerals of medium density, including feldspars and carbonates, are primarily reflected in LCP stream sediments and soils.
4) The 4 groups of materials are statistically distinct with some degree of overlap between LCP and UCP soils and LCP and UCP stream sediments. There is minimal overlap between stream sediments and soils in both depositional environments. The elements that best discriminate among these groups are As, Th, La, Nd, Ce, Y, Mg, Ca, Li, Na, P, Ba, Sr and K.
5) The most significant influence in the relation between geochemistry and the depositional environments appears to be the separation distance between stream-sediment and soil pairs. From some elements, there are significant correlations between stream sediment – soil pairs at separation distances of less than 2500 m. However, the correlation between the stream sediment – soil pairs is different between the UCP and LCP. Generally, the correlations between the LCP stream sediment – soil pairs are higher.
6) From Figures 7 and 8, it appears that prediction of soil composition based on stream-sediment composition is dependant on the distances between stream sediment – soil pairs. However, the number of pairs from which each prediction is made decreases with decreasing separation distance of the sediment – soil pairs. Thus, such correlations must be interpreted cautiously. The winnowing index, shown by the size of the symbols in Figure 15, also influences the degree of correlation. Many more high values of the WI (larger symbols) occur outside the confidence intervals than low values. This pattern exists independently of pair separation distance. Thus, the prediction of a soil composition based on a stream-sediment composition will depend on the degree of reworking (winnowing, weathering) and proximity. These parameters should be measured and assessed prior any type of prediction. Garrett et al. (2005) did not utilize spatial analysis of the stream sediment – soil pairs, which has been done in this study. The results of

> evaluating the stream sediment – soil pairs as a function of separation distance has provided additional insight into the ability to predict one composition given the other. Therefore, using the stream sediment – soil pairs for separation distances of less than 2500 m has resulted in improved prediction, which is nonetheless quite low as seen in Table 3. Given the complex depositional history of these materials, as demonstrated in this study, such calculations are unlikely to yield accurate predictions. In areas where the depositional history is less complicated (i.e., little reworking or winnowing), prediction of soil composition may be more straightforward.

The use of a winnowing index, principal component analysis and linear discriminant analysis has enabled clear differentiation between the stream sediments and the soils from both the upper and lower coastal plains and has shown that their compositions are statistically distinct. This, in turn, has assisted in the definition of a process diagram as illustrated in Figure 16. This figure starts with the parent material at the top (west of the Fall Zone) followed by an idealized series of processes by which the material is weathered, transported, sorted, reworked and weathered again on the LCP. Throughout these successive and cyclical processes, the effect of groundwater interaction with the material (co-precipitation of oxy-hydroxides) is also important. This type of process diagram fits with the features observed above.

This study has described a systematic methodology for examining the relationships between stream sediments and soils in an environment that is unique to the southeastern United States. The influence of the reworking of weathered materials derived from the Piedmont region west of the Fall Zone, and depositional and erosional process within the Coastal Plain on either side of the Orangeburg Scarp have a clear influence on the geochemical relationships between stream sediments and soils in the different regions.

The use of log ratios removes the bias of closure and permits the evaluation of data across the full range of the real number space. The use of multivariate methods such as principal component analysis and linear discriminant analysis describes the character and uniqueness of the 4 groups of data. Results of the analysis also indicate that only some of the elements can be used to correlate between stream sediments and soils; the correlation is weak for the UCP and stronger for a few elements in the LCP. It is concluded that this approach to evaluating geochemical data yields maximum information from which geological and geochemical processes can be described.

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Figure captions

Figure 1. Location map, geological provinces, hydrology and topographic features of South Carolina.

Figure 2. Shaded relief digital elevation model of South Carolina with pseudocolour defining the elevation range. Sun azimuth 45 degrees; elevation-45 degrees.

Figure 3. Location of matched NURE stream sediment soil pair samples in South Carolina. Only one pair per catchment area.

Figure 4. Experimental semi-variograms of Al for UCP stream sediments (a), UCP soils (b), LCP stream sediments (c), and LCP soils (d) using a maximum lag of 80,000 m and lag interval of 10,000 m. The search was isotropic with a fitted exponential model. Distances in km.

Figure 5. Experimental semi-variograms of Th for UCP stream sediments (a), UCP soils (b), LCP stream sediments (c), and LCP soils (d) using a maximum lag of 80,000 m and lag interval of 10,000 m. The search was isotropic with a fitted exponential model. Distances in km.

Figure 6. Histogram of distances between matched stream sediment – soil samples. Paired samples with distances of less than 7,500 m were selected for further study

Figure 7. Correlation of stream sediment – soil pairs as a function of separation distance for Al (a), K (b), Fe (c) and Th (d) for the Upper Coastal Plain. Distances in meters.

Figure 8. Correlation of stream sediment – soil pairs as a function of separation distance for Al (a), K (b), Fe (c) and Th (d) for the Lower Coastal Plain. Distances in meters.

Figure 9. (a) Plot of Th versus Al (log centered coordinates). Symbols represent the source material as noted in the legend. Symbol sizes based on a winnowing index described in the text. (b) Quantile-quantile plot of the winnowing index. Symbol sizes based on a winnowing index described in the text.

Figure 10. Map of winnowing index values for the stream sediments and soils

Figure 11. Biplot of principal components 1 and 2 for the stream sediment – soil geochemistry pairs from the LCP and UCP. Symbol sizes are proportional to the ratio of Th/Al, the index of winnowing.

Figure 12. Plot of the linear discriminant scores for stream sediment – soil pairs with a separation distance of less than 7500 m. Symbol sizes are proportional to the ratio of Th/Al, the index of winnowing. Note the overall clear distinction between the 4 groups of data.

Figure 13. Plot of F-value from an analysis of variance of the 4 groups (UCP and LCP stream sediment – soil pairs).

Figure 14. Plot of the first two linear discriminant scores for the 88 UCP and LCP stream sediment – soil pairs for Al, K, Fe, Ce, Th and As. Symbol sizes are proportional to the ratio of Th/Al, the index of winnowing.

Figure 15. Predicted values of elements between stream sediments and soils from the LCP based on stream sediment – soil pair separation distances of less than 2500 m. All values are expressed in log-centred coordinates. Dashed lines on either side of the solid regression line represent the 90% confidence interval. Symbol sizes are proportional to the winnowing index. Note that for many of the observations outside the 90% confidence interval, the winnowing index is generally larger.

Figure 16. Proposed model of the relationship between stream sediments and soils. Stream sediment formation and soil formation are dependent on several processes including gravitational-fluvial processes, marine coastal reworking, in situ weathering and groundwater effects.

Table 1
Measures of accuracy derived from the linear discriminant analysis for stream sediment – soil pair separation distances of less than 7500 m. The analysis was applied to UCP and LCP stream sediments and soils.

468 observations
Elements: Al, Ca, Fe, K, Mg, Na, P, Ti, Ba, Ce, Cr, Cu, La, Li, Mn, Nb, Nd, Pb, Sc, Sr, Th, V, Y, Zn, As

Prior probabilities of groups:

LCP_Soil	LCP_Stream	UCP_Soil	UCP_Stream
0.36	0.36	0.14	0.14

Proportion of trace:

LD1	LD2	LD3
0.70	0.24	0.06

10-fold Cross Validation
Raw Confusion Matric

Type	LCP_Soil	LCP_Stream	UCP_Soil	UCP_Stream
LCP_Soil	157	1	10	0
LCP_Stream	9	146	0	13
UCP_Soil	12	0	53	1
UCP_Stream	1	13	3	49

Percentage

Type	LCP_Soil	LCP_Stream	UCP_Soil	UCP_Stream
LCP_Soil	93.45	0.60	5.95	0.00
LCP_Stream	5.36	86.90	0.00	7.74
UCP_Soil	18.18	0.00	80.30	1.52
UCP_Stream	1.52	19.70	4.55	74.24

error %	13.46
accuracy %	86.54

Table 2
Measures of accuracy derived from the linear discriminant analysis for stream sediment – soil pair separation distances of less than 2500 m. The analysis was applied to UCP and LCP stream sediments and soils using the elements Al, Fe, Ce, Th, K and As.

88 Observations
Elements: Al, K, Fe, Ce, Th, As

Prior probabilities of groups:

LCP_Soil	LCP_Stream	UCP_Soil	UCP_Stream
0.36	0.36	0.14	0.14

Proportion of trace:

LD1	LD2	LD3
0.80	0.18	0.02

Raw Confusion Matrix

Type	LCP_Soil	LCP_Stream	UCP_Soil
LCP_Soil	30	0	2
LCP_Stream	1	28	2
UCP_Soil	4	0	8
UCP_Stream	0	2	0

Percentage		Predicted	
Type	**LCP_Soil**	**LCP_Stream**	**UCP_Soil**
LCP_Soil	93.75	0	6.25
LCP_Stream	3.13	87.50	6.25
UCP_Soil	33.33	0	66.67
UCP_Stream	0	16.67	0

error %	13.64
accuracy %	86.36

Table 3
Regression results on LCP stream sediment – soil pairs with separation distances of less than 2500 m.

Regression of Stream Sediment on Soil

	F-value	r2	adj. r2	p-value
Al	10.67	0.21	0.19	0.00
Ce	11.24	0.22	0.20	0.00
K	10.91	0.21	0.19	0.00
Th	2.59	0.06	0.04	0.12
Fe	12.77	0.24	0.22	0.00
P	14.27	0.26	0.24	0.00
As	2.79	0.06	0.04	0.10
Ca	6.15	0.13	0.11	0.02
Zn	0.16	0.00	-0.02	0.69

Numerator Degrees of Freedom	1
Deonminator Degrees of Freedom	41

Fig.1

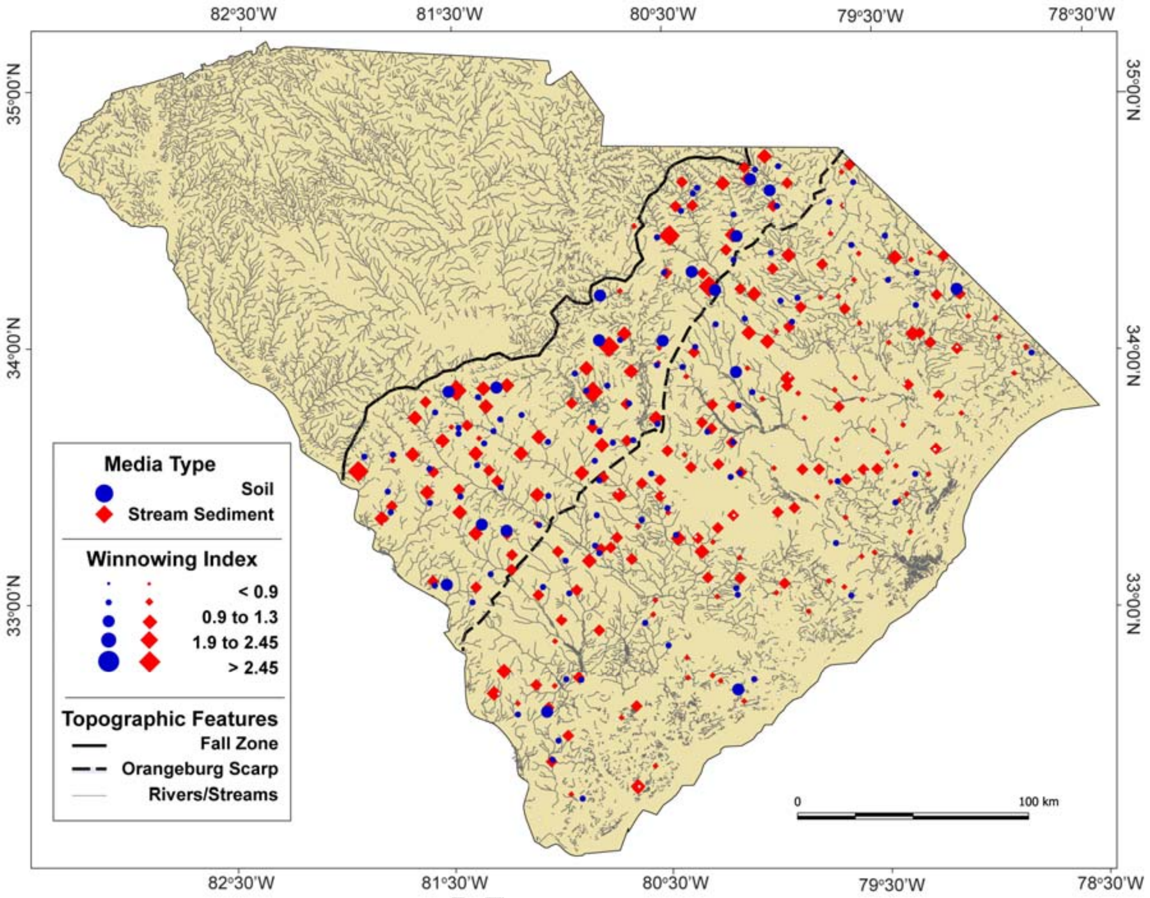

82°30'W
81°30'W
80°30'W
79°30'W
78°30'W
35°00'N
34°00'N
33°00'N
Media Type
Soil
Stream Sediment
Winnowing Index
< 0.9
0.9 to 1.3
1.9 to 2.45
> 2.45
Topographic Features
Fall Zone
Orangeburg Scarp
Rivers/Streams
0
100 km

Fig.2

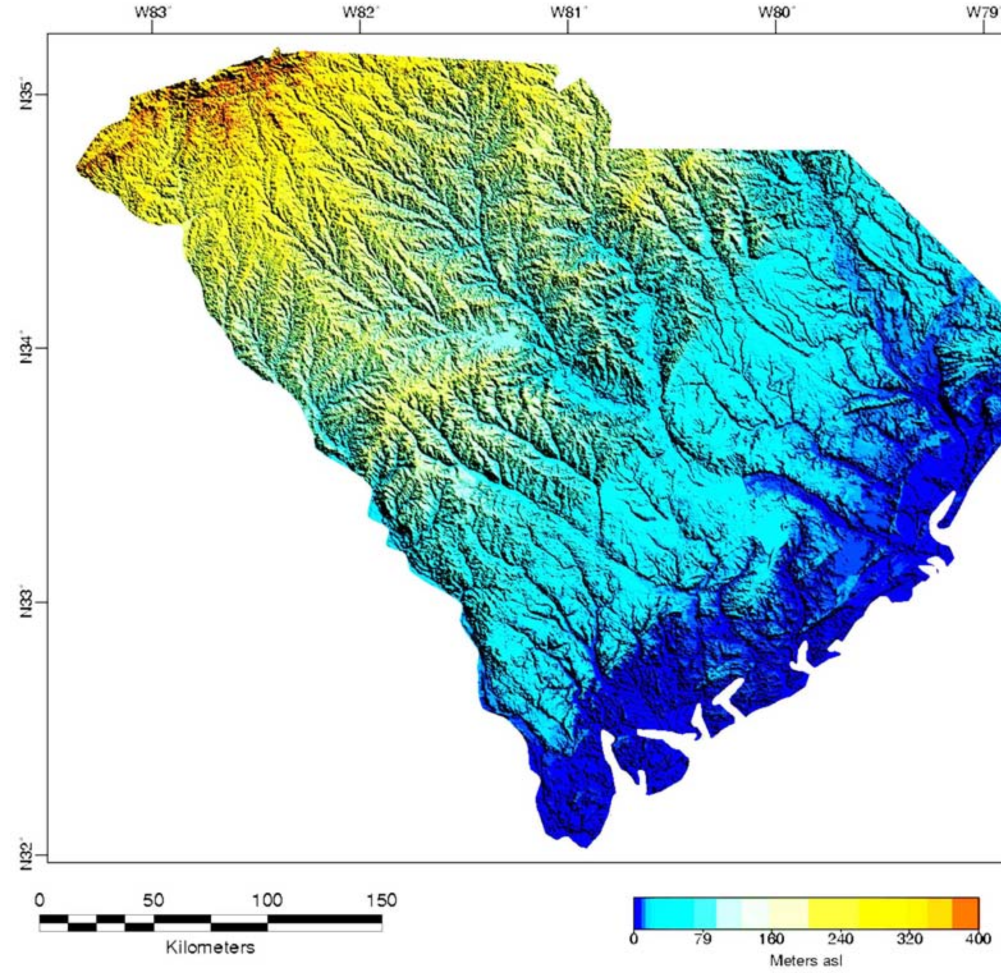

W83°
W82°
W81°
W80°
W79°
N35°
N34°
N33°
N32°
0
50
100
150
Kilometers
0
79
160
240
320
400
Meters asl

Fig.3

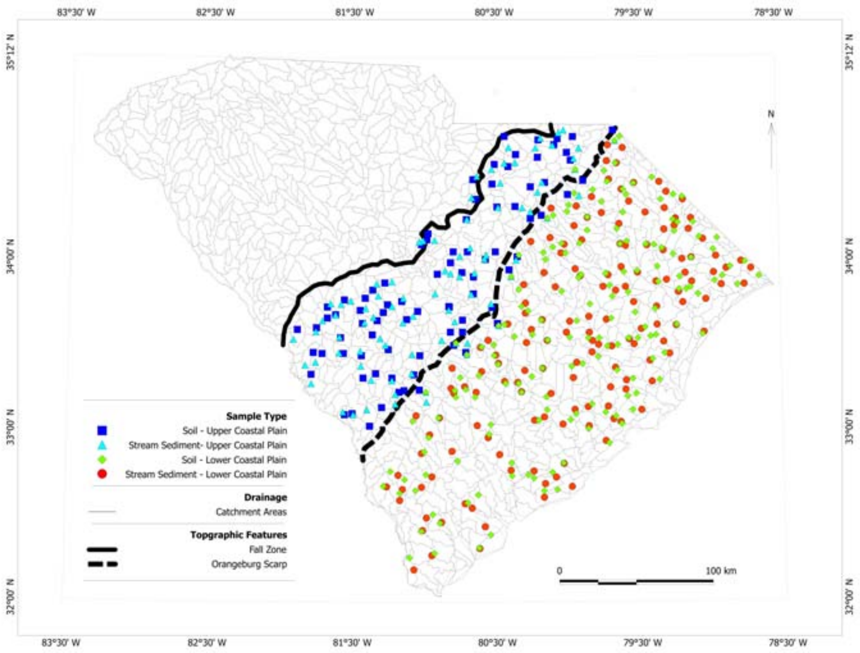

83°30' W
82°30' W
81°30' W
80°30' W
79°30' W
78°30' W
35°12' N
34°00' N
33°00' N
32°00' N
N
Sample Type
Soil - Upper Coastal Plain
Stream Sediment- Upper Coastal Plain
Soil - Lower Coastal Plain
Stream Sediment - Lower Coastal Plain
Drainage
Catchment Areas
Topgraphic Features
Fall Zone
Orangeburg Scarp
0
100 km

Fig.4

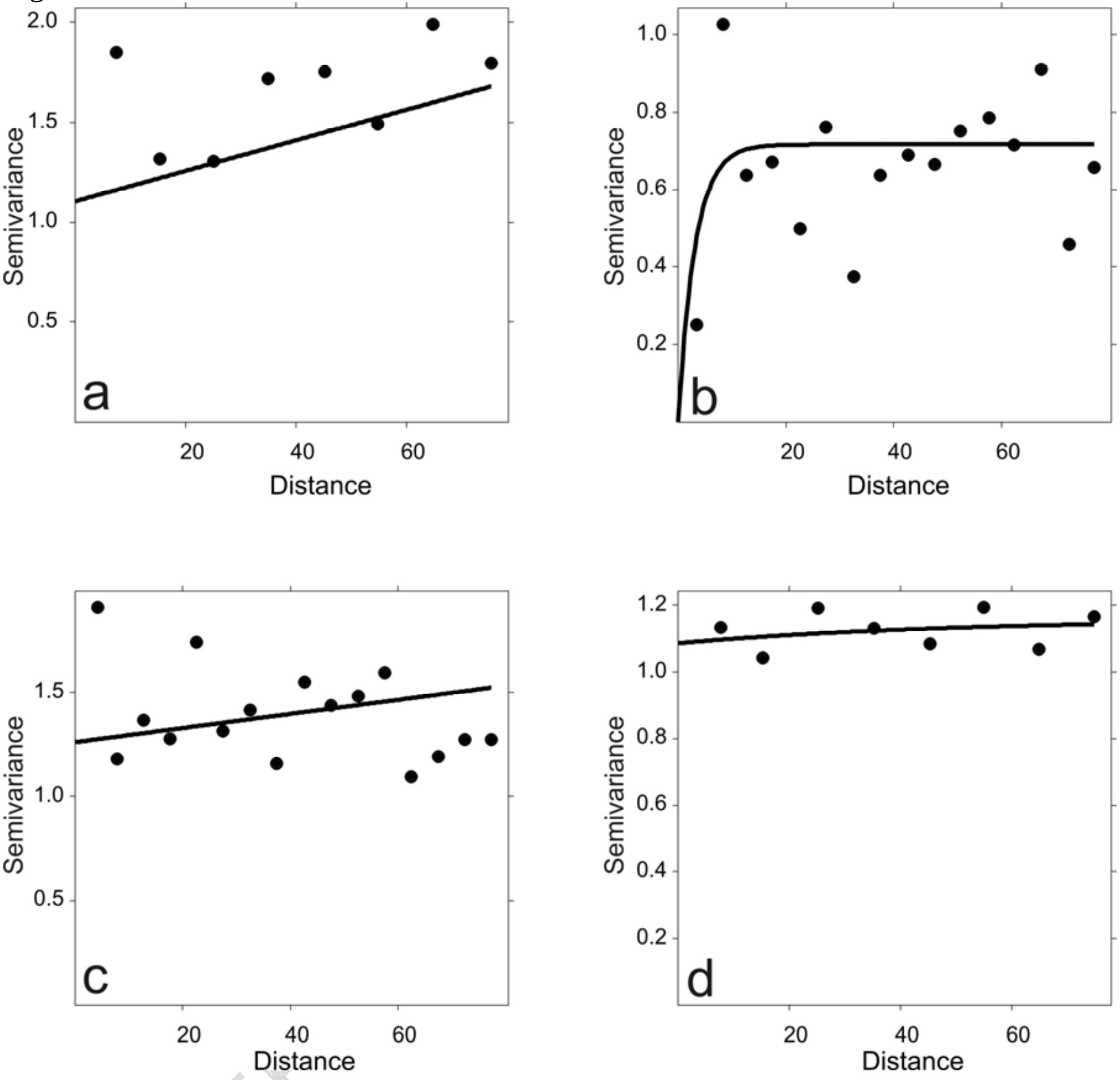

2.0
1.5
1.0
0.5
Semivariance
a
20
40
60
Distance
1.0
0.8
0.6
0.4
0.2
Semivariance
b
20
40
60
Distance
1.5
1.0
0.5
Semivariance
c
20
40
60
Distance
1.2
1.0
0.8
0.6
0.4
0.2
Semivariance
d
20
40
60
Distance

Fig.5

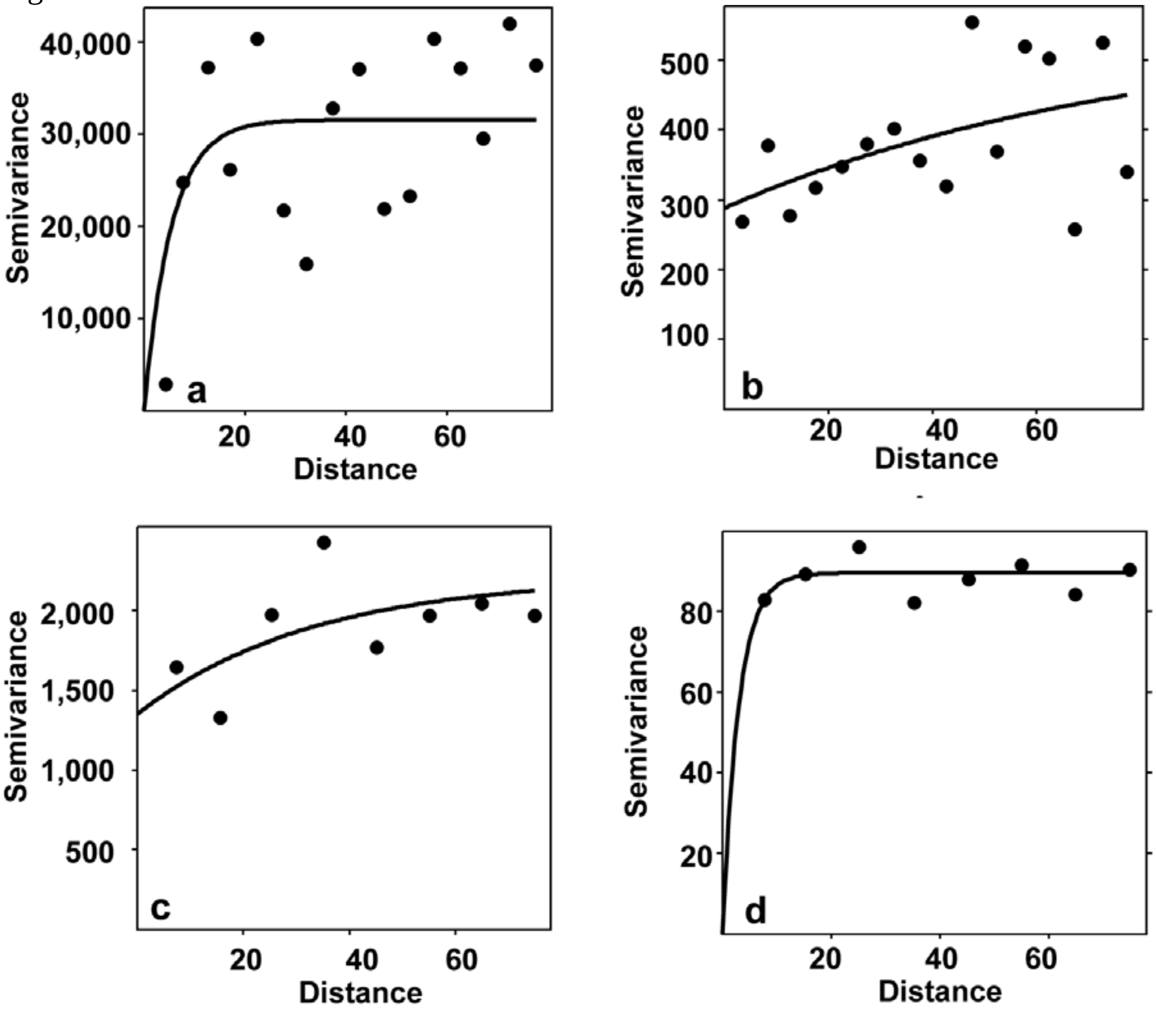

Semivariance
40,000
30,000
20,000
10,000
a
20
40
60
Distance
Semivariance
500
400
300
200
100
b
20
40
60
Distance
Semivariance
2,000
1,500
1,000
500
c
20
40
60
Distance
Semivariance
80
60
40
20
d
20
40
60
Distance

Fig.6

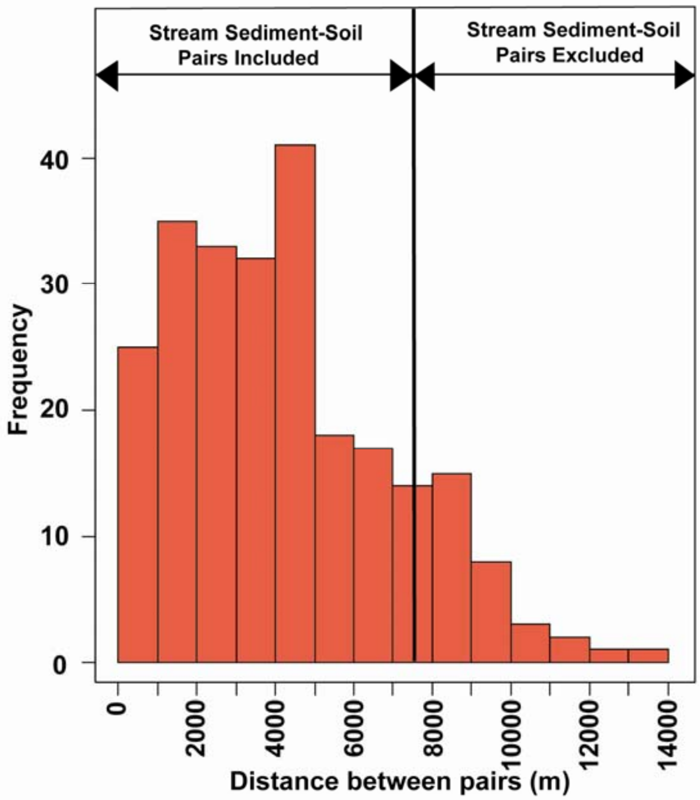

Stream Sediment-Soil Pairs Included
Stream Sediment-Soil Pairs Excluded
Frequency
0
10
20
30
40
0
2000
4000
6000
8000
10000
12000
14000
Distance between pairs (m)

Fig.7

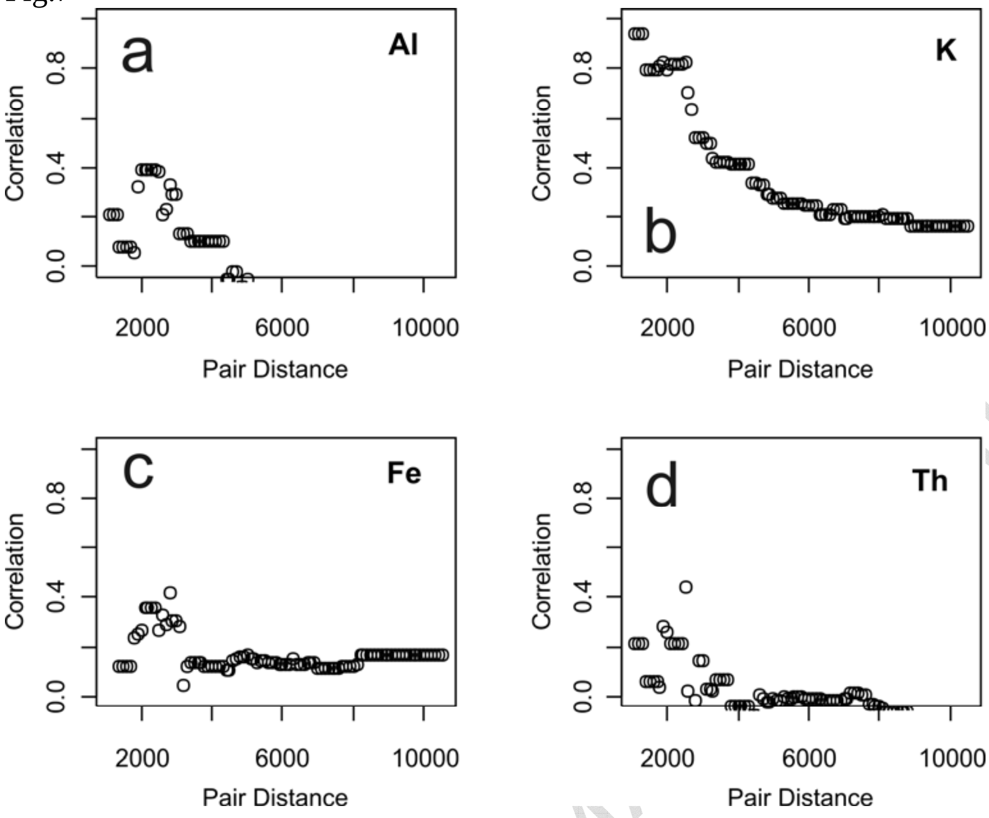

a
Al
b
K
c
Fe
d
Th
Correlation
0.0
0.4
0.8
Pair Distance
2000
6000
10000

Fig.8

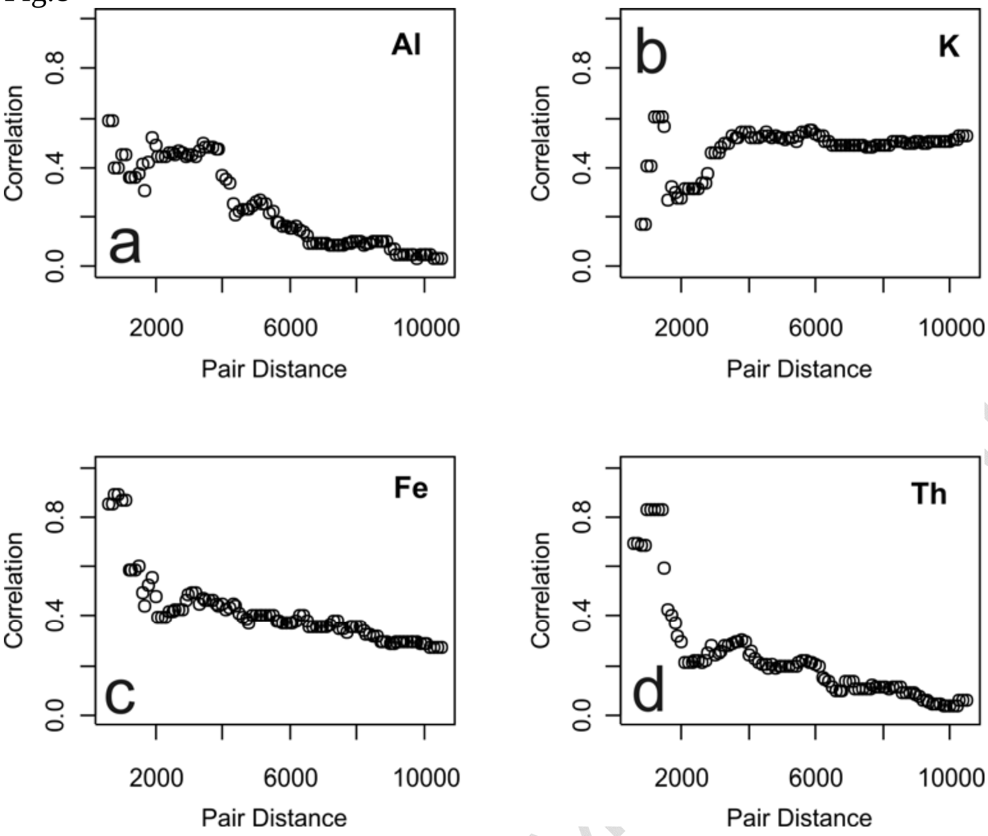

Al
a
b
K
Fe
c
Th
d
Correlation
0.0
0.4
0.8
Pair Distance
2000
6000
10000

Fig.9

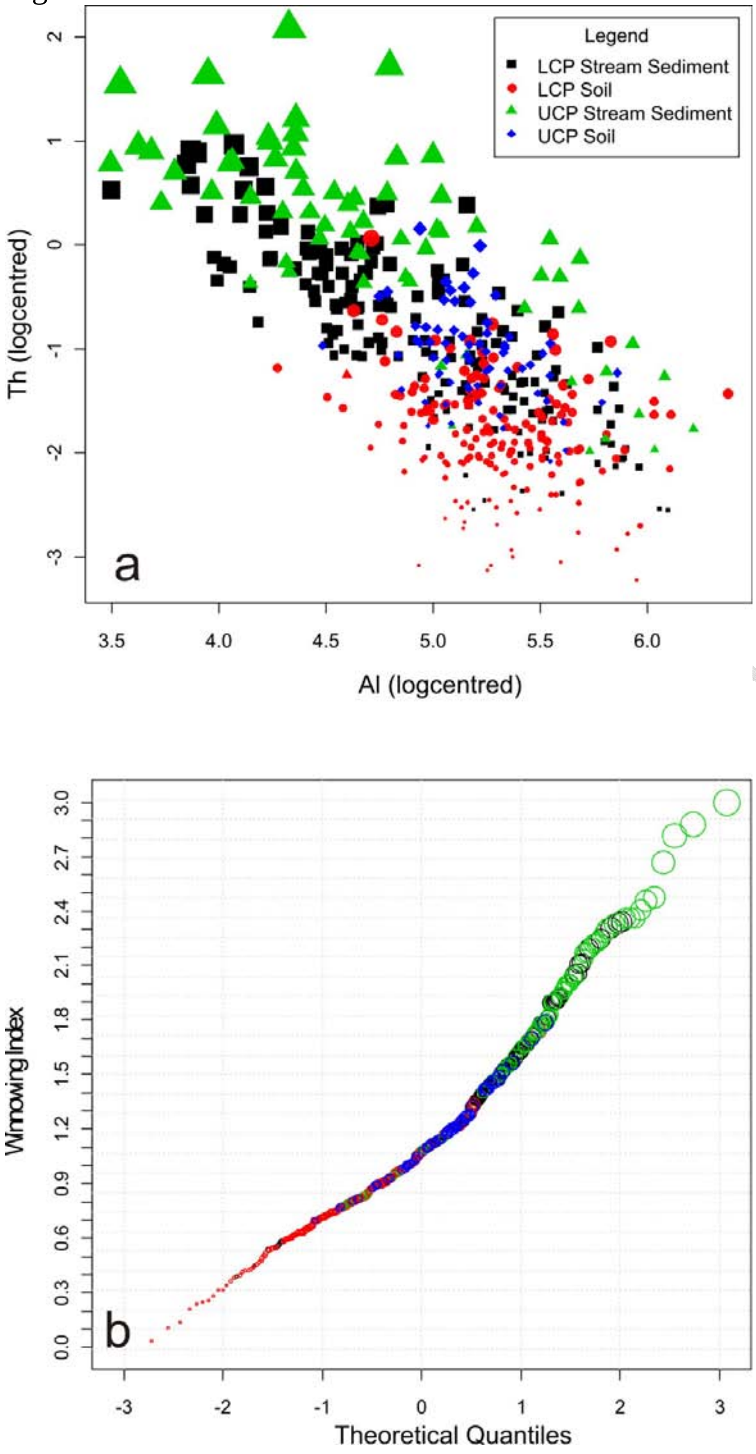

Legend
LCP Stream Sediment
LCP Soil
UCP Stream Sediment
UCP Soil
Th (logcentred)
2
1
0
-1
-2
-3
a
3.5
4.0
4.5
5.0
5.5
6.0
Al (logcentred)
Winnowing Index
3.0
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0.0
b
-3
-2
-1
0
1
2
3
Theoretical Quantiles

Fig.10

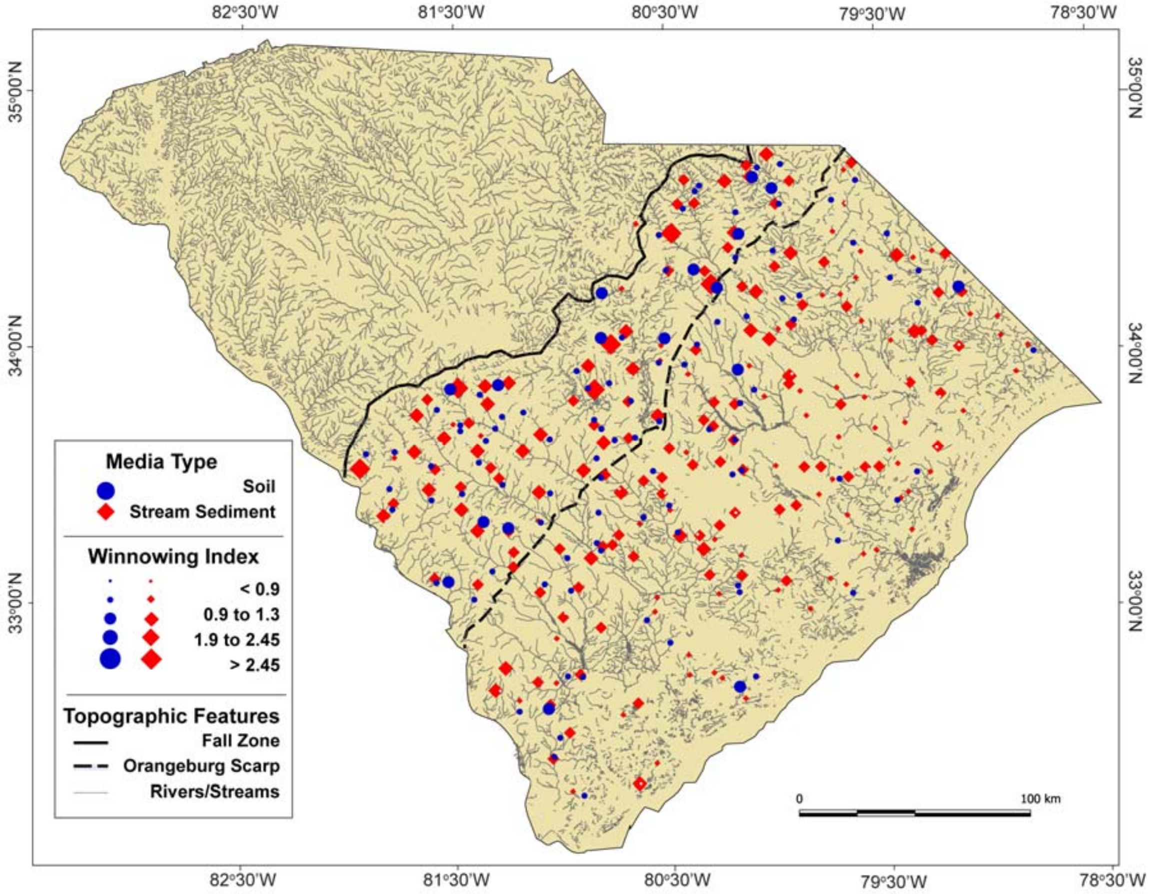
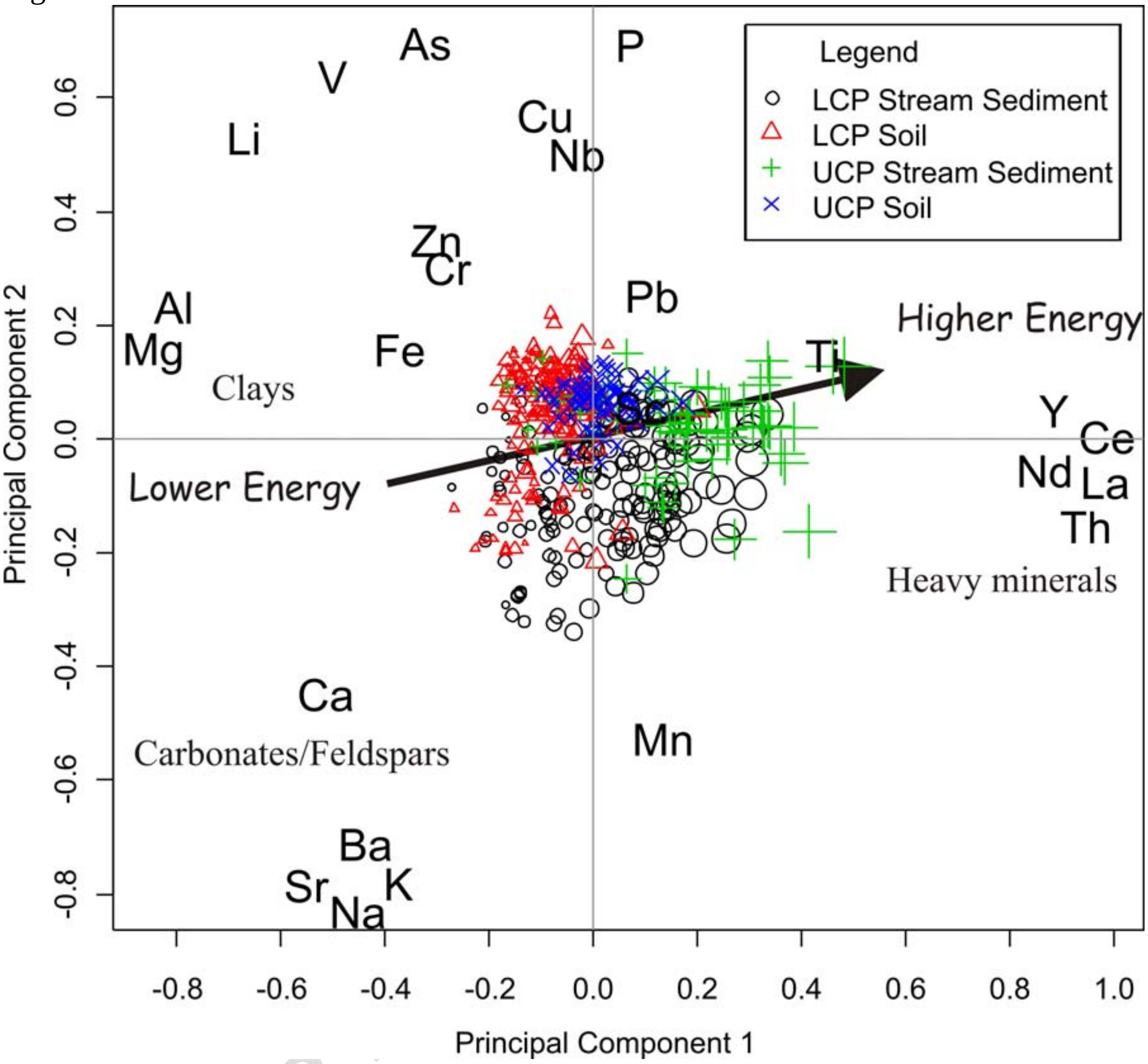

82°30'W
81°30'W
80°30'W
79°30'W
78°30'W
35°00'N
34°00'N
33°00'N
Media Type
Soil
Stream Sediment
Winnowing Index
< 0.9
0.9 to 1.3
1.9 to 2.45
> 2.45
Topographic Features
Fall Zone
Orangeburg Scarp
Rivers/Streams
0
100 km

Fig.11



Legend
○ LCP Stream Sediment
△ LCP Soil
+ UCP Stream Sediment
× UCP Soil
As
V
P
Cu
Li
Nb
Zn
Cr
Al
Mg
Fe
Pb
Higher Energy
Ti
Clays
Sc
Y
Ce
Lower Energy
Nd
La
Th
Heavy minerals
Ca
Carbonates/Feldspars
Mn
Ba
Sr
Na
K
Principal Component 2
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
Principal Component 1

Fig.12

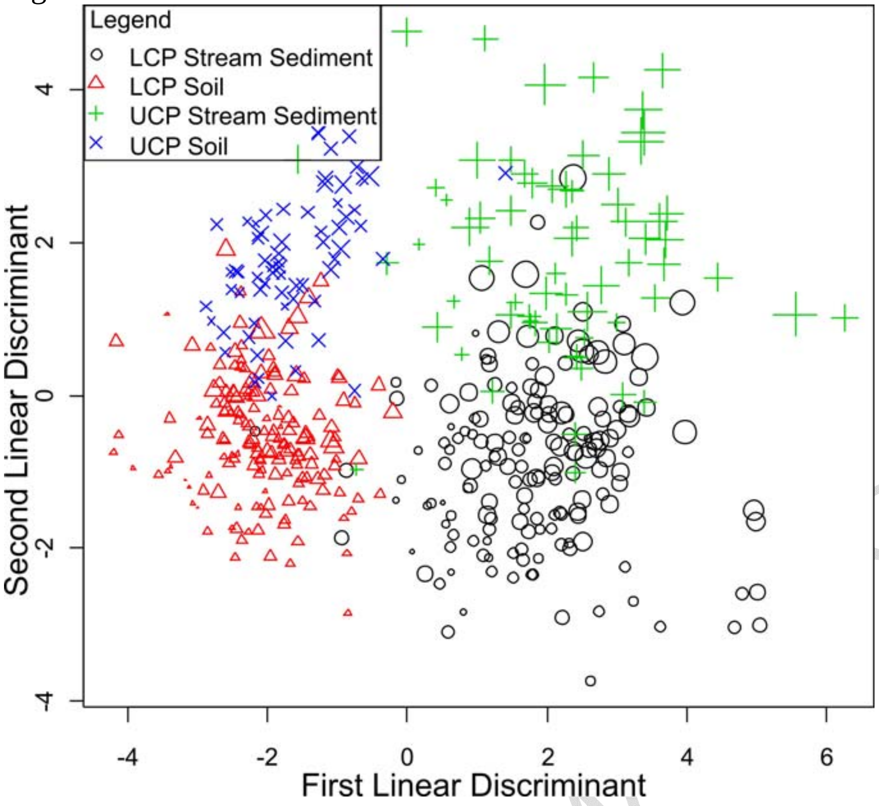

Legend
○ LCP Stream Sediment
△ LCP Soil
+ UCP Stream Sediment
× UCP Soil
Second Linear Discriminant
First Linear Discriminant
-4
-2
0
2
4
6
-4
-2
0
2
4

Fig.13

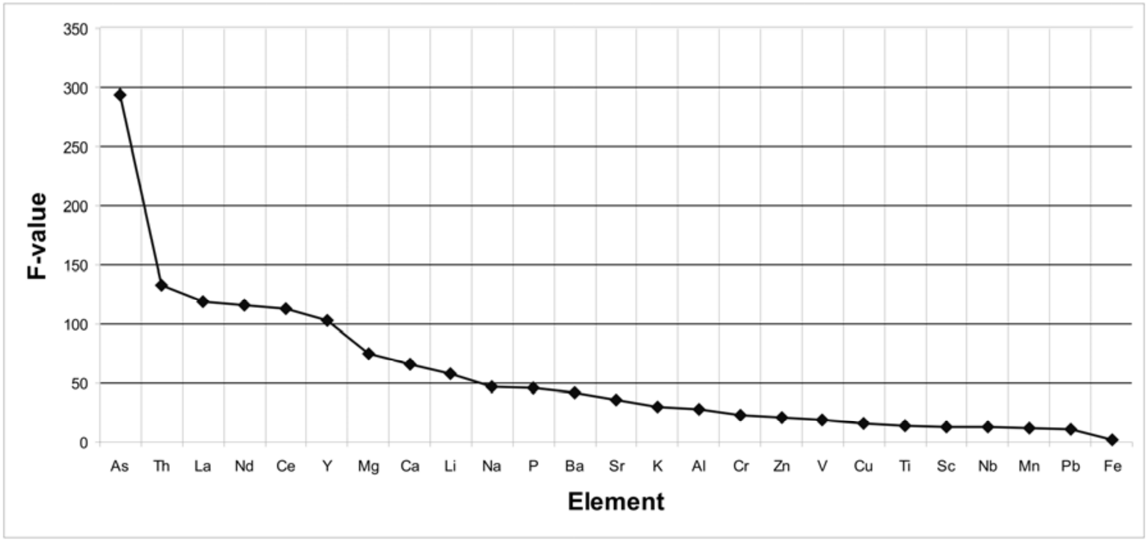

F-value
0
50
100
150
200
250
300
350
As
Th
La
Nd
Ce
Y
Mg
Ca
Li
Na
P
Ba
Sr
K
Al
Cr
Zn
V
Cu
Ti
Sc
Nb
Mn
Pb
Fe
Element

Fig.14

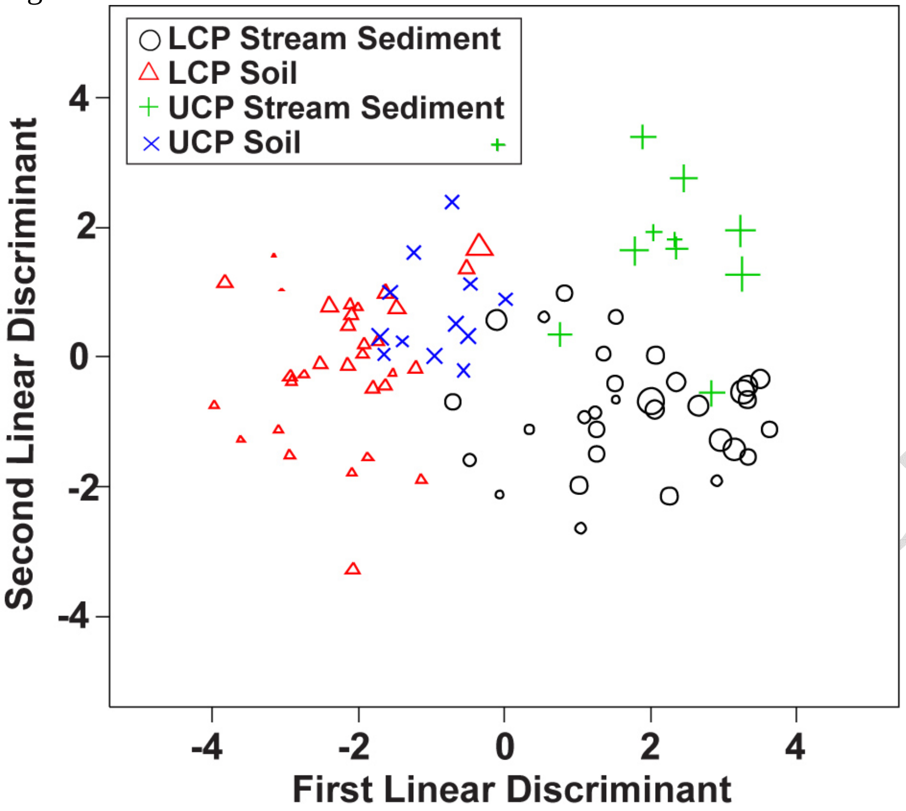

○ LCP Stream Sediment
△ LCP Soil
+ UCP Stream Sediment
× UCP Soil
4
2
0
-2
-4
Second Linear Discriminant
-4
-2
0
2
4
First Linear Discriminant

Fig.15

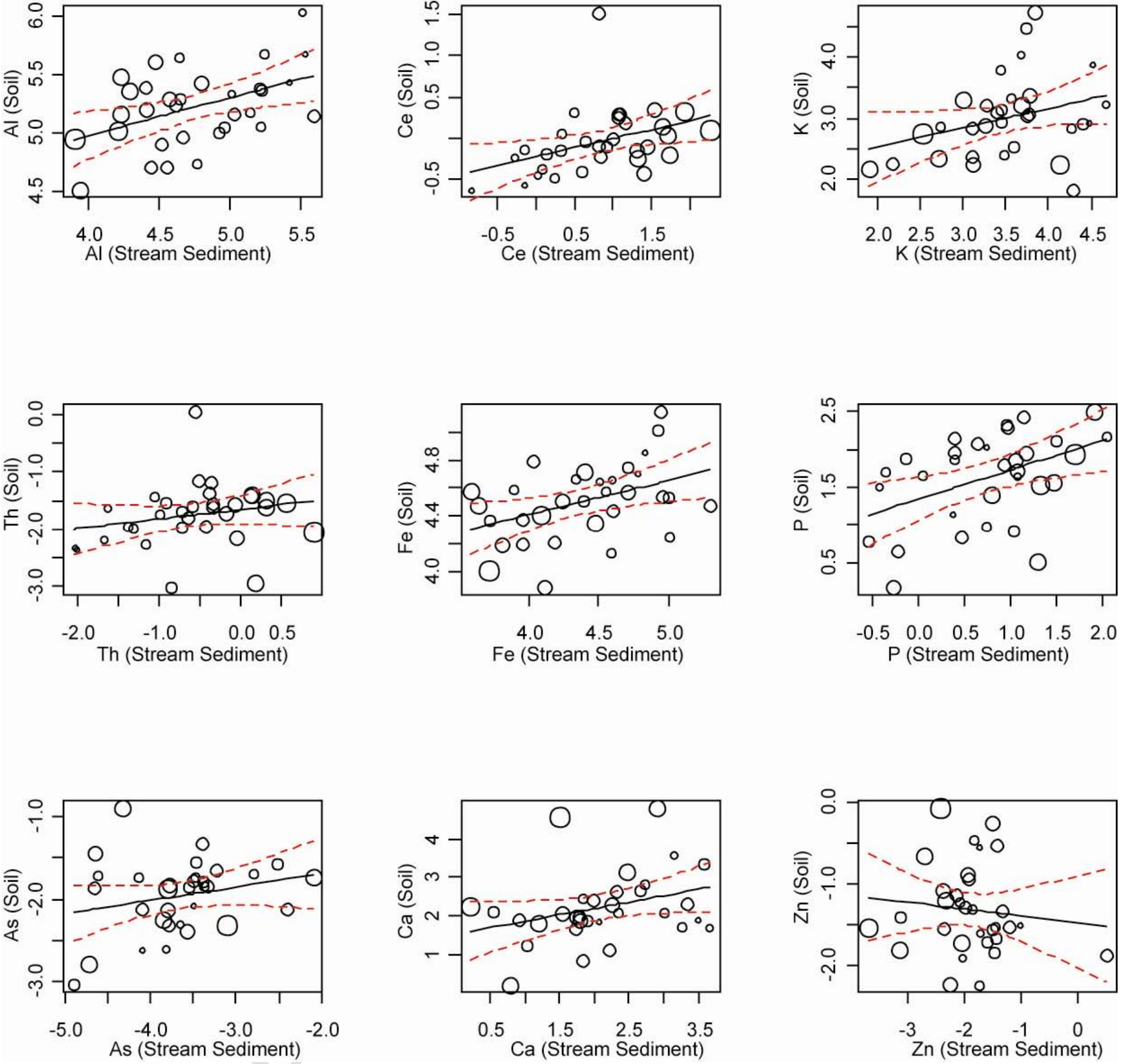
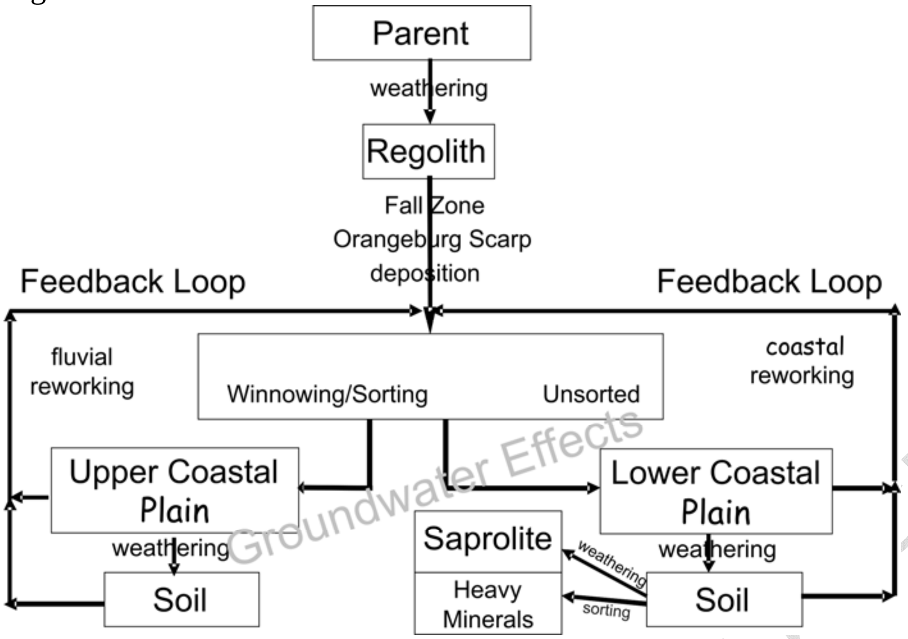

Al (Soil)
4.5
5.0
5.5
6.0
4.0
4.5
5.0
5.5
Al (Stream Sediment)
Ce (Soil)
-0.5
0.5
1.0
1.5
-0.5
0.5
1.5
Ce (Stream Sediment)
K (Soil)
2.0
3.0
4.0
2.0
2.5
3.0
3.5
4.0
4.5
K (Stream Sediment)
Th (Soil)
-3.0
-2.0
-1.0
0.0
-2.0
-1.0
0.0
0.5
Th (Stream Sediment)
Fe (Soil)
4.0
4.4
4.8
4.0
4.5
5.0
Fe (Stream Sediment)
P (Soil)
0.5
1.5
2.5
-0.5
0.0
0.5
1.0
1.5
2.0
P (Stream Sediment)
As (Soil)
-3.0
-2.0
-1.0
-5.0
-4.0
-3.0
-2.0
As (Stream Sediment)
Ca (Soil)
1
2
3
4
0.5
1.5
2.5
3.5
Ca (Stream Sediment)
Zn (Soil)
-2.0
-1.0
0.0
-3
-2
-1
0
Zn (Stream Sediment)

Fig.16


Parent
weathering
Regolith
Fall Zone
Orangeburg Scarp
deposition
Feedback Loop
Feedback Loop
fluvial
reworking
coastal
reworking
Winnowing/Sorting
Unsorted
Upper Coastal Plain
Lower Coastal Plain
Groundwater Effects
Saprolite
Heavy Minerals
weathering
sorting
weathering
weathering
Soil
Soil