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The Evaluation of a Chemical Fingerprinting Technique for Identifying the Sources of In-stream Sediments

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To the Graduate Council:

I am submitting herewith a thesis written by Robert Alexander Hull entitled "The Evaluation of a Chemical Fingerprinting Technique for Identifying the Sources of In-stream Sediments." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental and Soil Sciences.

Michael E. Essington, Major Professor

We have read this thesis and recommend its acceptance:

Forbes R. Walker, Carol P. Harden

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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The Evaluation of a Chemical Fingerprinting Technique for Identifying the Sources of In-stream Sediments

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Robert Alexander Hull
December 2008

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Abstract

Sediment is often listed as one of the main contributors to the impairment of surface waters throughout the United States. Sediment source identification is difficult in watersheds with complex combinations of land-uses and non-point sources because of the complexities involved in correlating water quality data, which are relatively easy to collect, to the source of a degrading component. The elemental properties of a particular soil on the landscape may be viewed as a “fingerprint”. A comparison of the elemental fingerprints of potential sources and in-stream sediment may be used to establish sediment source. The objectives of this investigation were to characterize the elemental content of suspended stream sediment and potential sources of sediment in an impaired watershed, Pond Creek watershed in east Tennessee (HUC: TN06010201013), and to use multivariate statistical techniques to identify and quantify sediment sources in the watershed. Potential sediment source samples were collected throughout the watershed and suspended sediment samples at two locations. Subsamples of the <53 µm material and suspended sediment were subjected to total dissolution, HNO_3-extraction, and Mehlich 3-extraction. Descriptive statistics suggested that each dataset contained considerable heterogeneity. The source samples were grouped according to land management and position in the landscape. The results of a Kruskal-Wallis rank test and discriminant function analysis indicated that for all three datasets the elemental variability of the samples was not sufficient to differentiate the source and sediment samples and characterize the suspended sediment sources using the initial group definitions. When using all available elemental data from each dataset the groups defined by cluster analysis and canonical discriminant analysis did not match the contents of the initially defined groups. The composition of the clusters varied from one dataset to another, making it difficult to draw conclusions concerning the cluster contents, or to identify sources of suspended sediment. The lack of elemental content variability for differentiating the source and sediment samples and characterizing the suspended sediment sources is likely an artifact of the watershed sampling procedure that was employed, which was directed towards sampling sources likely to be contributing to the suspended sediment load in Pond Creek.

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List of Abbreviations

Abbreviation	Definition
Al	Aluminum
As	Arsenic
Ba	Barium
BMPs	Best Management Practices
Ca	Calcium
CAN	Canonical variable
Cd	Cadmium
CDA	Canonical Discriminant Analysis
Ce	Cerium
Co	Cobalt
Cr	Chromium
Cu	Copper
CWA	Clean Water Act
EPA	Environmental Protection Agency
Fe	Iron
Hf	Hafnium
K	Potassium
KW	Kruskal-Wallis rank test
La	Lanthanum
Li	Lithium
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
Na	Sodium
NCDC	National Climatic Data Center
Nd	Neodymium
Ni	Nickel
NOAA	National Oceanic and Atmospheric Administration
P	Phosphorous
Pb	Lead
PC	Principal Component Variable
PCA	Principal Component Analysis
PCWC	Pond Creek Watershed Cooperative
Rb	Rubidium
S	Sulfur
Se	Selenium
Si	Silica
SNK	Student-Newman-Keuls multiple-range test

Sr	Strontium
TDEC	Tennessee Department of Environment and Conservation
TMDLs	Total Maximum Daily Loads
Ti	Titanium
V	Vanadium
Zn	Zinc
Zr	Zirconium

Introduction

Background

Sediment is one of the main contributors to the impairment of surface waters throughout the United States. The U.S. Environmental Protection Agency (U.S. EPA) estimated in 2002 that sediment and turbidity (siltation) were responsible for almost one-third of all impaired stream miles in the U.S (U.S. EPA, 2002). The term 'impaired' implies that a water body is not meeting all of its designated use requirements, one of which is habitat for fish and aquatic life (TDEC, 2008a). Siltation is usually assessed by visual surveys, measurement of total suspended solids, and biological surveys. The most emphasis is placed on the biological surveys as impairment is defined based on the occurrence of biological habitat degradation. Stream siltation is reported by more than 18 states, including Tennessee, as the principal cause of impairment (TDEC, 2006b). Of the estimated 97,400 km (60,500 mi) of streams in Tennessee, approximately 50,700 km (31,500 mi) have been assessed relative to the water quality criteria, and approximately 8,850 km (5,500 mi) of the assessed waterways are impaired by sediment (TDEC, 2008a).

Sediments are found in waterways as a result of both in-stream and landscape erosion, which are naturally occurring processes. Thus, sediments are found in even the most pristine streams and also are necessary for normal ecological function. However, the presence of excess sediments in water, often a result of human activities, can have adverse impacts on the biological, chemical, and physical properties of the water. The negative biological effects that sediments have on streams are numerous, and include smothering nests containing the eggs of fish and other species; transporting pollutants that can become toxic as they concentrate in the food chain; clogging the gills of aquatic species; covering and eliminating the habitat of aquatic insects on which fish feed; creating habitat that is advantageous to species that burrow, causing a reduction in biological diversity, and providing substrate favorable to underwater plants and algae, promoting their growth. The chemical effects that sediments have on waters may consist of inhibiting photosynthesis, decreasing levels of dissolved oxygen, promoting eutrophication by increasing nutrient levels, and carrying toxins into the water. The negative impacts that sediments have on the physical properties of water are reducing the penetration of light, altering temperature regimes, decreasing water depths, and shifting stream flow patterns (TDEC, 2008a).

Farnsworth and Milliman (2003) suggest that 80-90% of fluvial sediment reaching oceans is directly or indirectly linked to human activity. To minimize the negative impacts of sediments on streams, it is common practice to implement best management practices (BMPs) in areas of high priority (those contributing the most sediment). The aim of BMPs is to reduce the amount of sediment, nutrients, pathogens, and other contaminants entering a body of water to protect and improve water quality. ‘Best management practice’ is a broad term that encompasses almost any activity meant to protect or improve water quality. Some examples of commonly used best management practices in an agricultural setting are buffer strips, no-till cropping, proper fertilizer application, proper irrigation, contouring, water reuse, and maintenance of riparian buffers. All of these are aimed at improving water quality, yet, some may be better suited than others for use in a particular setting based on cost and efficiency. Successful application of BMP’s requires previous knowledge of the origin of the sediment in the stream to reduce in-stream sediment loads using the most cost effective strategies (Horowitz, 1991; Owens et al., 2001) Many attempts have been made to implement the types of strategies mentioned above. However, the evaluation of their effectiveness at the watershed scale can be very difficult due to the inherent problems associated with correlating water quality data with the source of the degrading component. The precise definition and identification of the potential sources of a pollutant can be complicated, and furthermore, it is generally very costly and time-consuming to accurately and quantitatively measure the contributions of each source due to the nature of the sampling required.

The objectives of this investigation are to (1) sample suspended stream sediment and the potential sources of stream sediment in an impaired watershed in east Tennessee; (2) determine the total elemental content of the watershed samples; (3) determine the extractable elemental content of the watershed samples; (4) investigate the variability of elemental concentrations in stream sediment source materials throughout the watershed; (5) group stream sediment source materials as a function of landscape position and land management practices; and (6) employ multivariate statistical techniques to identify and quantify the contributing sediment sources in the impaired watershed.

The technique used to identify sediment sources is a multivariate chemical fingerprinting approach. This approach is based on the idea that the elemental content of soils will differ depending on management history as well as landscape position and geology, and that the properties of the suspended sediment within a stream will reflect the properties of the sources from which it was derived. Furthermore, the characteristics that distinguish the approach used here from those that have been used previously are that the elemental analyses include common laboratory extraction and analytical procedures. In this study, watershed samples are subjected to total dissolution, nitric acid extraction, and Mehlich 3 extraction. Inductively coupled argon plasma – optical emission spectroscopy is then used to provide multi-elemental analyses, upon which the fingerprint approach is based. This procedure avoids the need for specialized analytical tools and techniques, such as isotopic, magnetic, or radiometric measurements.

Literature Review

The Clean Water Act (CWA) passed by Congress in 1977 amended the Federal Water Pollution Control Act of 1972, and eventually led to the establishment of water quality standards (U.S. EPA, 2008a) The law required that each state establish a set of standards on which to evaluate the quality of waters in that state. Water quality standards include four components (U.S. EPA, 2008b). The first component of water quality standards are the designated uses for a particular body of water. The second is a set of numeric and narrative water quality criteria that are established and must be met to protect the designated uses. An antidegradation policy, the next element is in place to maintain and protect the designated uses of a water body. The last component is general policies such as point source mixing zones, critical low flows, or temporarily relaxed water quality criteria that are typically put in place in special circumstances (U.S. EPA, 2008b). The regulatory agency of each state is then required to compile a list, known as the 303(d) list, of all water bodies not meeting the established water quality criteria and not supporting designated uses. For all waters contained within this list, a Total Maximum Daily Load (TMDL) must be developed for each pollutant negatively impacting a particular body of water (Hession et al., 2000). This requires that the pollutant and its sources be identified. The most common pollutants in streams are sediments, pathogens, and nutrients, but metals and organic toxins are also problematic in some cases (TDEC, 2008a). The importance of sediment as a pollutant is further enhanced by its ability to act as a vector for transport of a variety of nutrients, pathogens, and other environmental contaminants (metals, organic substances) (Carter et al., 2003). Consequently, sediment and associated contaminants can lead to alterations of the biological, chemical, and physical properties of a stream (TDEC, 2008a). The suspended sediment load carried by stream and rivers consists mostly of silt and clay size materials (<63μm), although exceptions do exist (Walling and Moorehead, 1989; Walling et al., 2000). Furthermore, this portion of the sediment load is particularly chemically reactive, and thus, is responsible for the retention and transport of many problematic substances (Salomans and Forstner, 1984; Horowitz et al., 1993, 1995; Foster and Charlesworth, 1996; Owens et al., 2001).

In Tennessee, waterways that have been evaluated are divided into three categories: (1) fully supporting its designated uses, (2) partially supporting designated uses, and (3) not supporting designated uses (TDEC, 2006a). Currently, an important component of the Tennessee Department of Environment and Conservation's (TDEC) strategy for combating pollution and improving water quality in Tennessee is the creation and implementation of TMDLs for point and non-point source pollutants identified on the Tennessee 303(d) list of impaired streams (TDEC, 2007). According to the CWA Section 502, point sources are "any discernible, confined and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, concentrated animal feeding operation, or vessel or other floating craft, from which pollutants are or may be discharged. This term does not include agricultural stormwater discharges and return flows from irrigated agriculture" (U.S. EPA, 2008a). Non-point sources of pollution, unlike point sources, are widely distributed and develop from runoff, precipitation, and groundwater movement rather than from a specifically identifiable point (U.S. EPA, 2008c). Since non-point source pollutants enter streams from many different locations they are difficult to identify and control. In the U.S., non-point source pollution affects approximately 40% of all waters (TDEC, 2006c). When creating TMDLs, states are required to consider both point and non-point sources of pollution.

A TMDL identifies the load of an individual pollutant that a stream can receive from all sources and still meet water quality standards, as well as to satisfy all of its use requirements as designated by the state (U.S EPA, 2006). A TMDL is pollutant specific and is calculated as:

$$\mathrm{TMDL} = \sum \mathrm{LA} + \sum \mathrm{WLA} + \mathrm{MOS} \qquad [1]$$

The $\sum$LA (load allocation) is the sum of the natural background levels present and the pollutant load entering from future and existing non-point sources. The $\sum$WLA is the sum of the pollutant loads entering from all point sources. The MOS (margin of safety) accounts for uncertainties in the load estimates of $\sum$LA and $\sum$WLA (TDEC, 2006d). The success of a TMDL depends on the accuracy of the load calculations, and the accuracy of these calculations relies solely on the proper identification of the specific sources of each pollutant. Furthermore, it is also important to define the relative importance of each contributing source. In general, it is difficult to accurately identify the sources of some of the most common non-point source pollutants, including nutrients and sediments, due to their wide spatial distribution on the landscape.

In the 2008 "Status of Water Quality in Tennessee" report, sediment or siltation is listed as one of the most commonly cited pollutants, impacting over 8,850 km (5,500 mi) of the 19,000 km (11,806 mi) of assessed streams and rivers listed as impaired or threatened in Tennessee (TDEC, 2008a). Sediments transported by a stream are typically derived from a variety of different locations and sources (Walling et al., 1999). Identification of sediment sources is essential for evaluating land management practices that may reduce sediment loads. Best management practices (BMPs), are commonly recommended by regulatory agencies (e.g., TDEC) to reduce sediment and contaminant loads in waterways (TDEC, 2007). Unfortunately, source identification is a particularly difficult task in watersheds with complex combinations of land uses and non-point sources of sediment (Mostaghimi et al., 1989). The importance of sediment source information when combating sediment loss using BMPs was illustrated by Wasson et al. (2002). They presented an example from Australia where BMPs were employed to revegetate bare and overgrazed slopes in the Lake Argyle watershed with hopes of reducing sedimentation. In their study, the revegetation program essentially had no effect on sedimentation rates because the BMPs did not target the main source of sediment in the watershed, which was gully and bank erosion. The finding of Inamdar et al. (2001) indicated that BMPs had little effect on annual sediment load and flow-weighted concentrations of some forms of nitrogen (N)and phosphorus (P) in a cropped agricultural watershed in Virginia. They monitored a stream at two locations before and after the implementation of agronomic (strip cropping, conservation tillage, nutrient management, integrated pest management) and structural (vegetative filter strips, grade stabilization structures, and drop structure) BMPs. They suggested that the results they reported may have been a consequence of the resuspension of sediment and increased streambank erosion due to more high intensity rainfall events and higher streamflows during the post-BMP period during which they monitored. They also noted that the influence of BMP implementation may be better evaluated by including a comparison of edge-of-field suspended solid measurements with those of in-stream suspended solids. Similar results were reported by Edwards et al. (1997). They studied two primarily pastured agricultural watersheds within the Lincoln Lake watershed of northwestern Arkansas. They found no significant change in the amount of suspended solids in the two streams monitored after the implementation of BMPs aimed to manage pasture and hayland, as well as nutrients. The results of these studies illustrate the importance of correctly identifying the sources of in-stream sediment before implementing potentially costly and time-consuming BMPs. Sediment source information is also needed for a variety of other applications, which include determining sediment budgets for watersheds, validating erosion prediction models, and determining guidelines for design and implementation of sediment and pollution control strategies (BMPs) (Collins et al., 2001). Clearly, the lack of information regarding sediment sources is often a constraint in these applications (Walling, 1990).

It is difficult to link water quality data, which are relatively easy to collect, to the source of a degrading component at the watershed scale. Traditionally, direct monitoring techniques, such as erosion pins and troughs, and sediment load measurements, have been used to assess sediment sources and their relative significance. However, the high costs and time-consuming nature of employing these techniques, as well as operational difficulties and associated sampling constraints, have led to the development of less labor-intensive and more cost-effective means for determining the sources of sediments (Collins et al., 1997c). These new techniques recognize that the chemical and mineralogical properties of soils are spatially variable depending on landscape position and current and past management (soil forming factors). Because the behavior of each chemical element differs relative to the soil forming factors, the multi-elemental content of a soil may be viewed as a 'fingerprint' (Kelley and Nater, 2000). If the chemical fingerprints of soils on a landscape are known, and assuming that it is possible to confidently differentiate between the fingerprints of the sediment sources, it is hypothesized that the chemical fingerprint of suspended stream sediment will proportionally reflect the properties of the sources from which it is derived (Krause et al., 2003; Collins et al., 2001).

The underlying principle for this approach is that sediment sources can be characterized based on their chemical properties, which can then be compared with the chemical properties of suspended sediments in order to predict the relative importance of contributions from different sources. The soil and sediment properties used in the fingerprinting technique will depend on the nature of the sources in a watershed (Walling et al., 1999). The two basic steps used to apply this technique are: (1) to identify properties that can clearly discriminate between potential sources, such as mineralogy, elemental concentrations, and color; and (2) to compare individual fingerprint properties with the corresponding fingerprint of suspended sediment samples to identify the source of the sediment (Collins et al., 1997b). The application of this approach has been successfully demonstrated in a number of studies (Collins and Walling, 2002).

Many approaches have shown promise for determining the sources of sediments, confirming that a variety of sediment-tracing characteristics may be used. However, a single source or sediment property that is widely applicable for differentiating sediment sources has yet to be identified. Thus, the use of a single tracer property is seen as unrealistic (Collins and Walling, 2004). Some of the first sediment sourcing studies used mineralogical properties to provide information for sediment sourcing. Klages and Hsieh (1975) used the mineralogy of drainage areas having differing geologies to infer the sources of suspended sediment in a southwestern Montana watershed. By comparing the mineralogies within the watershed with the mineralogy of the suspended sediment they were able to infer which part of the watershed was providing the majority of the sediment. However, they note that the method was most applicable to small watersheds with only a few sources, and where the distance between sampling points was short. Wall and Wilding (1976) used a similar method in a northwestern Ohio watershed to differentiate between surface and subsurface sources of sediment. They indicated that mineralogy was useful as an index for differentiating surficial and geologic materials, and concluded that the suspended sediment load in the watershed was primarily derived from surficial sources. They also indicated that the sediment load was likely a mixture of the different sources and that precise differentiation between sources was not possible. Garrad and Hey (1989) also used mineralogy to evaluate the sources of suspended sediment and to determine changes in the source of deposited sediment over time in the Norfolk Broads in the eastern part of England. They used a linear numerical model to determine the relative proportions of three major mineral groups (illite, montmorillonite, and kaolinite/chlorite) in sediment and sources. They found that the source of suspended sediment differed seasonally, with stream bank material dominating in the summer and bed material dominating in winter, and also the sedimentation rates had increased from the 1800's on. Furthermore, they noted that both the total composition and the composition of the inorganic component of deposited sediments had changed over time, and suggested that the seasonal differences in suspended sediment were primarily due to the influence of boat traffic. The differences exhibited in deposited sediments were also a result of increased boat activity, as well as land drainage, and water pH changes due to the growth of phytoplankton. The authors noted that the confident application of their model required identification all possible sources of sediment.

The mineral-magnetic properties of sediments have also been used to identify sediment sources. Dearing et al. (1986) used magnetic measurements, including magnetic susceptibility, frequency dependent susceptibility, isothermal remanence magnetization, viscous remanence magnetization, and three demagnetization parameters, to trace the movement of topsoil. They showed that the magnetic properties of soils are variable with depth in a profile, indicating that these properties could be used to elucidate differences in sediments derived from surface versus subsurface sources. They also indicated that particle size and mineralogy influence magnetic parameters and can complicate the interpretation of magnetic data. Thus, they recommended an evaluation of the relationships between particle size, mineralogy, and the magnetic parameters when evaluating sediment sources using magnetic data. Walden et al. (1997) and Slattery et al. (2000) also use magnetic measurements, including magnetic susceptibility, frequency dependent susceptibility, and isothermal remanence magnetization, to identify the sources of suspended sediment. In addition, they expanded upon the method of Dearing et al. (1986) by including a quantitative linear mixing model for determining the relative contributions of each potential source in the suspended sediment. They found by applying a variety of statistical analyses, including simple bivariate plots and multivariate analyses (R and Q-mode factor analysis), that using magnetic measurements allowed them to differentiate between three potential sources of suspended sediment based on soil taxonomy (Aberford topsoil, Aberford bank material, and Banbury soil-topsoil and bank). Furthermore, they show that successfully grouping the data into the various sources using multivariate techniques is critical for the application of the mixing model. For instance they could infer from the factor analysis that the Banbury soil made the smallest contribution to the suspended sediment load based on where these samples plotted in factor space in relation to the suspended sediment samples. They also observed that when using a linear mixing model it was important to consider the number of parameters measured (dimensionality of the data) when deciding how many sources to include. Since they only measured a small number of magnetic parameters, only a small number of sources could be considered.

Walden et al. (1997) and Slattery et al. (2000) computed hypothetical source mixtures using the mean values for each of the three source materials to represent the measured magnetic parameters. These were used to test the reliability of their mixing model for calculating source proportions. Based on the fact that the hypothetical mixtures were successfully ‘unmixed’ by the model in the correct proportions, they concluded that the model functioned satisfactorily. However, they did point out a number of short-comings that may present themselves when using the linear mixing model. First, the identification of potential sediment sources is difficult in a larger watershed. Second, some suspended sediment samples may be described by the model as being derived from more than one set of possible mixtures. In such cases, the multivariate analyses results can provide insight into the most probable source mixture. The authors also stated that problems may arise when the parameters used in a model range over orders of magnitude. Overall, however, they concluded that their modeling approach resulted in a realistic identification of stream sediment sources and their relative contributions.

Brown (1985) studied pollen as an organic indicator of sediment origin, since organic material often makes up a significant portion of the suspended load. He found that, although the types of pollen present differ with location, vegetation, and soil depth, their concentrations differed greatly with the seasons. Thus, Brown was unable to make strong conclusions about sediment source, although, he argued that the successful modeling of pollen transport and storage could lead to prediction of suspended sediment sources. Grimshaw and Lewin (1980) used sediment color (based on Munsell color charts) to distinguish between “channel” and “non-channel” sources of suspended sediment. They plotted sediment concentration versus sediment color to estimate the primary sources of sediment, and concluded that non-channel sediment contributions from hillside erosion were greatest during summer months when rainfall was greater. They also suggested that the inclusion of a mineralogical analysis could allow for the identification of additional sediment sources.

Chemical data have also been used to derive information about stream sediment sources. Symader and Thomas (1978) studied a watershed in the Eiffel Mountains, Germany. Watershed samples, including stream water, suspended material, bed sediment, and soils, were analyzed for nine metals. Hierarchical cluster analysis was used to analyze the data and to group the subwatersheds according to metal content. Based on the results of the cluster analysis, they differentiated four types of subwatersheds: catchments influenced little by human activity, catchments with metals mainly derived from subsoil, catchments affected by domestic sewage, and catchments affected by industrial waste waters. Jones et al. (1991) used copper (Cu) and zinc (Zn) concentration data from sediment cores taken from Llangorse Lake, Wales, along with historical inferences, to explain changes in sediment deposition over time. They found that increases in surficial deposition of Cu and Zn corresponded with large increases in smelting activity in the 17th and 18th century. They also surmised that increased agricultural production and erosion from exposed arable soils added to the metal burden of the lake sediment. As the smelting industry declined, so did agriculture in the watershed, resulting in decreased concentration of Cu and Zn in the associated sediment cores.

The physical properties of sediments have also been used to determine the source of sediments. However, they are only useful when used in conjunction with other sediment properties. Collins et al. (1997a) used physical parameters (i.e., absolute particle size), along with chemical and radiometric characteristics to quantify sources of suspended sediment using a multivariate mixing model. They did not use particle size as a parameter in the mixing model; however, they used it to calculate a particle size correction factor to use in the model to weight the potential sources and ensure that the sources and suspended sediments were directly comparable. The correction factor for each source was calculated as the ratio of the specific surface area of each individual suspended sediment sample to the mean specific surface area of each individual source type. The need for the inclusion of this correction factor could have been eliminated by sieving all source samples to <53μm, since suspended sediment consists almost exclusively of this size class.

Several studies have used the radiometric properties of sediments to derive information about their source. Walling and Woodward (1992) used radiometric fingerprints developed using measurements of the fallout radionuclides cesium-137, lead-210, and beryllium-7. Potential sediment source materials (soils from cultivated, pasture, forest lands, and subsurface) were sampled within three watersheds. Suspended sediment was recovered from the outlet of each watershed during storm events. The three-component fingerprints were then used to examine the relationships between the suspended sediments and the sources using bivariate plots. Their analyses indicated that fallout radionuclides could be used to source the suspended sediments. They also suggested that additional sediment properties should be used to allow for further clarification of the contributing sources. Wallbrink and Murray (1993) also used radiometric measurements of fallout radionuclides to differentiate between surface and subsurface sources of sediment from simulated rainfall plots. Their findings suggested that sediment source shifted from sheet to rill erosion under continuous rainfall. They also found that gully walls were a more significant source of sediment than were upslope soils. Douglas et al. (1995) used measurements of strontium-86 and -87, and rubidium-87 activities to estimate sediment sources for two large rivers. They concluded that the preferential weathering of sedimentary materials occurred, and that the river sediment had little or no isotopical relationship to the source rock. They also stated that the relationship of sediment to source may become more complicated over time. Matisoff et al. (2002) used cesium-137, lead-210, and beryllium-7 meaurements to evaluate the sediment sources in an Ohio watershed. The source groups included were undisturbed soils, no-till soils, and tilled soils. Using the radiometric measurements it was possible to distinguish between the source groups. They also found that the tilled areas had higher sediment yields and erosion depths. However, the fact that they only examined a single storm event and looked only at surficial sources seems problematic, since the nature of a storm event may affect sediment source variability, and subsurface sources, such as stream banks, may often contribute significant amounts of sediment.

Recently, Wallbrink (2004) quantified sediment sources in two watersheds of the Moreton Bay, Southeast Queensland, Australia using radium-226 and cesium-137. The source groups used in this study were uncultivated soil, cultivated soil, and subsurface soil. The mean values of the radiometric measurements for each source group were used in a mixing model to estimate the relative contributions from each group. They found that the subsurface soil was the greatest contributor to suspended sediment (66%), with cultivated soils and uncultivated soils contributing 33% and <1%. Wallbrink (2004) also noted that it is important to consider the residence time of sediment in the watershed when evaluating the effectiveness of BMP's, since this will affect how long it takes to see improvements. Although the use of isotopes for sourcing sediments has shown potential, their principal usefulness has been for discriminating between surface and subsurface sources. In many cases, a more detailed assessment of sources and sediments may be necessary for precisely determining areas of highest priority for reducing sediment loss and implementing BMPs.

In general, the above cited studies illustrate that the examination of a relative few properties may effectively be used to discriminate potential sources of suspended sediment in a watershed (Collins and Walling, 2002). However, the use of a single diagnostic property is increasingly seen as unrealistic. Instead, employing an array of properties is seen as providing a number of predictive benefits, including a reduction in the occurrence of false relationships between suspended sediment and potential sources, and allowing a greater number of sources to be discriminated (Collins and Walling, 2002). The multiple property fingerprinting technique has been used in numerous studies to determine the relative contributions of potential sediment sources to the suspended sediment load of streams and rivers (Collins et al., 1997a; 1997b; 1997c; 1998; 2001; Owens et al., 1999; Walling et al., 1999). Collins et al. (1997a,b,c;1998) used combinations of chemical elemental analyses, along with inorganic and organic analyses of carbon (C), nitrogen (N), and phosphorus (P), a radiometric analyses, and a particle size analyses to fingerprint suspended sediment sources. These studies were conducted in similar watersheds located in southwest England. Collins et al. (1997a and 1997c), defined potential sources as forest, pasture, cultivated soils, and subsurface material. Collins et al. (1997b), defined the sources of sediment based on subwatershed type: low altitude steeply sloping pasture areas; high altitude more gently sloping mixed arable and pasture areas; high altitude typical of transition between mixed agricultural land and moorland in lower reaches; and high altitude moorland sub-basin areas. In another study, Collins et al. (1998), sampled different land uses (forest, pasture, and subsurface) within different geological systems (Devonian, Carboniferous, and Permian). In each study, sediment properties exhibiting statistically significant discrimination power were input into a multivariate mixing model to determine the relative contributions of each potential sediment source to suspended sediment. The measured sediment properties were compared to the values predicted by the mixing model using source properties. The predicted values were typically in the range of ±10% of the actual values.

Collins et al. (2001) conducted a similar study on a tropical watershed in the Southern Province of Zambia. Sediment sources were defined as surface and subsurface materials and were characterized using an array of chemical and radiometric properties. The ability of each property to discriminate the sources was statistically verified using the Kruskal-Wallis *H*-test and a stepwise multivariate discriminant function analysis. The optimum group of chemical characteristics (fingerprint) identified by these tests was then used in the multivariate mixing model to quantify the contributions of the sediment sources. They reported relative error values of ±15%, indicating that the model provided reliable predictions of source contributions. Walling et al. (1999) used the same methodology to identify suspended sediment sources in the River Ouse watershed, Yorkshire, UK. Source samples were collected from within each geologic zone from woodland, cultivated, uncultivated, and subsurface materials. They used the statistical process of Collins et al. (2001) to identify the optimum fingerprint, which was then used in a multivariate mixing model to determine source contributions. They reported relative errors for their predictions ranging from ±8% to ±15%. Owens et al. (1999) also collected sediment samples from within three different geologic zones (Permian, Triassic, and Jurassic) from woodland, cultivated, uncultivated, and subsurface materials in the River Ouse watershed, Yorkshire, UK. They also collected floodplain sediment cores at seven sites (cultivated and uncultivated) in the study area susceptible to regular overbank flooding. Environmental radionuclide analysis of the cores was used to determine the rate of sedimentation due to overbank flooding. All samples were analyzed for magnetic properties and elemental content. The statistical procedures used were the same as those described in Walling et al. (1999), leading to a relative error of prediction that ranged from ±7% to ±14%. They found that the relative contributions from topsoil sources increased in the late 19th through the early 20th century, but that in recent years the contribution of bank material had become more significant, possibly due to increased awareness and management of surface erosion on agricultural land. They also documented changes in the sources of sediment within each of the different geologic areas, as well as variations in the relative importance of each geologic area as a source, and suggest that this is likely a result of land use changes within each area.

Kelley and Nater (2000) used a chemical mass balance method to determine the sources of lake bed sediments in Lake Pepin, in the Upper Mississippi River basin. Sediment sources were defined as the three contributing watersheds (the headwater of the Mississippi River, the Minnesota River watershed, and the St. Croix River watershed). A 3.5m sediment core was collected from within Lake Pepin. Sedimentation rates and core dating were established using radiometric and magnetic data, as well as pollen analysis and loss-on-ignition. Unlike other studies, they focused only on the heavy-density silts (2-63µm, >2.95 g cm^{-3} density), which were typical of lakebed deposits. After the removal of carbonates, organic matter, and iron oxides, the heavy silts from the sediment and core samples were analyzed for 42 elements. The U.S. EPA chemical mass balance (CMB) air quality receptor model was used to determine the sources of the lakebed sediments. Similarly to the multivariate mixing models used by others (Walling et al., 1999; Owens et al., 1999; Collins et al. 2001), this model consists of a set of linear equations (one for each parameter analyzed) solved simultaneously to determine the relative source contributions. They tested the mass balance model using known masses from each source and found that the average deviation of the calculated from the actual source proportions to be 3.2%. However, they noted that problems arose in the model when the source properties were not adequately different to allow for differentiation by the algorithms of the model. Thus, due to similarities in the lithology of two of the source watersheds, they were only able to distinguish between two of the three groups of potential sources of sediment using the model. They report significant changes in the contribution of the Minnesota River after European settlement. Using recent sediments (1992), the model indicated that the sediment contributions from the Minnesota

River were 92% (8% from the other two watersheds combined). These estimates corresponded well with suspended sediment loads from the watersheds.

Recently, Rhoton et al. (2008), conducted a sediment sourcing study in the Walnut Gulch Experimental Watershed (WGEW) of Arizona, which encompasses the town of Tombstone. They focused on six subwatersheds with the WGEW, each of which was instrumented with a supercritical flume. Suspended sediments were collected at the flume with an automated sampler during flow events, while soil samples were collected from the surface within the subwatersheds based on their relative acreage and according to slope position, class, and aspect. A particle size distribution, the water dispersible clay component, soil mineralogy, and magnetic susceptibility were all measured. A range of chemical analyses were also performed. Since vegetation within the subwatersheds differed, they used the mass balance equation of Boutton (1996) to estimate the relative contribution of C3 and C4 plants to the overall $\delta^{13}C$ concentration in the sediments. The chemical and physical parameters measured were then used in a multivariate mixing model to estimate the relative contributions of each subwatershed to the sediment load leaving the watershed. Their results indicated that the two subwatersheds with the most highly erodible soils contributed 68% of the sediment load. For most of the measured properties, the predicted values when compared with the measured values were exceptionally close. However, for magnetic susceptibility the model underpredicted the measured values by 12%. They noted that their mixing model has the potential to provide reasonably accurate estimates of the portions of the watershed contributing the greatest amounts of sediment, although it does not allow for the estimation of streambank versus upland sediment contributions. They evaluated only some of the total subwatersheds in WGEW, which encompassed 65% of the total area, and assumed that the sediment contributed from the subwatersheds not evaluated in the study is similar to that from those that they did use since the parent materials, landforms, mapping units, and land-use were essentially identical. This may have lead to erroneous estimates since it is possible that the subwatersheds not evaluated are contributing some amount of sediment, which may or may not be identical to the sediment from the watersheds evaluated. They also only sieved the soil samples to <2mm, which may not allow for a direct comparison to suspended sediments that usually are <53μm in size. Finally, they did not provide any evidence of statistical analyses to validate the use of a mixing model.

While each one of these studies has provided valuable insight into the origin of suspended sediment, there still exists a need for a more widely applicable method for sourcing suspended sediment, as well as one that provides more detailed sediment source information for developing TMDLs and successfully implementing BMPs. Based on this need and the apparent success of the fingerprinting technique for providing sediment source information in various watersheds, this study was developed to evaluate the technique for a sediment-affected watershed in East Tennessee.

Objectives

The results of a previous study in the Pond Creek watershed indicated that the total elemental contents of the sediments can be used to develop fingerprints, rather than using properties that are difficult to measure and require special instrumentation, such as magnetism, isotopics, and radionuclides (Hull et al., 2007). In addition, it was hypothesized that extractable elemental data may also be effective for fingerprinting. The objectives of this investigation were to (1) sample suspended stream sediment and the potential sources of stream sediment in an impaired watershed, the Pond Creek watershed in east Tennessee (HUC: TN06010201013); (2)

determine the total elemental content of the watershed samples; (3) determine the extractable elemental content of the watershed samples; (4) investigate the variability of elemental concentrations in stream sediment source materials throughout the watershed; (5) group stream sediment source materials as a function of landscape position and land management practices; and (6) employ multivariate statistical techniques to identify and quantify the contributing sediment sources in the impaired watershed.

Previous Pond Creek Study

In the previous evaluation of the Pond Creek watershed (Hull et al., 2007), 20 surface soil samples were collected from the top 2 cm of eight different defined sediment sources. The sources were: edge of roadbed, cattle path, stream sediment (bottom and bars), stream bank, cattle trampled, abandoned barite mine, corn field, and pasture (forage) and sod (Table 1). The samples were sieved to 53µm, subjected to a complete digestion procedure (dissolution) and a Mehlich 3 extraction, and then analyzed using inductively coupled argon plasma-optical emission spectroscopy (ICP-OES). Samples were analyzed for 29 elements, and 24 were above detectable concentrations: Al, As, Ba, Ca, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Nd, Ni, P, Pb, S, Sr, Ti, V, Zn, and Zr. Each sample had a unique elemental composition, which may be viewed as a fingerprint (Fig. 1).

To determine if elemental concentrations differed significantly among the source groups, the 24 detectable elements were tested using the parametric Kruskal-Wallis rank test and a significance level of $P<0.05$. A discrimination analysis (STEPDISC procedure in SAS) was then used to determine for each element whether the variability in concentration was able to afford optimum discrimination of the source groups. The variability of K, Mg, and P in the Pond Creek

Table 1. Grouping and description of surface materials collected from the Pond Creek watershed during a preliminary study.

Group number	Description	Number of samples	Sample number
1	Edge of roadbed (road bank)	1	2
2	Cattle path	2	1, 9
3	Stream sediment	4	4, 5, 17, 18
4	Stream bank	3	6, 16, 19
5	Cattle trampled	2	3, 7
6	Abandoned barite mine	3	11, 12, 13
7	Corn	1	14
8	Pasture (forage) & sod	4	8, 10, 15, 20

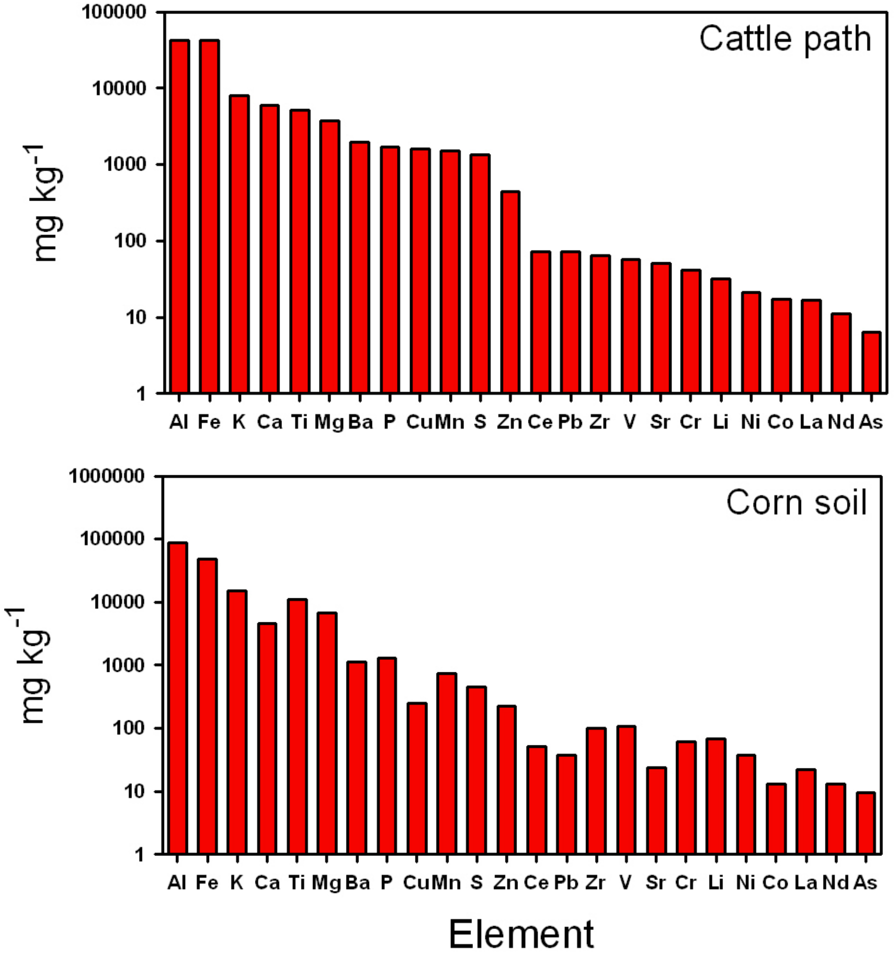


Figure 1. The histograms illustrate the elemental composition (fingerprint) of a cattle path and a corn soil sample.

materials can be used as an example of the importance of different elements (Fig. 2). Potassium concentrations were found not to differ significantly among groups and did not offer the power to discriminate between the groups, while magnesium concentrations did not differ significantly among the groups, but did offer the power to discriminate the groups. Phosphorus concentrations were both significantly different among some groups and could be used to discriminate between the groups. These two initial tests indicated that 15 elements were significantly different among some source groups (Al, As, Ca, Ce, Co, Cr, Fe, Li, Mn, Nd, P, Pb, S, Zn, and Zr); 12 elements could be used to discriminate between the source groups (Al, As, Ce, Cr, Li, Mg, Mn, P, Pb, Sr, Ti, and Zr); and nine elements had both characteristics (Al, Ca, Cr, Li, Mn, P, Pb, S, and Zn).

The power of the nine elements that were significantly different between some source groups and could be used to discriminate between source groups in the Pond Creek watershed was further evidenced by a principal component analysis (PCA) (PRINCOMP procedure in SAS). This analysis reduced the large amount of variability in the chemical concentrations of the samples to a small number of variables (principal components). As Fig. 3 illustrates, 82.1% of the variability in the chemical compositions of the Pond Creek samples could be explained by three principal components; PC1, PC2, and PC3. The arrows illustrate the impact that each element had on sample discrimination. For example, the variability in P concentrations differentiates the samples almost solely along the PC1 axis; whereas, the Mn, Pb, and Zn concentrations are principally responsible for discriminating (pulling apart) the samples along the PC2 axis. In general, the samples from a particular source group (Table 1) clustered together in principal component space. One obvious example was the barite mine (blue circles) and creek bank samples (upside down triangles), which each formed tightly clustered groups (Fig. 3). The clustering illustrates similarities in the elemental compositions (fingerprints).

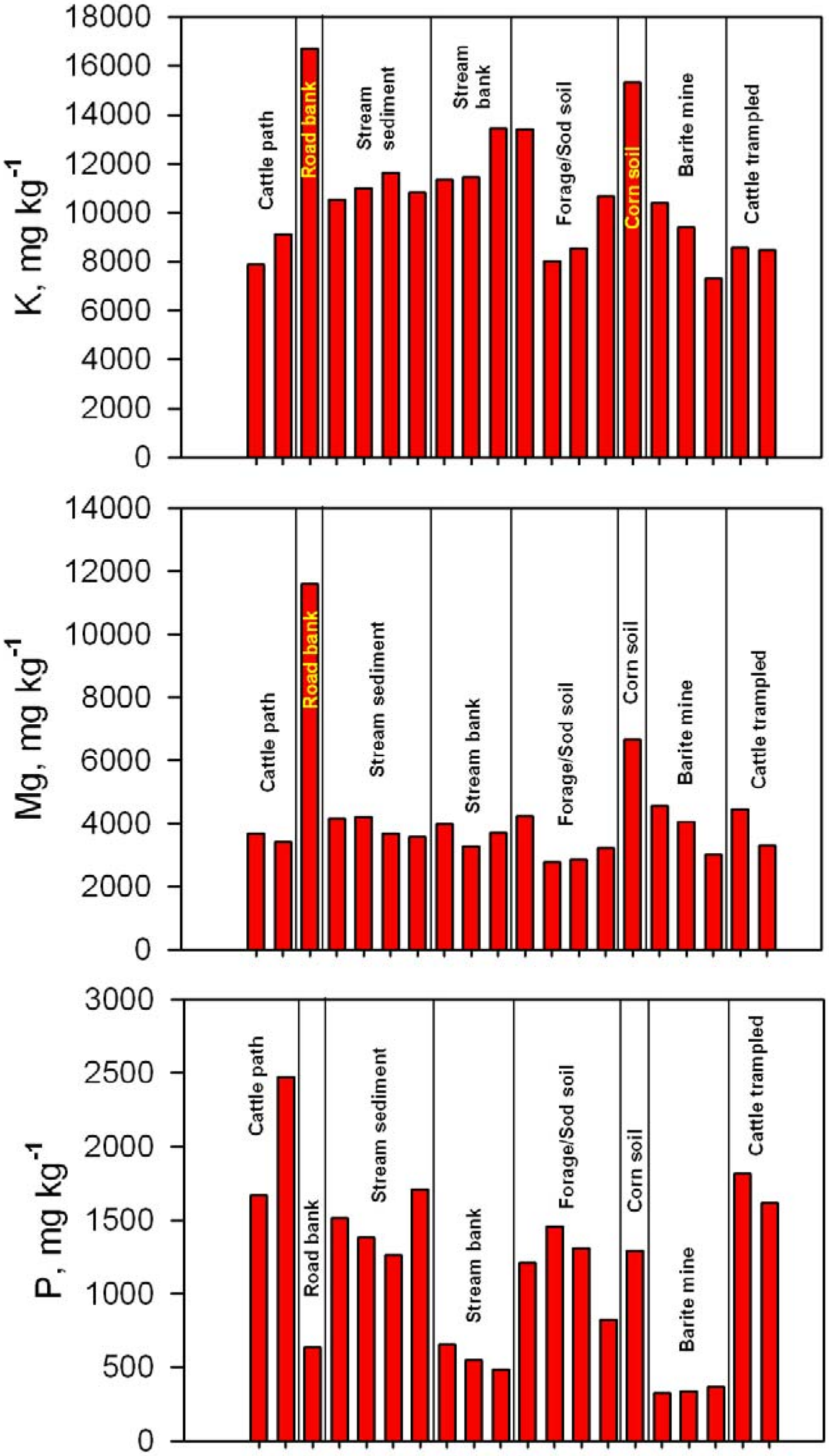


Figure 2. The histograms illustrate the distribution of potassium (K), magnesium (Mg), and phosphorus (P) in the Pond Creek watershed samples as a function sample type and grouping.

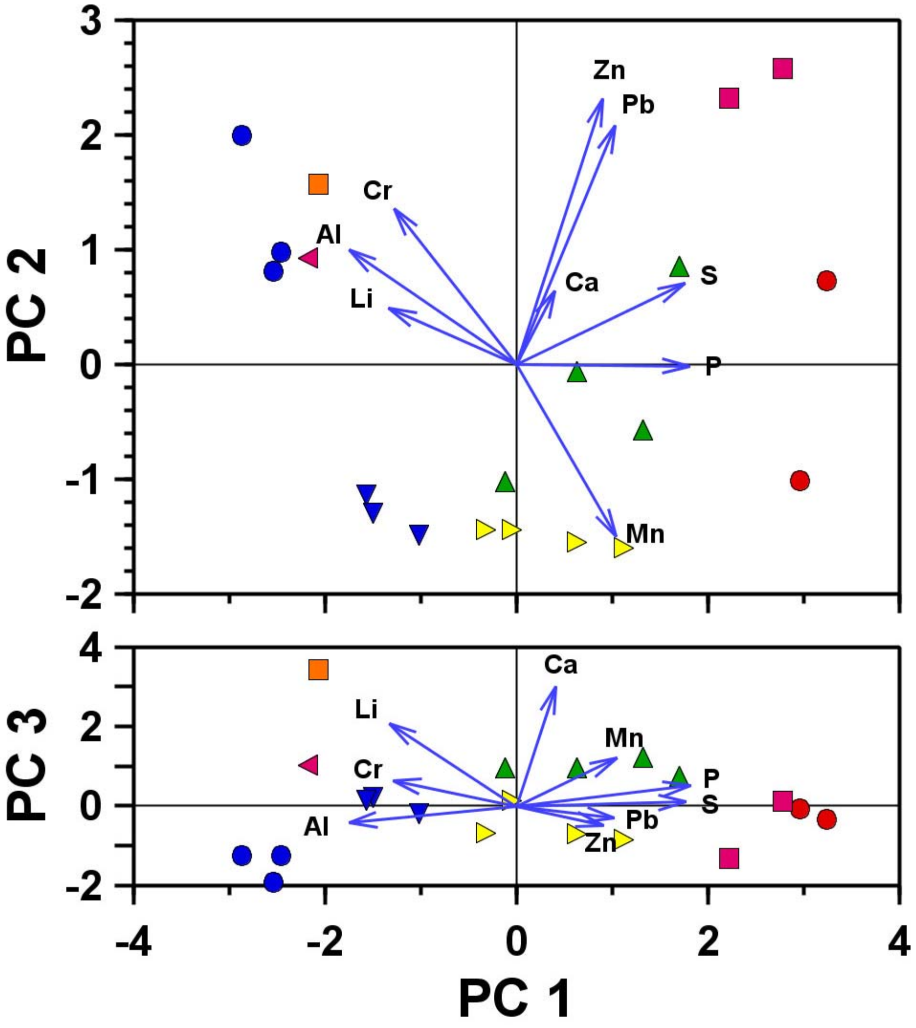


Figure 3. The PC1 vs. PC2 and PC1 vs. PC3 diagrams illustrate the results of a principal component analysis of the Pond Creek samples using the nine elements that are both significantly different among the sample sources and that are discriminatory. The cumulative variability captured by the three principal component axes is 82.1 % (PC1: 43.4 %; PC2: 22.7 %; PC3: 15.9 %). The data points represent the individual soil or sediment samples and the arrows illustrate the impact of each element on sample discrimination (samples with the same shape and color represent a unique group, as indicated in Table 1).

Another way to examine the clustering presented in Fig. 3 is to use a dendrogram derived through divisive hierarchical cluster analysis (Fig. 4). The mechanism used to differentiate the samples in Fig. 4 is similar to that used to develop Fig. 3. In both figures the similarities between samples are evident. In Fig. 3 the barite mine (blue circles), corn soil (left-facing triangle), and road bank material (orange square) are adjacent to one-another in PC1 – PC2 space. Similarly, in Fig. 4 all of these samples are found on the lower branch of the dendrogram (Fig. 4).

Another dimension reduction technique that can be used to group samples into statistically similar groups is canonical discriminant analysis (CDA), which is related to (and employs) PCA. PCA produces principal components that capture the greatest degree of variability in the data, while CDA creates canonical variables having the highest possible multiple correlations with groupings of observations. The same nine elements used in the PCA were used in the CDA analysis. In this analysis six unique clusters were created (Fig. 5). Three unique clusters were formed containing the barite mine, cattle trampled, and road bank materials. The stream sediment materials clustered with soils to which they were proximate on the landscape (Fig. 6). For example, in Fig. 5 the group that is identified by red circles contains one sample from a cattle path and one from a sediment bar. In this case, the path is upslope and proximate to the bar (red circles in Fig. 6). Furthermore, the forage soil and cattle path samples are clustered with the two stream sediment samples (orange circles in Fig. 5, yellow squares in Fig. 6). The PCA (Fig. 3) and CDA (Fig. 5) analyses provided similar, although slightly different associations. The overall indication was that elemental variability of the field soils, creek bank, and creek sediment (bottom and bars) samples was somewhat similar, and that the road bank, barite mine, and cattle trampled samples were chemically distinct.

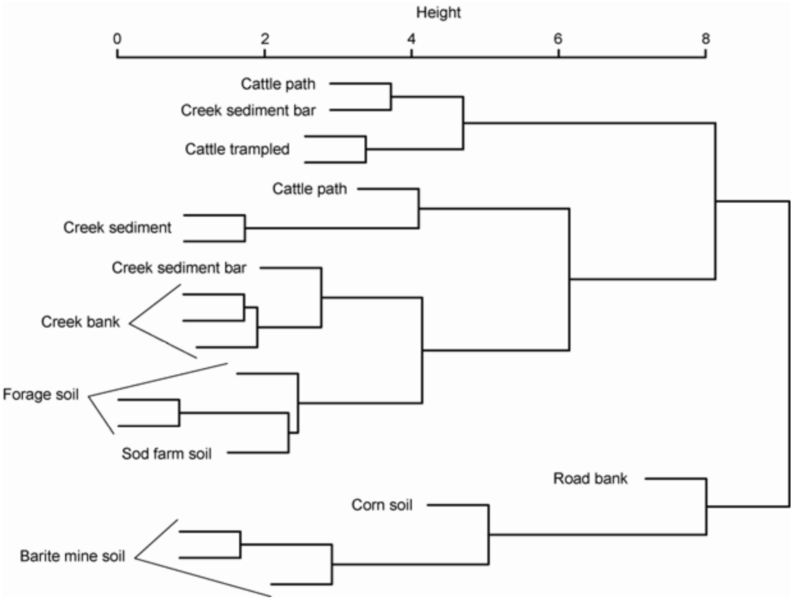


Figure 4. Divisive hierarchical cluster analysis using the elements with significant discrimination power and differences among sources results in the dendrogram that illustrate the Pond Creek sample associations.

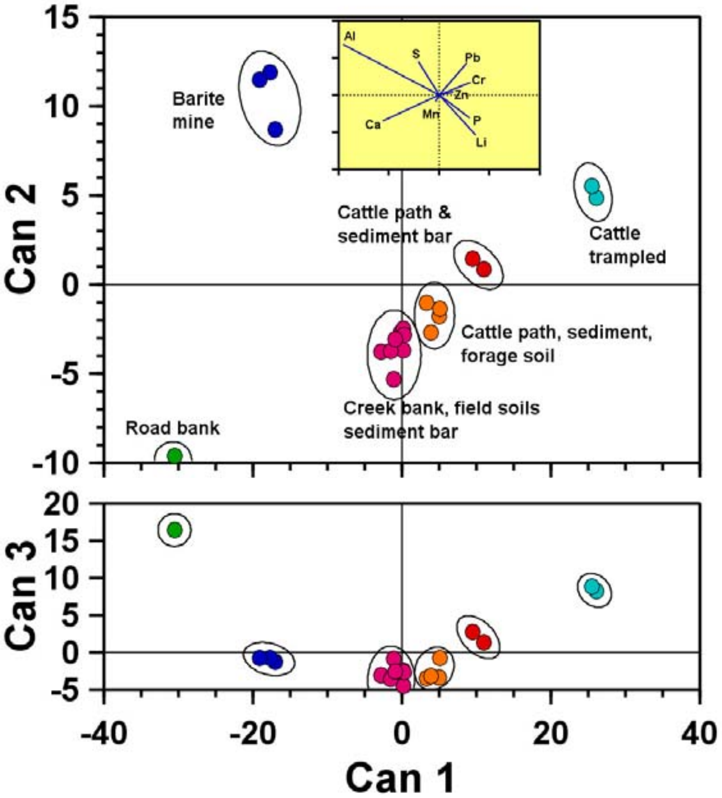


Figure 5. The Pond Creek soils and sediments are clustered into canonical groups by canonical discriminant analysis. The inset illustrates the influence of the elements on the discrimination.

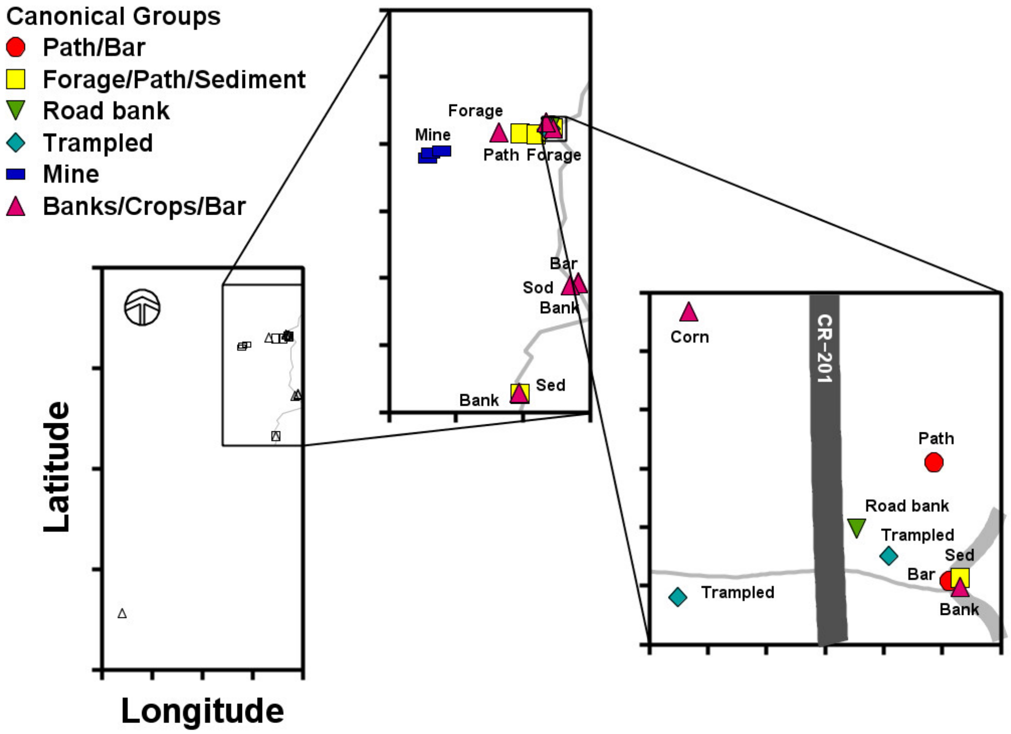


Figure 6. Spatial distribution of soil and sediment samples collected during preliminary studies, as differentiated by canonical groups in the Pond Creek watershed (Hull et al., 2007).

The observation that the road bank and barite mine were chemically distinct from the other samples means they impart considerable variability into the elemental data. This could cause the remaining samples to cluster together and diminish the capabilities of the discrimination procedures. Thus, they were removed from the analysis and the statistical process described above was repeated. In this second analysis only six of the 24 elements were significantly different among some source groups and could provide significant discrimination power: Ba, Co, P, Pb, S, and Zn. In this analysis, the PCA resulted in the generation of three PC variables that accounted for 90.2% of the variability in the elemental concentrations (Fig. 7). The differentiation of the samples in this analysis appears to be stronger than when the road bank and barite mine samples were included. This is evidenced by the fact that when they were omitted from the analyses, the first three principal components explained 90.2% of the elemental variability; but when they were included, only 82.1% of the elemental variability was explained by the first three principal components. The hierarchical cluster analysis suggested that the sediment bar materials were associated with the cattle paths and the forage soils (Fig. 8). However, there was no clear association between the sediment on the bottom of the stream and any other source. A close examination of the dendrogram created when the barite mine and road bank samples were excluded (Fig. 8) from the analysis indicated that their omission did in fact improve the ability to differentiate the samples. In general, the corn field, creek bank, forage soils, creek sediment, cattle trampled soil, and cattle path samples all occupied separate branches of the dendrogram, excepting the sod farm soil and the sediment bars. Although the two dendrograms (Fig. 4 and Fig. 8) look similar, the omission of the road bank and mine samples (Fig. 8) allowed for greater separation of the remaining samples, while still generating sensible clusters based on source groups. The CDA (Fig. 9) indicated that the stream sediment clustered

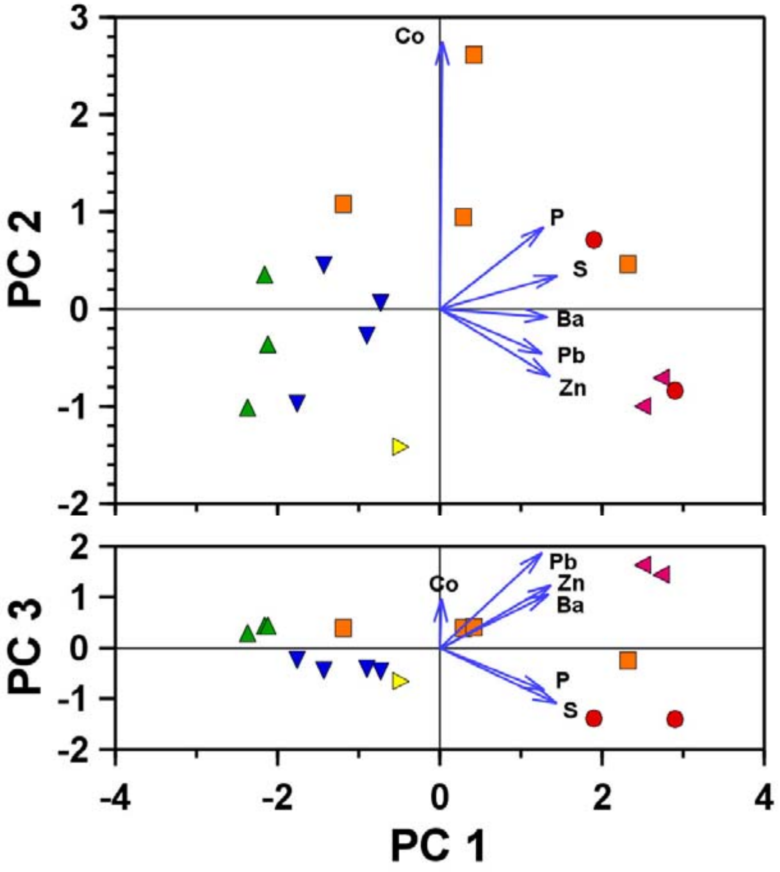


Figure 7. Principal component analysis of the Pond Creek samples (excluding the barite mine and road bank samples) using the six elements that are both significantly different among the sample sources and that are discriminatory. The cumulative variability captured by the three principal component axes is 90.2 % (PC1: 60.2 %; PC2: 28.2 %; PC3:11.9 %). The data points represent the individual soil or sediment samples and the arrows illustrate the impact of each element on sample discrimination (samples with the same shape and color represent a unique group, as indicated in Table 1).

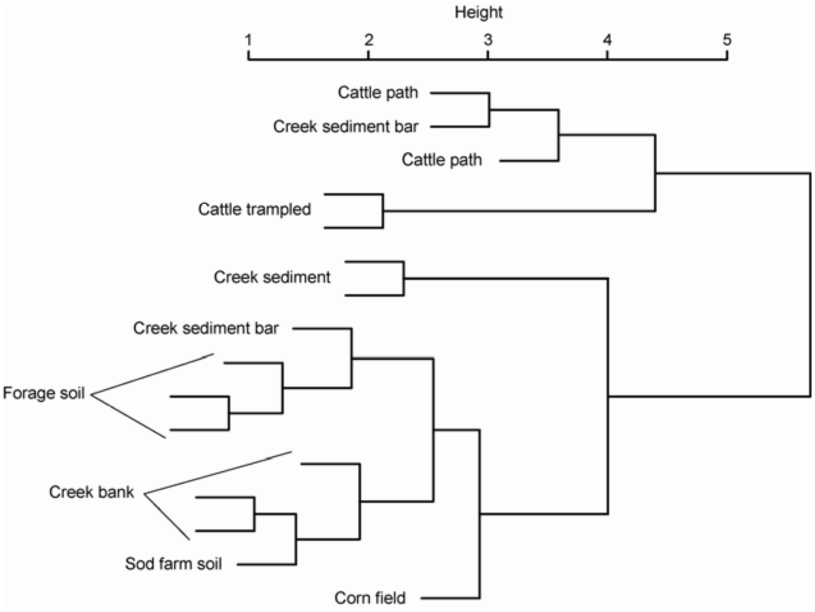


Figure 8. Divisive hierarchical cluster analysis using the six elements with significant discrimination power and differences among sources (mine and road bank excluded).

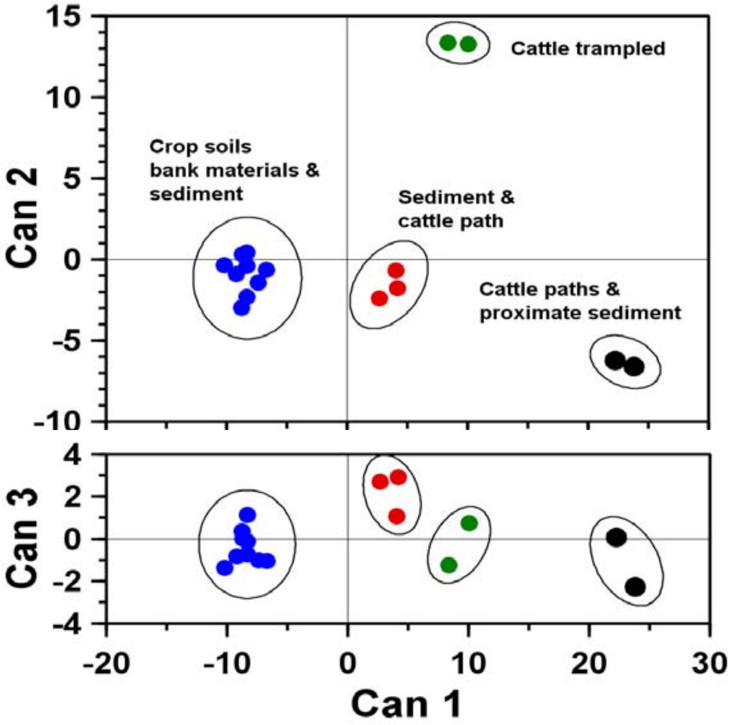


Figure 9. Clustering of Pond Creek soils and sediments into canonical groups by canonical discriminant analysis using the six elements that are both significantly different among the sample sources and that are discriminatory (mine and road bank excluded).

with a proximate cattle path, and that the sediment bar materials were closely associated with cattle paths and proximate forage soils. Although these clusters (Fig. 9) appear similar to the clusters in Fig. 5, excluding the barite mine and road bank clusters, the samples could have been differentiated into a larger number of groups because, when using CDA, the number of groups formed is preselected. Although the exclusion of the barite mine and road bank samples did reduce the overall variability of the elemental composition data, it did not appear to diminish the ability of the statistical analysis technique to differentiate and group the samples.

These preliminary evaluations indicated that surficial materials in the Pond Creek watershed could be characterized by a chemical fingerprint consisting of the concentrations of 24 elements. Based on the statistical analyses, it is apparent that the elemental concentrations of the samples provided sufficient variability and hence, discrimination power to separate the samples into statistically similar groups or clusters. Furthermore, when statistically separated into groups, samples collected from areas under similar current and past management, and in similar landscape positions tended to cluster together, indicating similarities in their chemical composition (Hull et al., 2007).

The Mehlich 3 extraction procedure (Mehlich, 1984) was also used to obtain elemental composition data for the 20 preliminary soil samples. These data were subjected to similar statistical analyses to the data acquired using the total dissolution procedure (Ammons et al., 1995). Fig. 10 shows the samples grouped into four statistically similar clusters. Once again, the barite mine samples clustered independently of all the other samples. Although not shown, it is likely that, had the barite mine samples been removed from this analysis, it would have been possible to further discriminate the samples into clusters containing samples mostly from similar types of locations. Furthermore, the clusters created using the Mehlich data correspond to some degree with the clusters generated using the total dissolution data. The fact that it was possible to differentiate the samples using Mehlich 3 extraction data, and that the clusters were somewhat similar to those from the totals data indicates that much simpler extraction procedures may also be viable tools for discriminating surficial sediment materials and possibly for identifying the sources of sediments.

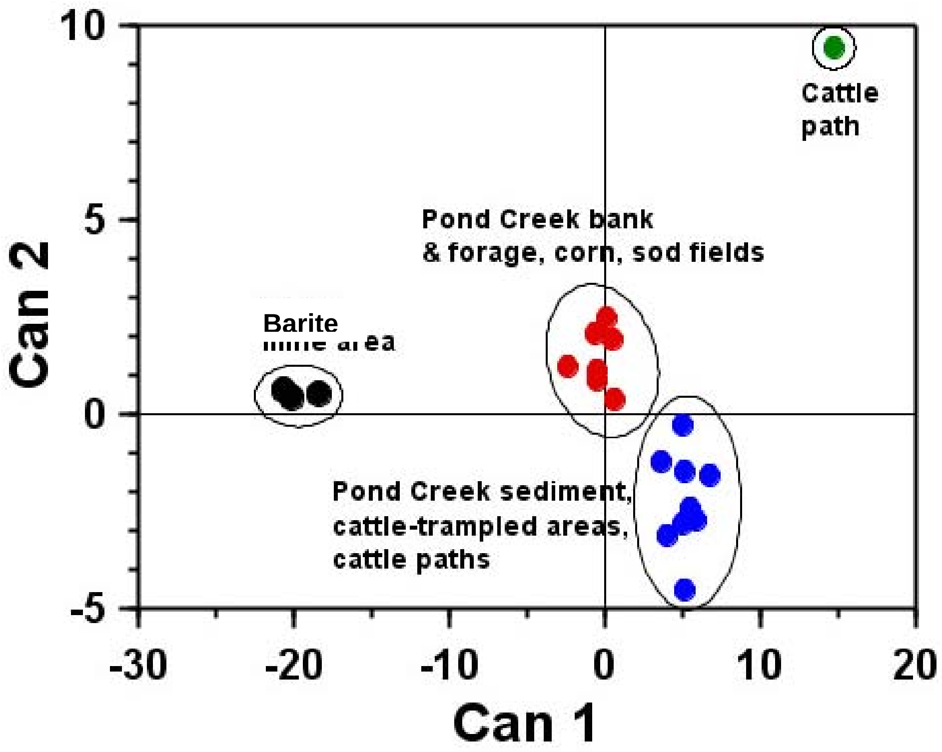


Figure 10. The Pond Creek soils and sediments are clustered into canonical groups by CDA using Mehlich 3 extractable element data.

Materials and Methods

Study Area

Pond Creek watershed (HUC: TN06010201013) encompasses approximately 9,542 ha in Loudon, Monroe, and McMinn counties in the Valley and Ridge physiographic region of east Tennessee. It is a subwatershed within the Watts Bar/Fort Loudoun Watershed (HUC 06010201), located between the metropolitan areas of Knoxville and Chattanooga near the city of Sweetwater (Fig. 11). Pond Creek has been further divided into 19 subwatersheds based on its tributary streams (Fig. 12). The location (and elevation) of the headwaters of Pond Creek is 35°36’38” N, 84°31’01” W (290 m) and that of its mouth at the Tennessee River is 35°44’48” N 84°25’47” W (225 m). The topography is mostly low rolling ridges and valleys with a few steep ridges. The underlying bedrock consists of both Quaternary cherty clay solution residuum and Ordovician dolomite and limestone. The soils of the region are primarily in the order Ultisols and of the series Fullerton, Dewey, Decatur, Bodine, and Waynesboro (Table 2). These soils are excessively to well drained with mostly moderate permeability. The annual rainfall ranges from 101-137 cm. The average temperature in the summer ranges from 19-30.5 °C, and in the winter ranges from 3-7°C (Hagan and Walker, 2006).

The primary land use in the watershed is pasture (forage) for family-based dairy and beef cattle operations (Fig. 13) (Hagan and Walker 2006). The area is rural and contains no municipal separate storm sewer systems. It was estimated by Hagan and Walker (2006) using Tennessee Valley Authority (TVA) integrated pollutant source inventory (IPSI) data that there were 59 beef cattle operations and 12 dairy operations in the watershed, consisting of 1,960 beef cattle; 960

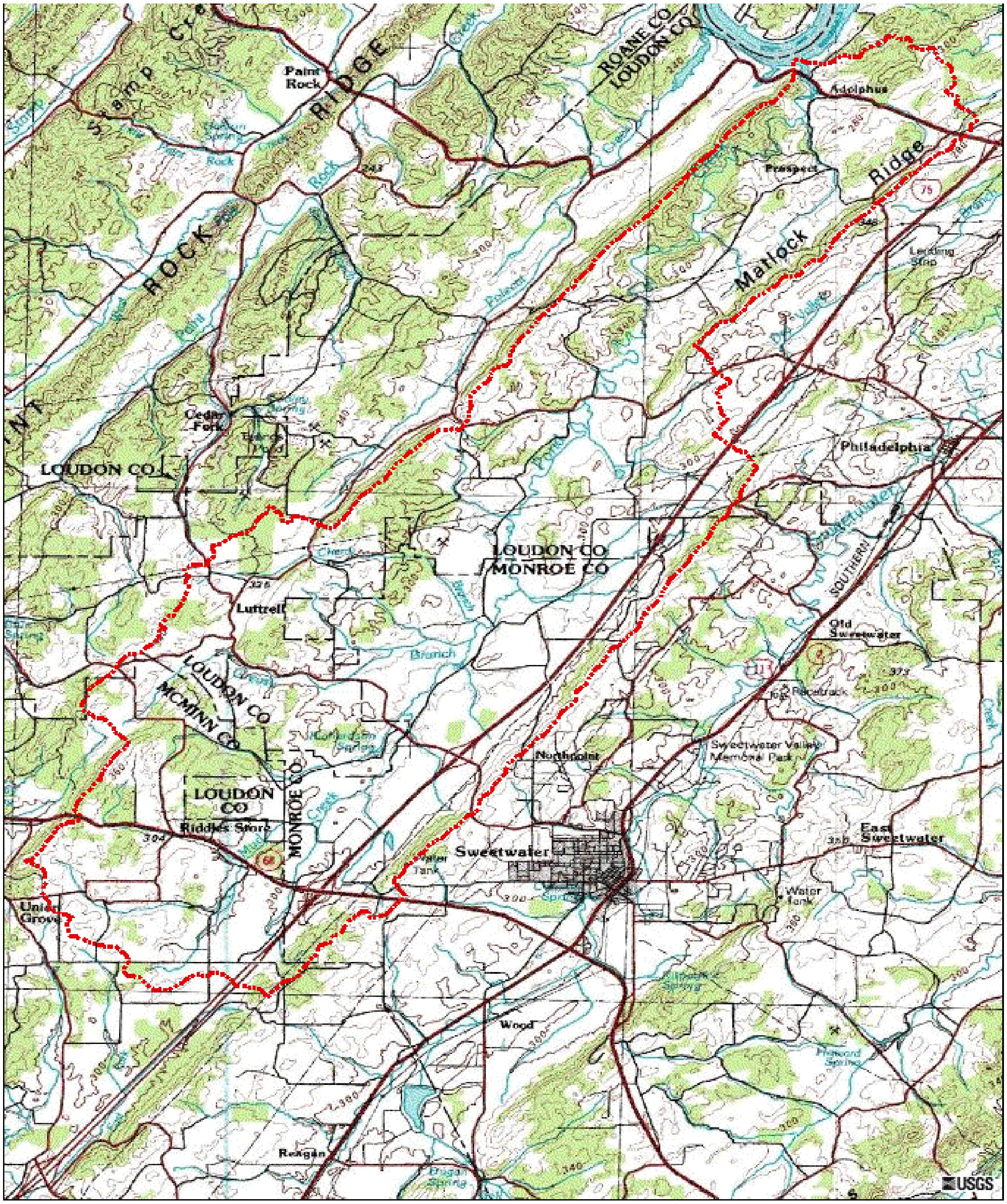


Figure 11. Topographic map with the Pond Creek watershed outlined in red.

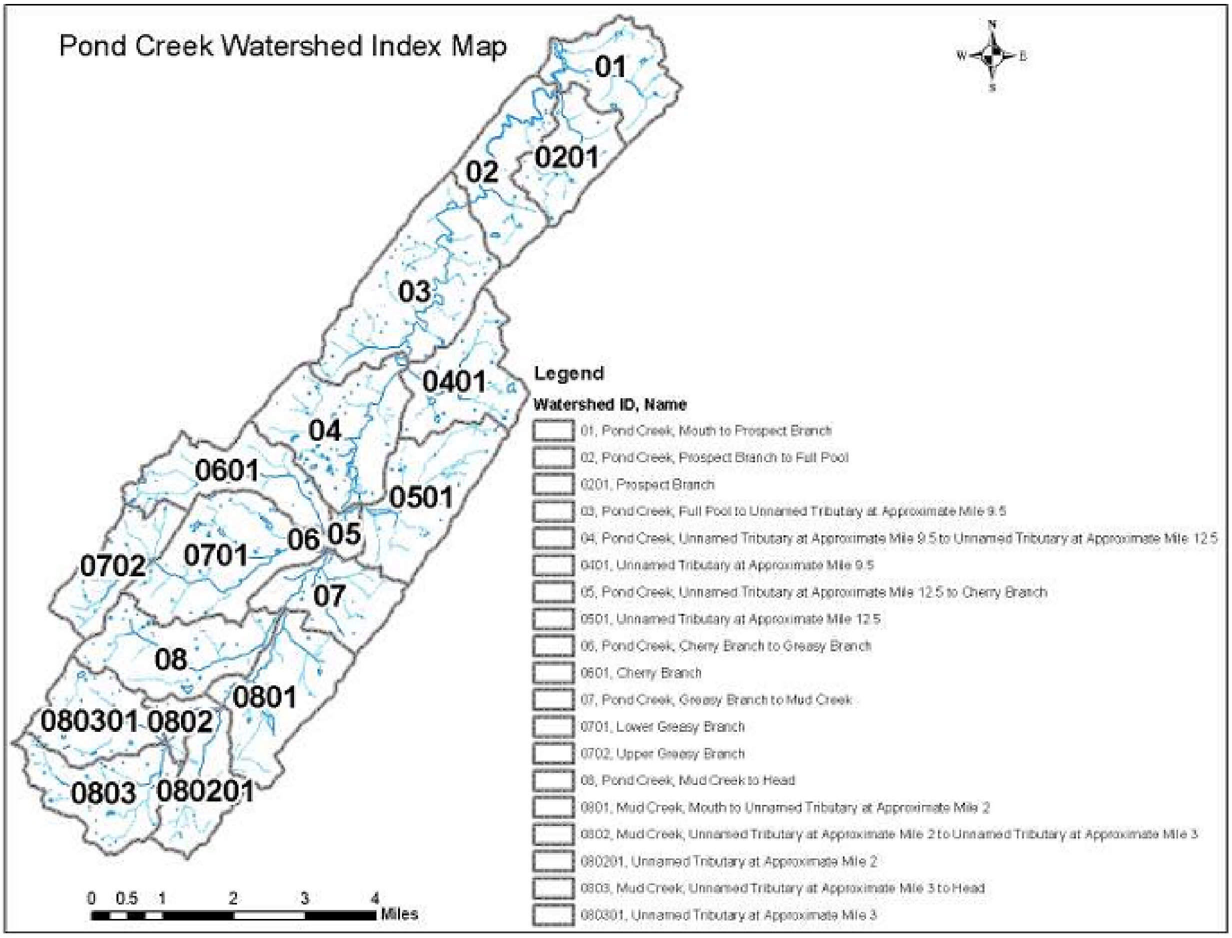


Figure 12. Pond Creek Watershed index map defining subwatershed locations and HUC codes.

Table 2. Classification and description of soil series within Pond Creek watershed; adapted from NRCS (2008).

Series	Depth	Drainage Class	Permeability	Landscape Position	Parent Material	Taxonomic Class
Bodine	Very deep'; C horizon >60in	Excessively drained	Moderately rapid	Ridge crests, shoulder slopes, side slopes	Derived from cherty limestone and dolomite	Loamy-skeletal, siliceous, semiactive, thermic Typic Paleudults
Decatur	Very deep'; to bedrock: 4-14ft; C horizon >67in	Well drained	Moderate	Ridge crests and side slopes	Old alluvium or colluvium underlain by residuum derived from limestone or dolomite	Fine, kaolinitic, thermic Rhodic Paleudults
Dewey	Very deep'; to bedrock: 5-20ft; C horizon >70in	Well drained	Moderate	Ridge crests and side slopes	Old alluvium underlain by residuum derived from limestone or dolomite	Fine, kaolinitic, thermic Typic Paleudults
Fullerton	Very deep'; to bedrock: 10-40ft; C horizon >60in	Well drained	Well-drained	Ridge crests, shoulder slopes, side slopes	Derived from cherty limestone or dolomite	Fine, kaolinitic, thermic Typic Paleudults
Waynesboro	Very deep'; to bedrock: 2-20ft; C horizon >60in	Well drained	Moderate	Ridge crests, stream terraces, side slopes	Old alluvium derived from sandstone, shale, and limestone	Fine, kaolinitic, thermic Typic Paleudults

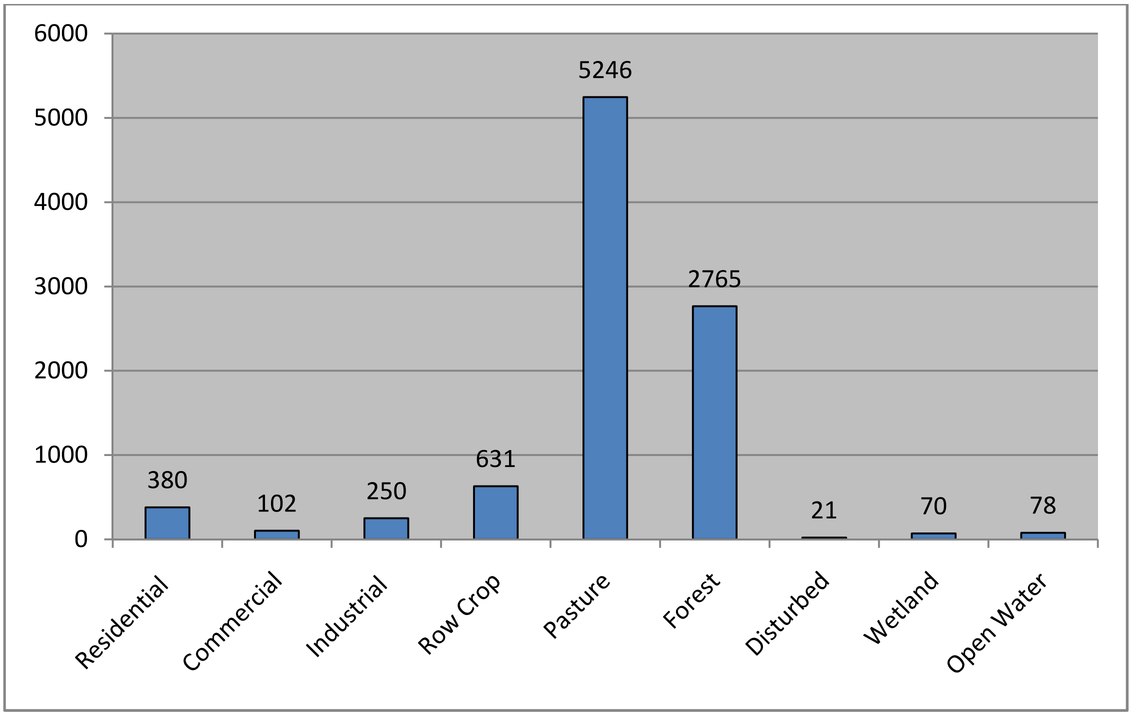


Figure 13. Major land use distribution (in hectares) within Pond Creek watershed (PCWC, 2008).

calves and dry dairy cows; 1,575 mature, lactating dairy cows; and 45 horses. The majority of the dairy operations are considered large, containing 150 or more animals per site.

The Pond Creek watershed was selected for this study because its land use is very typical of the Appalachian region, and further, because it has been listed on the 303(d) lists of impaired streams prepared by TDEC since 1998. Therefore, it can be considered a model system for evaluating the effectiveness of BMPs for improving water quality in the Valley and Ridge physiographic region. Furthermore, the watershed is also currently being studied to determine the sources of pathogens found within Pond Creek. The first draft of the 2008 303(d) list of impaired streams prepared by TDEC lists Pond Creek and two of its tributaries, Greasy Branch and Mud Creek, as only partially supporting their designated uses (TDEC, 2008b). Pond Creek is identified as an impaired stream because it has been affected by a number of pollutants, particularly pathogens, sediments, and nutrients as a result of pasture grazing, livestock in stream, and animal feeding operations (TDEC, 2008b). However, no direct identification of pollutant sources has been established, a difficulty inherent to non-point source pollutants.

Currently, the primary concern in the watershed is elevated pathogen levels from both human and animal sources. A TMDL for pathogens has already been developed for the Pond Creek watershed. Pond Creek is monitored monthly for pathogens, nutrients, and total suspended solids. There is also a significant amount of University of Tennessee Agricultural Extension effort in the watershed to convince producers to adopt management practices that will help improve Pond Creek water quality. Although sediments are considered a pollutant independently, they are often a medium for transport of pathogens and an array of other pollutants, including nutrients, heavy metals, and organics. Thus, it is important to identify the source of sediments in order to successfully control the quantities of other contaminants reaching Pond Creek. A number of BMPs have been employed in the watershed to improve stream quality by reducing the amount of sediment and pathogens entering the stream (TDEC, 2006a). In particular, the BMP's employed have been aimed at restricting cattle access to the stream, as well as improving pastures and tillage management practices, establishing riparian buffers, and reducing the size of livestock loafing areas. Water quality monitoring data indicate that the BMP's employed in Pond Creek have been relatively effective for reducing sediment and pathogen loads within the stream (Hagan and Walker, 2006).

Field Sampling Methodology

The potential sources of suspended sediments in the watershed are numerous. Sources include gravel roads, cattle paths, in-stream sediments (bottom and bars), subsurface materials, cattle trampled areas, tilled fields, drainage ditches, and forested areas. Sediment source sampling involved the collection of representative samples from the potential source locations described in Table 3 on February 8, 2007. Care was taken to ensure that only material susceptible to erosion (top 1-2 cm) was collected. Stream bank material was collected from subsurface material that was exposed and likely to be eroded. In stream sediment samples were collected from the top 1-2 cm of the exposed surface of bars and the bottom of the stream. Sampling included sites that encompassed all of the areas within the watershed that were accessible and proximate to the stream and appeared to be particularly susceptible to erosion processes. All surface sediment sampling sites were georeferenced using GPS technology (Fig. 14). Overall, 47 sediment source samples representing a variety of potential contributing sources, and four suspended sediment samples were collected (Table 4).

Representative suspended sediment sampling involved the collection of grab samples from the middle of the stream at two locations in Pond Creek (AJ and EMU-Fig. 14). This procedure was chosen because it was necessary to collect large volumes of stream water (approximately 60 L) in order to obtain a sufficient mass of suspended sediment (approximately 5 g) for chemical analysis. One collection site was near the middle of the watershed (35°38’46.15” N, 84°29’7.77” W) and the other was closer to the mouth (35°41’18.28” N, 84°27’59.80” W). The bulk water samples were collected during two separate high (storm) flow events. The first suspended sediment samples were collected on March 1, 2007 immediately after a significant rain event had passed through the area. At a Lenoir City, TN weather station approximately 30 km from Pond Creek, 28.7 mm of precipitation was recorded following this event (NCDC, 2008). On this sampling date Pond Creek was well above its bank full elevation at both sampling locations. The second set of suspended sediment samples were collected on July 11, 2007 after a short but intense thunderstorm had passed through the watershed. On this date,

Table 3. Pond Creek surface sediment source sampling site descriptions. The numbers indicate sample location within the watershed, while the letters indicate that multiple different samples were taken at the same location. Coordinates of each location are shown in decimal degrees.

Site #	Description of sample collection location	Latitude	Longitude
1A	An in-stream sediment bar just upstream from where an unnamed tributary enters the Pond Creek tributary Mud Creek.	35.6104	-84.5164
1B	A streambank adjacent to the sediment bar (1A) just upstream from where an unnamed tributary enters the Pond Creek tributary Mud Creek.		
1C	A cattle path entering the unnamed tributary of Mud Creek adjacent to the sediment bar (1A).		
1D	A portion of the in-stream sediment bar (1A) that had been trampled by cattle exactly where the cattle access path (1C) entered the unnamed tributary.		
2	An unvegetated portion of a pasture that had been completely trampled by cattle and was situated approximately 100 meters NW of the bank of the unnamed tributary of Mud Creek (1B).	35.6107	-84.5166
3	A cattle path leading to the cattle trampled area (2) situated in a vegetated area approximately 50 meters SW of site 2.	35.6105	-84.5167
4A	A dirt road parallel and immediately next to Pond Creek just where the dirt road exited a paved road.	35.6196	-84.52
4B	A cut bank adjoining the dirt road where sample 4A was taken.		
4C	A drainage ditch just below and in the downstream direction of the cut bank (4B). This sampling location was also receiving runoff via a culvert from a small area on the other side of the dirt road.		
5A	An in-stream sediment bar in Pond Creek that was heavily trampled by cattle.	35.6271	-84.5042
5B	A streambank of Pond Creek immediately adjacent to the in-stream bar (5A).		
6	A cattle path entering Pond Creek just upstream of the in-stream sediment bar (5A).	35.6269	-84.5041
7A	A cattle path within a heavily cattle trampled and largely unvegetated area approximately 50 meters from a small unnamed tributary of Pond Creek.	35.6277	-84.5055
7B	The heavily cattle trampled and largely unvegetated area surrounding the cattle path from which sample 7A was collected		
8	Sediment from the bottom of the small drainage ditch/unnamed tributary (7A) of Pond Creek. This unnamed tributary was situated directly behind a manure storage pit an began precisely where the drain for the manure storage pit was located.	35.6275	-84.5057
10	A drainage ditch exiting from a small wetland area and entering Pond Creek approximately 50 meters downstream.	35.639	-84.4914
11	A Pond Creek streambank just upstream of where the drainage ditch (10) enters. The sample was taken from the outside cut bank of a meander.	35.6391	-84.4917

Table 3. continued.

12	An instream sediment deposit along the inside edge of the meander adjacent to the streambank from which sample 11 was collected.	35.6391	-84.4919
13	A heavily traveled cattle path along side a paved road approximately 200 meters E of Pond Creek.	35.6426	-84.4873
14	A Pond Creek streambank just upstream of where the tributary Greasy Branch enters. The sample was collected on the outer wall of a meander.	35.6431	-84.4892
15A	An in-stream sediment bar located just downstream of where Greasy Branch enters Pond Creek.	35.6437	-84.4892
15B	A cattle travel path along the edge of Pond Creek just downstream of where Greasy Branch enters Pond Creek.		
16	A largely unvegetated area along the bank of Pond Creek that had been heavily trampled by cattle.	35.6464	-84.4849
17A	An in-stream sediment bar slightly downstream from where sample 16 was collected.	35.6467	-84.4849
17B	A largely unvegetated area along the bank of Pond Creek that had been heavily trampled by cattle slightly downstream from site 16 and within the floodplain of Pond Creek.		
18	A slightly sloping tilled corn field situated approximately 50 meters from Pond Creek.	35.6665	-84.4831
19	A slightly sloping tilled wheat field on which biosolids had been heavily applied, approximately 150 meters from Pond Creek.	35.6615	-84.485
20	A cattle feeding area that had been heavily trampled and was largely unvegetated located across the road from site 19 and approximately 100 meters from Pond Creek.	35.6614	-84.4843
21	A relatively flat tilled field in a corn/soybean rotation on which there was nothing planted at the time.	35.6553	-84.4873
22	A dirt road leading to a farm and situated alongside the tilled field from which sample 21 was collected.	35.6557	-84.4874
23	A cattle loafing area that was heavily trampled and completely unvegetated. It was situated downhill from a cattle milking barn.	35.6479	-84.4761
24	A drainage ditch situated below and receiving all the runoff from the cattle loafing area (23).	35.649	-84.4774
25	A tilled field in a corn/soybean rotation on which biosolids had been applied. This sample was collected from a portion of the field on top of a ridge.	35.647	-84.4807
26A	The surface layers of sediment from a drainage ditch that runs along the edge of a tilled field on which corn/fescue rotation was being used.	35.6516	-84.4729
26B	The subsurface (15cm) layers of sediment from a drainage ditch that runs along the edge of a tilled field on which corn was grown.		
27	A dirt road along a perpedicular edge of tilled field along which the drainage ditch (26) runs.	35.6518	-84.4731

Table 3. continued.

28	The tilled field in a corn/fescue rotation, and currently planted in fescue along the edges of which samples 26 and 27 were collected.	35.6519	-84.4729
29	A sloping tilled corn field that had no vegetation and had been recently tilled.	35.6567	-84.4684
30A	A cattle loafing area that was heavily trampled and completely unvegetated, and situated adjacent to a milking barn. This sample was collected from a disturbed surface consisting of pushed up clumps of soil generated from large numbers of cattle exiting the barn. This was likely subsurface material.	35.662	-84.4693
30B	A hard scraped surface just outside of the milking barn close to where 30A was collected.		
31	A cattle travel path within the loafing area (30) approximately 100 meters from the milking barn.	35.6633	-84.4686
32	A cattle travel path within the loafing area (30) but approximately 50 meters upslope from where sample 31 was collected.	35.6633	-84.4694
33	A unvegetated refuse pile consisting of subsurface material just outside of the milking barn very close to where sample 30 was collected. This material had been removed when the milking barn was constructed.	35.6623	-84.4693
34	A forested area situated alongside an unnamed tributary of Pond Creek towards the mouth of Pond Creek.	35.6973	-84.4725
35	A forested area situated alongside an unnamed tributary of Pond Creek closer to the mouth of Pond Creek than 34.	35.7049	-84.4621
36A	A cut bank along a pave road even closer to the mouth of Pond Creek than 35.	35.7222	-84.4381
36B	A forested area just upslope from the cut bank on which (36A) was collected.		
AJ	A suspended sediment sampling location situated approximately in the center of the watershed	35.6462	-84.4855
EMU	A suspended sediment sampling location situated towards the mouth of Pond Creek in relation to the AJ site.	35.6884	-84.4666

* Samples 23-33 were collected within a subwatershed drained by an unnamed tributary of Pond Creek. The reason that this area was heavily sampled is that it was thought to be a major contributor of in-stream sediment, based on land-use practices in the area.

Coordinates are in decimal degrees.

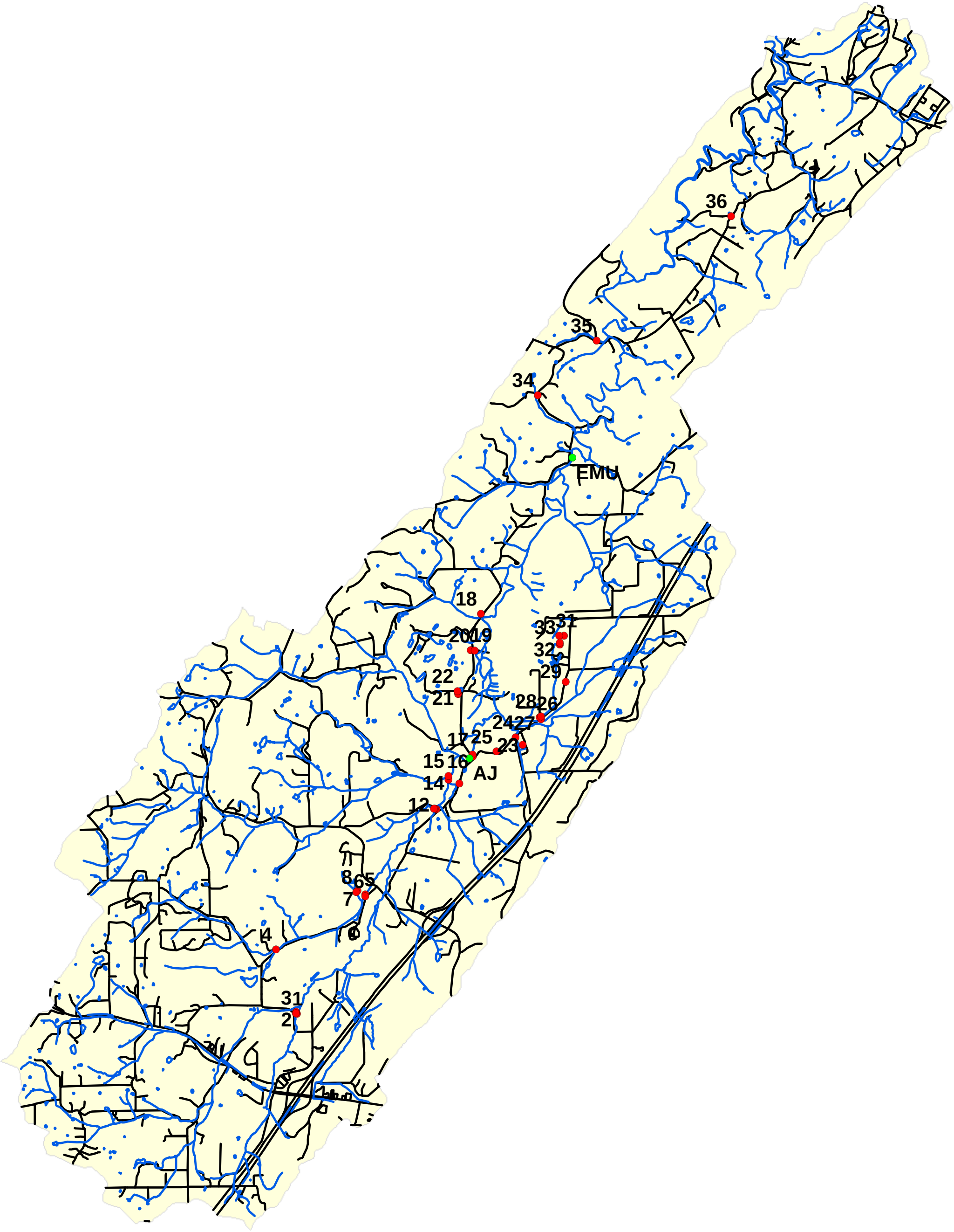


Figure 14. Map of the Pond Creek watershed showing streams in blue and roads in black. Surface and subsurface sediment sampling sites are indicated by red points and suspended sediment sampling sites are indicated by green points. All points are labeled according to Table 3.

Table 4. Grouping and description of surface materials collected from the Pond Creek watershed. Sample ID corresponds with the sampling locations (Table 3; Figure 14).

Group	Description	Number in Group	Sample ID
1	Cattle Path	8	1C, 3, 6, 7A, 13, 15B, 31, 32
2	Gravel Roads	3	4A, 22, 27
3	Forested Areas	3	34, 35, 36B
4	Tilled Fields	6	18, 19 ,21 ,25, 28, 29
5	Subsurface	8	1B, 4B, 5B, 11, 14, 30B, 33, 36A
6	Cattle Trampled Areas	7	2, 7B, 16, 17B, 20, 23, 30A
7	Drainage Ditches	6	4C, 8, 10, 24, 26A, 26B
8	Instream Sediment	6	1A, 1D, 5A, 12, 15A, 17A
9	Suspended Sediment	4	AJ1, AJ2, Emu1, Emu2

* The 1 and 2 associated with the suspended sediment samples indicates the first and second date on which suspended sediment samples were collected.

the water in Pond Creek was higher than normal; however, it was still well below bank full elevation at both sampling locations. Approximately 7 mm of precipitation were recorded at the Lenoir City, TN weather station following this event (NCDC, 2008).

Laboratory Methodologies

The surface samples from potential sediment sources were air dried and then disaggregated using a mortar and pestle. Next, they were subjected to particle size fractionation by wet sieving through a 53-µm sieve to isolate the clay and silt-sized material. The size separation was performed because suspended sediments typically consist only of clay- and silt-sized materials (<63 µm) (Collins et al., 1997c). Thus, the suspended sediment samples can be directly compared with the source samples. The suspended sediments were isolated from the bulk water samples by centrifugation. After sieving and centrifugation, all samples were freeze-dried using a Labconco Freezone 4.5.

Subsamples (0.2 g) of the <53-µm material and suspended sediment (3-fold replication) were subjected to microwave dissolution in *aqua regia* (a mixture of concentrated nitric acid and concentrated hydrochloric acid in a ratio of 1:3) and HF (hydrofluoric acid) (Ammons et al., 1995). After the neutralization of excess HF with boric acid and filtering through Whatman 42 (>2.5 μm) filters, the elemental composition was determined using inductively coupled argon plasma-optical emission spectroscopy (ICP-OES) (Spectro CIROS ICP-OES). The watershed materials were also subjected to chemical extractions, including the nitric acid extraction method of Chang et al. (1984) and the Mehlich 3 extraction (Mehlich, 1984) to evaluate the potential for using these safer and less time-consuming methods for characterizing watershed source materials. In the Chang method, 3.5 g subsamples of the <53-μm material and suspended sediment (3-fold replication) were extracted by refluxing overnight in 21 mL 4M HNO_3. Extracts were then diluted to 35 mL and filtered through Whatman 42 (>2.5 μm) filters. The extracts were analyzed using ICP-OES. In the Mehlich 3 extraction procedure, 2.5 g subsamples of the <53-μm material and suspended sediment (3-fold replication) were extracted in 25 mL of the Mehlich 3-extractant (0.2M CH_3COOH – 0.25M NH_4NO_3 – 0.015M NH_4F – 0.013M HNO_3 – 0.001M EDTA). Samples were shaken for five minutes and then filtered through Whatman 42 (>2.5 μm) filters. The extracts were analyzed using ICP-OES. The total dissolution samples were analyzed for 31 elements (Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hf, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Rb, S, Se, Si, Sr, Ti, V, Zn, Zr), while the extracts were analyzed for the same elements, excluding Na and Si. For quality assurance/quality control (QA/QC), the order of sample analysis was randomized. Further, ISO (International Organization for Standardization) certified standards (VHG Labs, Inc.) were used to calibrate the instrument every 10 samples. Recalibration was also triggered when the coefficient of variation in the ICP-OES response for any element exceeded 20%.

In order to evaluate the reliability of the data generated by the ICP-OES analysis of the samples, the average percent relative standard errors for each element for the replicates of each sample were calculated. The %RSE values for the total dissolution data are presented in Table 5. They range from 2.45% to 15.71% and fall within the acceptable error limit of 20%. The %RSE values for the nitric acid extraction data range from 2.06% to 13.69% (Table 6). The %RSE values for the Mehlich 3 extraction data are also <20%, ranging from 1.27% to 5.34% (Table 7).

Table 5. Average percent relative standard error values (%RSE) for each element for the replicate total dissolution analysis of each sample.

Element	%RSE	Element	%RSE
Al	3.39	Mn	3.34
Ba	3.83	Na	2.46
Ca	3.24	Nd	4.15
Cd	5.69	Ni	15.71
Ce	4.79	P	2.67
Co	6.13	Rb	4.01
Cr	14.96	Si	6.11
Cu	4.56	Sr	3.55
Fe	3.52	Ti	4.64
K	2.72	V	3.40
La	5.99	Zn	3.39
Li	3.27	Zr	3.40
Mg	3.25		

Table 6. Average percent relative standard error values (%RSE) for each element for the replicate HNO_3-extraction analysis of each sample.

Element	%RSE	Element	%RSE
Al	4.30	Mg	3.53
Ba	2.28	Mn	2.06
Ca	2.14	Mo	13.69
Cd	3.81	Nd	2.16
Ce	4.49	Ni	4.00
Co	2.25	P	2.47
Cr	5.15	Rb	2.34
Cu	3.19	S	2.50
Fe	2.77	Sr	3.08
Hf	8.21	Ti	7.58
K	4.77	V	2.86
La	3.01	Zn	2.95
Li	4.45	Zr	3.35

Table 7. Average percent relative standard error values (%RSE) for each element for the replicate Mehlich 3-extaction analysis of each sample.

Element	%RSE	Element	%RSE
Ba	2.08	Mn	1.34
Ca	1.46	Nd	2.81
Cd	2.02	Ni	5.34
Ce	4.76	P	1.79
Co	1.46	Rb	2.35
Cr	3.28	S	4.18
Cu	2.49	Sr	1.67
Fe	1.69	V	3.21
Hf	2.22	Zn	1.55
K	1.29	Zr	4.55
Mg	1.27		

Statistical Methods

Statistical analyses were performed using SAS 9.1 (SAS Institute, 2005). Descriptive statistics (e.g., mean, median, mode, standard deviation) were calculated for each element using PROC CAPABILITY. Elemental fingerprinting involved a series of nested multivariate statistical procedures. First, the elemental data were examined to identify those elements whose concentrations differed significantly with sediment source group (Table 4), with source groups defined initially as cattle paths, cattle trampled areas, tilled fields, forested areas, subsurface material, in-stream sediment, drainage ditches, and suspended sediment. The nonparametric Kruskall-Wallis rank test (nonparametric one-way ANOVA) with $P< 0.05$ was one method used to make this determination. The results of this test determine with 95% confidence whether significant differences exist among any of the groups for each element. Secondly, the Student-Newman-Keuls multiple-range test (parametric ANOVA) was used to examine significant differences among groups, and to identify between which groups differences exist. The results of this test confirm with 95% probability whether the differences in the mean elemental concentrations for each element in each arbitrary group are the result of random variations. Next, a multivariate discriminant function analysis (PROC STEPDISC) was used to establish a set of elements that was capable of optimum discrimination among the source groups. This was done using a stepwise selection algorithm based on the minimization of Wilks' lambda (Collins et al. 1997a). The chemical information for all elements and for all watershed samples was used in each of these two steps. Elements whose compositional variables failed to distinguish between source types and did not vary significantly among groups were initially excluded from the next stage of analysis (sediment sourcing). The above process was also conducted with the source groups defined as surface material, subsurface material, in-stream sediments, and suspended sediments.

Multivariate techniques, including principal component analysis (PCA), divisive hierarchical cluster analysis (a type of factor analysis) and canonical discriminant analysis (CDA) were employed to examine relationships among the elemental composition variables and identify statistically similar groups of sediment source samples. Principal component analysis is a statistical method used to reduce the complexity of data containing a large number of variables to a small number of variables (principal components), while at the same time allowing for little loss of information. Hierarchical dendrograms are another way to conveniently view the clustering that occurs within principal component space. Another statistical method that is related to (and employs) principal component analysis is CDA. While PCA creates variables that account for the greatest degree of variability in the data, the variables produced by CDA have the highest possible multiple correlations with groupings of observations. The clusters or groups that were created by these multivariate techniques were closely evaluated to determine if they were similar to the defined sediment source groups. The PCA analysis is also be useful for examining the relationships between the sediment source samples and the suspended sediment samples. The relative distance between two samples in principal component space indicates how similar or different their elemental compositions are. If suspended sediment samples plot close to a particular group of source samples in principal component space, then they are similar in elemental composition to those samples, and it is logical to conclude that that source is the dominant contributor of suspended sediment material. The groups created by CDA are also particularly important to evaluate because this analysis is conducted completely independent of previously defined groups. Thus, the groups created by CDA can be compared with the groups defined based on the watershed land uses, as well as the groups defined by surface versus subsurface origin.

If distinguishable groups were established using the multivariate techniques that match the defined sediment source groups, then the significant elements identified using the Kruskall-Wallis rank test and the multivariate discriminant function analysis could be applied to a multivariate mixing model similar to those used in other studies that have quantified suspended sediment sources (Collins et al., 1997a; 1997b; 1997c; 1998; 2001; Owens et al. 1999; Walling et al., 1999). In the model a linear equation was constructed for the mean values of each property in each group in order to relate the concentration of that property to the mixture of properties represented in the suspended sediment samples. The set of linear equations representing the composite fingerprint was then used to determine the relative contributions of each source type to the suspended sediment collected from the stream. The same type of model may also be applied using principal components rather than elemental concentrations as the variables for the set of equations used to determine relative source contribution.

This type of model is only applicable if a number of criteria are met. First, it is important to identify all the sources contributing to the suspended sediment load because the sources represent ‘end members’ of the model and influence the relative proportions calculated for each contributing source for a particular suspended sediment sample in the model output (Walden et al., 1997). For example, when all of the samples are plotted using CDA, the suspended sediment samples should plot in a region of canonical space that is representative of a combination of the chemical properties of the defined contributing sources. If this is not the case then it is likely that there are other contributing sources. Secondly, it is necessary for the maximum number of sources to be realistic with respect to the dimensionality of the data. The number of parameters used to characterize the sediment sources restricts the number of sources (end members) that can be used in this type of modeling. The number of numerical variables used in the model to characterize the sources must be greater than or equal to the number of sources. Furthermore, as stated above, it is important to use an initial qualitative and statistical analysis to evaluate whether or not a data set can be realistically applied to a quantitative model (Walden et al., 1997). It must be possible to differentiate the groups using statistical analyses, otherwise, a multivariate mixing model of this type provides no utility.

Results and Discussion

Total Elemental Data

Descriptive Statistics

Of the 31 elements analyzed, 25 were above detectable concentrations in all of the Pond Creek samples (Table 8). Based on the coefficient of variation (%CV, 100 times the standard deviation divided by the mean) values, there is considerable heterogeneity in the elemental data. According to Mulla and McBratney (2000), %CV values can be used to describe the heterogeneity of a soil property. Soil elemental data that are described by %CV values that are <15% are identified as having little variability. Elemental data with moderate variability have %CV values between 16 and 35%, and highly variable data has %CV values >36%. Hence, the higher the value for the %CV, the more heterogeneous the data for a particular element. With the exception of Si, which had little variability in the watershed (10.7 %CV), the elements are in the moderate to highly variable groups, ranging from 17.6% (Zr) to 150.3% (Ni). For example, the %CV values for Cr and Ni are approximately 150, indicating that the concentrations of these two elements in the watershed are highly heterogeneous. The %CV values for Cu, Mn, and P are between 50 and 60 and indicate very heterogeneous distributions. In contrast, the %CV values for Zr and Li are much lower, ranging from 17% to 22%, indicating that these populations display only moderate variability. Although %CV values are only one criteria for evaluating the heterogeneity of the soil elemental content, these values suggest that more than one population, or sediment source groups, of soil samples may exist in the watershed.

Table 8. Descriptive statistics of the total elemental data for the Pond Creek watershed samples.

Element	N	Mean	Median	Std. Deviation	Variance	Min	Max	%CV	X^2
g kg^{-1}									
Al	44	59.21	57.1	19.42	377272.6	20.46	111.33	32.81	0.249
Ca	44	4	4.12	1.9	3595.25	0.77	8.45	47.41	0.761
Fe	44	36.06	34.35	12.18	148354.1	10.86	72.77	33.77	0.06*
K	44	10.69	11.17	2.43	5912.35	6.05	14.27	22.75	0.083*
Mg	44	3.93	3.91	1.21	1461.31	1.25	6.46	30.75	0.086*
Si	44	213.51	216.94	22.78	518890.3	169.61	260.74	10.67	0.976
Ti	44	2.23	2.18	0.53	285.01	1.36	3.34	23.93	0.005*
mg kg^{-1}									
Ba	44	420.59	414.61	145	21024.31	116.91	974.66	34.48	<.001*
Cd	44	3.04	2.79	1.23	1.5	1.06	8.76	40.28	<.001*
Ce	44	73.32	68.87	24.99	624.6	17.14	156.95	34.09	<.001*
Co	44	17.97	17.79	6.46	41.68	2.87	30.54	35.94	0.801
Cr	44	226.42	57.82	337.02	113580.1	17.56	1413.5	148.85	<.001*
Cu	44	104.28	86.31	52.4	2745.26	23.07	253.02	50.25	0.002*
La	44	36.59	36.29	12.59	158.46	8.08	74.24	34.4	0.02*
Li	44	51.55	51.9	11.07	122.58	25.69	70.41	21.48	0.078*
Mn	44	1918.77	1750.4	971.06	942959.2	326.58	3967.15	50.61	0.198
Na	44	872.44	866.25	246.2	60616.49	391.23	1473.62	28.22	0.658
Nd	44	22.31	23.17	7.59	57.55	6.33	37.18	34	0.807
Ni	44	131.04	36.5	196.96	38793.27	3.26	842	150.3	<.001*
P	44	1325.29	1227.6	783.73	614232.7	168.57	3875	59.14	<.001*
Rb	44	86.35	81.35	30.14	908.57	25.94	179.12	34.91	0.016*
Sr	44	31.69	30.09	8.66	75.08	14.18	55.53	27.34	0.179
V	44	76.45	76.27	22.67	513.93	35.29	131.5	29.65	0.607
Zn	44	146.75	133.75	64.65	4180.07	44.61	356.17	44.06	<.001*
Zr	44	113.62	112.33	19.98	399.17	84.08	165.72	17.58	0.181

*Elemental data are not normally distributed at P<0.1

The chi-square distribution coefficient values (X^2) show that a majority of the elements are not normally distributed in the watershed (Table 8). This also indicates that the elemental content of soils may be used for discriminating sediment source groups. In general, elements that are normally distributed, such as Al and Sr (Fig. 15), are also less variable in the watershed. Chromium and Ni are highly variable, and their distributions are both highly skewed (Fig. 16). Two other elements that do not fit a normal distribution are Li and K. These two elements can be described as having several modes (Fig. 17). The multi-modal distributions suggest that the data contain more than one population. Thus, these elements may provide significant power for discriminating the various types of sediment samples collected in the watershed because an element (or variable) that has discrimination power is defined as having the ability to differentiate between groups within a population.

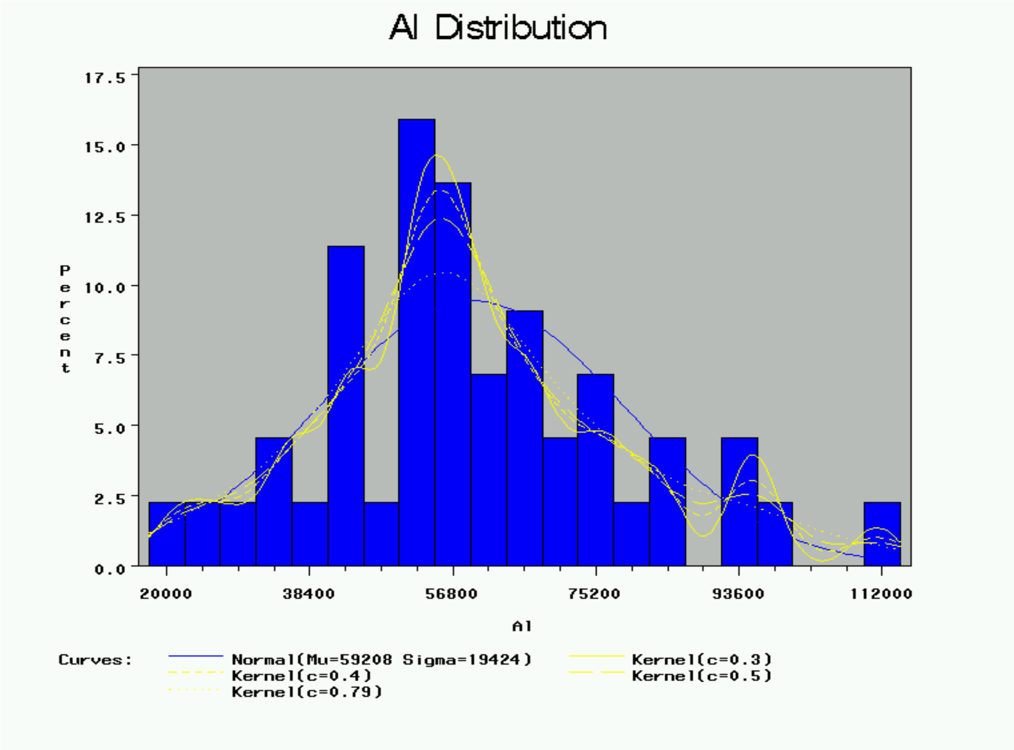
Sediment Source Discrimination

The elemental content of each soil sample is unique and can be described as a fingerprint of the sample. Two examples of soil sample fingerprints are illustrated for a cattle trampled area and a subsurface sample (Fig. 18). To differentiate the various potential stream sediment sources using the elemental fingerprint data, the following stipulations were assumed:

(1) Potential stream sediment source samples could be placed into source groups based on the current and past management, location in the landscape, or depth of the soil sample.

(2) A group of elements could be identified as having significantly different concentrations among the defined source groups.

(3) A group of elements could be identified as having significant power to discriminate the defined source groups.



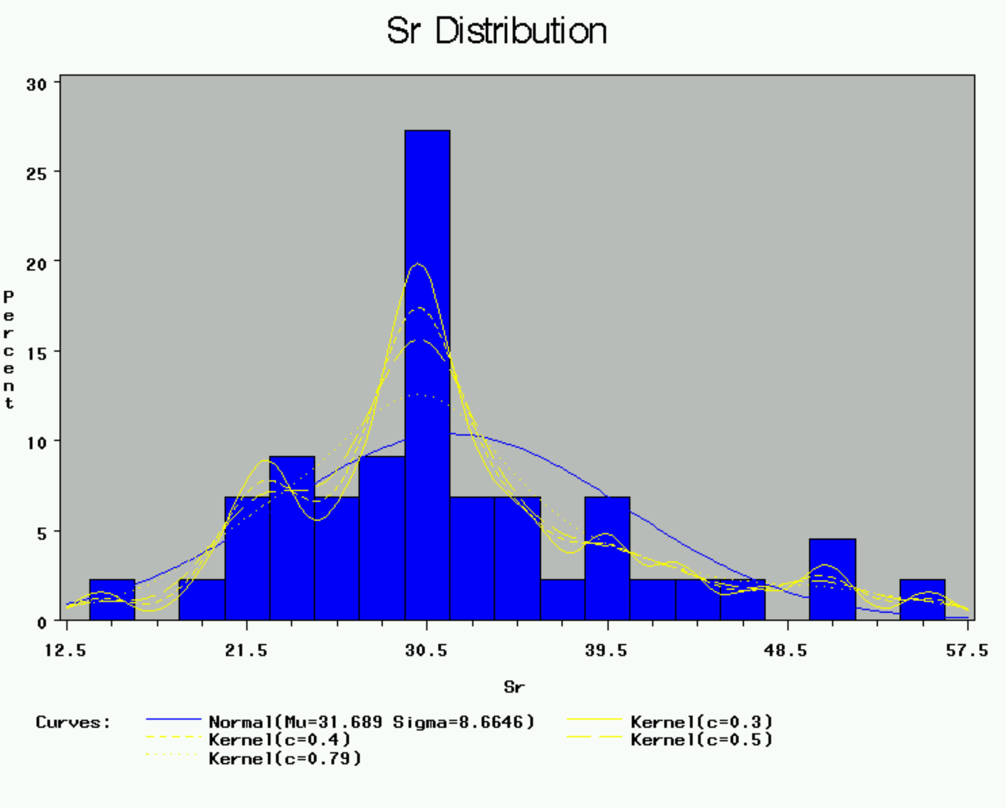
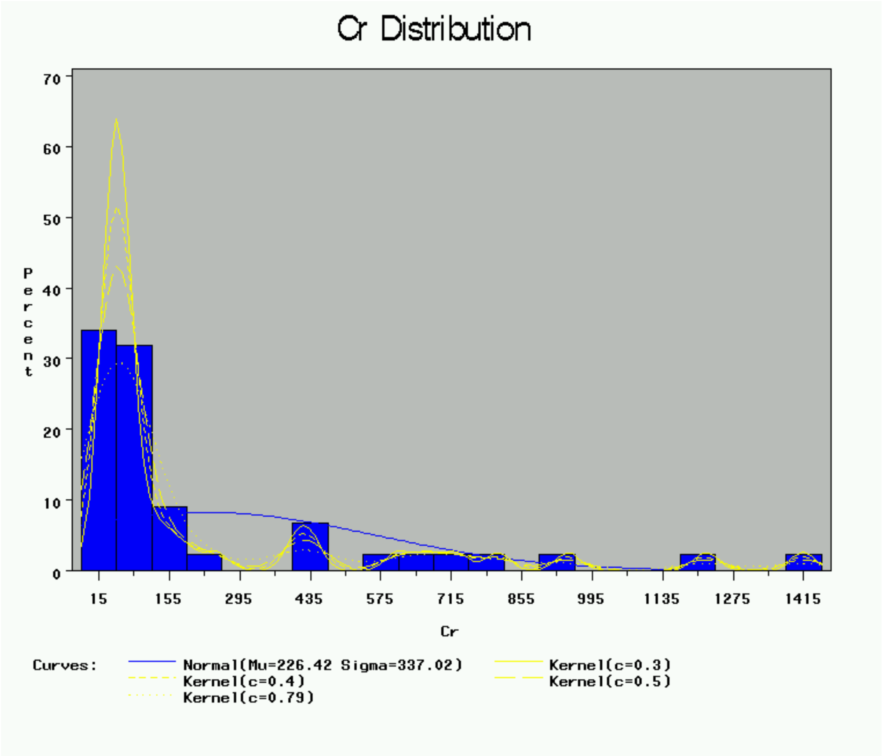


Figure 15. Frequency distributions for the total concentrations of Al and Sr in the Pond Creek watershed. These two elements are described by a normal distribution.



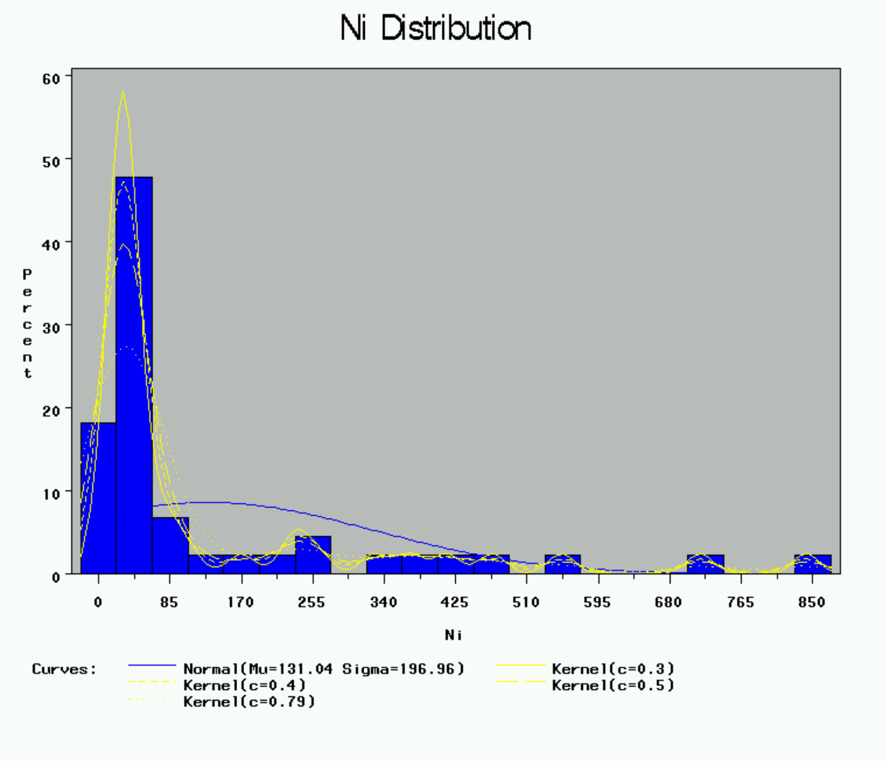


Figure 16. Frequency distributions for the total concentrations of Cr and Ni in the Pond Creek watershed. These two elements are not described by a normal distribution and their distributions are highly skewed.

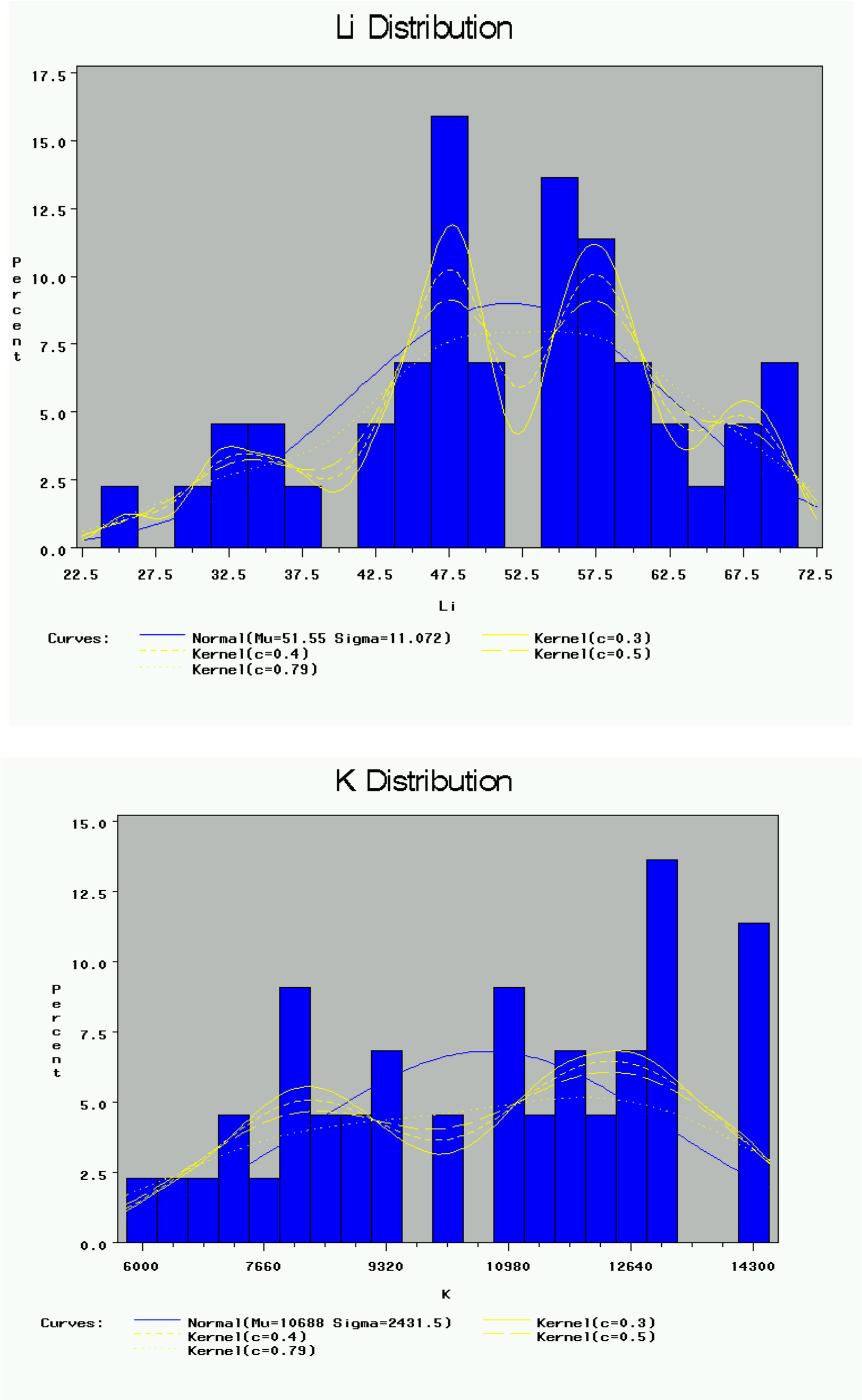


Figure 17. Frequency distributions for the total concentrations of Li and K in the Pond Creek watershed. These two elements are not described by a normal distribution, and their distribution is characterized as containing several modes.

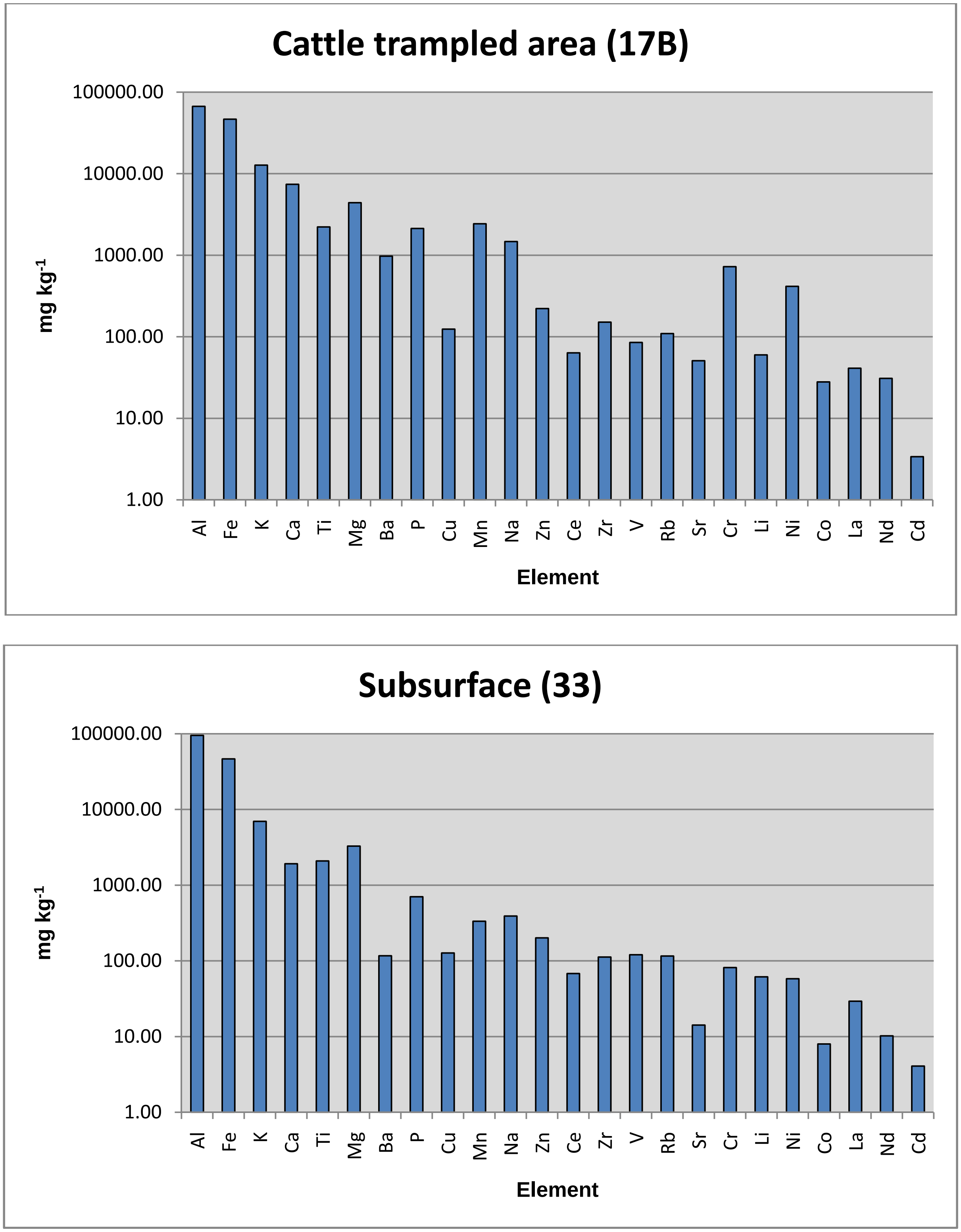


Figure 18. The histograms illustrate the total elemental composition (fingerprint) of a cattle trampled area and a subsurface sample.

To test for significant differences in the concentrations of each element among the defined groups (suspended sediment and sources) (Table 4) both a Kruskal-Wallis rank test (KW) with $P < 0.05$ and a Student-Newman-Keuls (SNK) multiple-range test with $P < 0.05$ were used. The former is a non-parametric test, and the latter is parametric. Secondly, a stepwise discriminant analysis was used to identify those elements that were useful for discriminating among the source groups. Using all nine groups (eight source groups and a suspended sediment group, Table 4), nine elements (Al, Ca, Cu, K, Mg, P, Ti, V, Zr) were found to have significant differences among the source groups by the KW test (Table 9), and seven elements (Al, K, Mg, P, Rb, Ti, Zr) were shown to afford discriminatory power among the groups (Table 10). Six elements had both characteristics (Al, K, Mg, P, Ti, Zr). The results of the SNK test (Table 11) indicated that significant differences existed between the means of groups for Ba, Ca, Cd, K, Mg, P, Sr, Ti, and Zr. For Ba, Ca, Mg, and Sr the mean of the gravel road samples was significantly different from all of the other groups, and there were no differences between the means of any of the other groups. For Cd, K, P, Ti, and Zr there were significant differences in the means of more than one group (Table 11).

Due to the considerable variability imparted on the elemental data set by the gravel road samples (Fig. 19), they were excluded from further consideration. The rank test, multiple-range test, and discrimnant analysis were then repeated. As a result, only seven elements (Al, Ca, Cu, P, Ti, V, Zr) were found to exhibit significant differences among the eight sediment source groups by the KW test (Table 12), and seven elements (Al, K, Li, P, Sr, Ti, Zr) afforded discriminatory power among these source groups (Table 13). Four elements had both characteristics (Al, P, Ti, Zr). For example, consider the concentrations of Fe, Ca, Li, and Ti in the Pond Creek materials. Iron concentrations did not significantly differ among any of the

Table 9. Results of the Kruskal-Wallis rank test using all nine initially defined groups (Table 4) and total elemental concentrations.

Kruskal-Wallis Test

Element	X^2	DF	Pr>X^2
Al*	19.6944	8	0.0116
Ba	5.6183	8	0.6899
Ca*	24.9141	8	0.0016
Cd	12.8868	8	0.1158
Ce	9.566	8	0.2968
Co	4.7564	8	0.7833
Cr	7.1341	8	0.5222
Cu*	18.6279	8	0.017
Fe	11.6468	8	0.1677
K *	16.2195	8	0.0393
La	10.5313	8	0.2297
Li	14.5141	8	0.0693
Mn	8.4068	8	0.3948
Mg*	17.9854	8	0.0213
Na	8.2769	8	0.4069
Nd	5.5438	8	0.6982
Ni	7.2972	8	0.5049
P*	26.5039	8	0.0009
Rb	10.8642	8	0.2095
Si	8.0132	8	0.4322
Sr	6.6576	8	0.574
Ti*	24.1042	8	0.0022
V*	16.208	8	0.0395
Zn	7.6587	8	0.4675
Zr*	22.0882	8	0.0048

*Indicates elements that exhibited significant differences among the groups at P<0.05.

Table 10. Results of the discriminant function analysis using all nine initially defined groups(Table 4) and total elemental concentrations.

Discriminant Function Analysis			
Element	R^2	F	Pr>F
Al*	0.4558	3.77	0.0027
Ba	0.0821	0.39	0.9177
Ca	0.0312	0.14	0.9966
Cd	0.2246	1.27	0.2916
Ce	0.067	0.31	0.9555
Co	0.1287	0.65	0.7335
Cr	0.1974	1.08	0.4018
Cu	0.1284	0.64	0.7349
Fe	0.1254	0.63	0.7491
K*	0.469	3.98	0.0019
La	0.249	1.45	0.2108
Li	0.253	1.48	0.1993
Mg*	0.4676	3.95	0.0019
Mn	0.1249	0.62	0.7516
Na	0.0914	0.44	0.8885
Nd	0.2111	1.17	3440
Ni	0.2005	1.1	0.3882
P*	0.3964	2.96	0.012
Rb*	0.3663	2.6	0.0235
Si	0.1406	0.72	0.6759
Sr	0.0384	0.17	0.9929
Ti*	0.4041	3.05	0.01
V	0.2254	1.27	0.2887
Zn	0.1786	0.95	0.4886
Zr*	0.3589	2.52	0.0275

*Indicates elements that provided power for discriminating the groups. Pr>F values must be below 0.15 for an element to be considered to provide discrimination power.

Table 11. Results of the Student-Newman-Keuls multiple-range test using all nine initially defined groups (Table 4) and total elemental concentrations. For each element, groups identified by the same letter are not significantly different at the P<0.05.

Student-Newman-Keuls multiple-range test

Aluminum				Barium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	72727	8	Subsurface	A	7981.4	3	Gravel roads
A	72022	6	Tilled fields	B	529.6	7	Cattle trampled areas
A	69737	7	Cattle trampled areas	B	478.6	4	Suspended sediment
A	65269	6	Drainage ditches	B	449.4	6	Instream sediment
A	63855	4	Suspended sediment	B	418.7	8	Cattle paths
A	58742	8	Cattle paths	B	418.1	3	Forested areas
A	47980	6	Instream sediment	B	405.1	6	Tilled fields
A	34616	3	Gravel roads	B	398.6	6	Drainage ditches
A	30747	3	Forested areas	B	334	8	Subsurface
Cadmium				Calcium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	4.42	4	Suspended sediment	A	68156	3	Gravel roads
AB	3.41	7	Cattle trampled areas	B	5232	7	Cattle trampled areas
AB	3.33	6	Tilled fields	B	5060	4	Suspended sediment
AB	3.29	8	Subsurface	B	4675	6	Instream sediment
AB	3.1	6	Drainage ditches	B	4612	6	Drainage ditches
AB	2.94	6	Instream sediment	B	3888	8	Cattle paths
AB	2.92	8	Cattle paths	B	3290	6	Tilled fields
AB	1.98	3	Gravel roads	B	2285	8	Subsurface
B	1.66	3	Forested areas	B	2060	3	Forested areas
Cerium				Chromium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	88.83	6	Tilled fields	A	572.3	3	Forested areas
A	88.66	4	Suspended sediment	A	503.3	7	Cattle trampled areas
A	78.97	6	Drainage ditches	A	498.4	8	Subsurface
A	75.3	8	Cattle paths	A	274.7	6	Instream sediment
A	70.17	7	Cattle trampled areas	A	245.2	6	Drainage ditches
A	68.22	8	Subsurface	A	227.8	8	Cattle paths
A	66.07	6	Instream sediment	A	187.8	6	Tilled fields
A	58.75	3	Forested areas	A	108.1	3	Gravel roads
A	56.19	3	Gravel roads	A	53.7	4	Suspended sediment

Table 11 continued.

Cobalt				Copper			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	21.31	3	Gravel roads	A	176.92	8	Cattle paths
A	20.03	6	Drainage ditches	A	173.67	3	Forested areas
A	19.76	6	Instream sediment	A	132.38	6	Instream sediment
A	19.5	4	Suspended sediment	A	132.09	8	Subsurface
A	18.96	7	Cattle trampled areas	A	130.2	6	Drainage ditches
A	17.97	8	Cattle paths	A	94.23	7	Cattle trampled areas
A	17.65	6	Tilled fields	A	87.91	6	Tilled fields
A	16.76	8	Subsurface	A	69.51	3	Gravel roads
A	12.52	3	Forested areas	A	30.11	4	Suspended sediment

Iron				Lanthanum			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	46549	7	Cattle trampled areas	A	53.7	3	Forested areas
A	42786	8	Subsurface	A	50.56	4	Suspended sediment
A	41705	6	Tilled fields	A	43.27	6	Tilled fields
A	40336	8	Cattle paths	A	40.26	7	Cattle trampled areas
A	38942	6	Drainage ditches	A	39.42	6	Drainage ditches
A	34739	4	Suspended sediment	A	36.65	8	Cattle paths
A	32795	3	Gravel roads	A	35.7	8	Subsurface
A	32695	6	Instream sediment	A	34.09	6	Instream sediment
A	16935	3	Forested areas	A	19.36	3	Gravel roads

Lithium				Magnesium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	57.97	6	Tilled fields	A	10994	3	Gravel Roads
A	56.96	6	Drainage ditches	B	4988	4	Suspended sediment
A	56.43	8	Subsurface	B	4641	7	Cattle trampled areas
A	56.25	4	Suspended sediment	B	4151	6	Drainage ditches
A	54.61	7	Cattle trampled areas	B	4099	8	Cattle paths
A	51.37	8	Cattle paths	B	4004	6	Instream sediment
A	49.21	6	Instream sediment	B	3985	6	Tilled fields
A	37.72	3	Gravel roads	B	3803	8	Subsurface
A	32.95	3	Forested areas	B	1790	3	Forested areas

Table 11 continued.

Manganese				Neodymium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	3048.9	4	Suspended sediment	A	39.92	3	Forested areas
A	2389.1	3	Forested areas	A	25.05	4	Suspended sediment
A	2251.8	6	Instream sediment	A	24.99	6	Instream sediment
A	2110.1	6	Tilled fields	A	24.61	7	Cattle trampled areas
A	1992	8	Cattle paths	A	24.15	8	Cattle paths
A	1987.7	3	Gravel roads	A	22.99	6	Drainage ditches
A	1720.5	6	Drainage ditches	A	22.12	8	Subsurface
A	1498.3	8	Subsurface	A	22.11	6	Tilled fields
A	1466.5	7	Cattle trampled areas	A	13.32	3	Gravel roads
Nickel				Phosphorus			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	329.2	3	Forested areas	A	2200	7	Cattle trampled areas
A	290.3	7	Cattle trampled areas	AB	1824.1	6	Drainage ditches
A	286.5	8	Subsurface	AB	1764.3	8	Cattle paths
A	162	6	Instream sediment	AB	1412.9	6	Instream sediment
A	142.3	6	Drainage ditches	AB	1235.2	4	Suspended sediment
A	125.4	8	Cattle paths	AB	1189.1	6	Tilled fields
A	106.7	6	Tilled fields	AB	775.9	8	Subsurface
A	53.8	3	Gravel roads	B	615.2	3	Gravel roads
A	32.7	4	Suspended sediment	B	463.1	3	Forested areas
Potassium				Rubidium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	13217	4	Suspended sediment	A	114.14	7	Cattle trampled areas
AB	11661	6	Instream sediment	A	102.75	8	Subsurface
AB	11503	8	Cattle paths	A	100.81	6	Tilled fields
AB	11440	7	Cattle trampled areas	A	95.75	8	Cattle paths
AB	11265	6	Drainage ditches	A	91.75	6	Drainage ditches
AB	10239	8	Subsurface	A	83.68	4	Suspended sediment
AB	9775	6	Tilled fields	A	80.03	6	Instream sediment
B	7960	3	Gravel roads	A	77.99	3	Gravel roads
B	6844	3	Forested areas	A	38.38	3	Forested areas

Table 11 continued.

Silica

SNK Group	Mean	N	Groups
A	226850	6	Instream sediment
A	217755	4	Suspended sediment
A	214780	3	Forested areas
A	211527	8	Subsurface
A	210849	6	Drainage ditches
A	207225	8	Cattle paths
A	203243	3	Gravel roads
A	198641	6	Tilled fields
A	193412	7	Cattle trampled areas

Sodium

SNK Group	Mean	N	Groups
A	1061.6	7	Cattle trampled areas
A	1017.4	8	Cattle paths
A	982.7	6	Instream sediment
A	880.9	4	Suspended sediment
A	837	8	Subsurface
A	828.4	6	Drainage ditches
A	807.4	6	Tilled fields
A	785.2	3	Forested areas
A	680.1	3	Gravel roads

Strontium

SNK Group	Mean	N	Groups
A	245.57	3	Gravel roads
B	42.02	7	Cattle trampled areas
B	39.12	8	Cattle paths
B	32.43	6	Instream sediments
B	31.72	6	Drainage ditches
B	30.67	3	Forested areas
B	30.21	8	Subsurface
B	30.17	6	Tilled fields
B	29.98	4	Suspended sediment

Titanium

SNK Group	Mean	N	Groups
A	2916.3	6	Tilled fields
AB	2446.4	6	Drainage ditches
ABC	2303.3	7	Cattle trampled areas
ABC	2261.2	8	Cattle paths
ABC	2177.7	4	Suspended sediment
BC	2075.3	8	Subsurface
BC	1775.1	3	Forested areas
BC	1728.2	6	Instream sediment
C	1517.6	3	Gravel roads

Vanadium

SNK Group	Mean	N	Groups
A	98.07	6	Tilled fields
A	92.38	8	Subsurface
A	86.96	7	Cattle trampled areas
A	81.5	6	Drainage ditches
A	77.57	8	Cattle paths
A	73.82	4	Suspended sediment
A	61.33	6	Instream sediment
A	55.11	3	Gravel roads
A	45.02	3	Forested areas

Zinc

SNK Group	Mean	N	Groups
A	201.98	7	Cattle trampled areas
A	181.81	4	Suspended sediment
A	179.85	6	Drainage ditches
A	156.91	3	Gravel roads
A	149.8	3	Forested areas
A	146.6	6	Tilled fields
A	137.01	8	Cattle paths
A	135.63	8	Subsurface
A	124.36	6	Instream sediment

Table 11 continued.

Zirconium			
SNK Group	Mean	N	Groups
A	134.08	7	Cattle trampled areas
A	128.65	6	Tilled fields
A	128.41	8	Cattle paths
AB	118.93	8	Subsurface
AB	112.35	6	Drainage ditches
AB	111.84	6	Instream sediment
AB	93.48	3	Forested areas
AB	90.33	4	Suspended sediment
B	74.88	3	Gravel roads

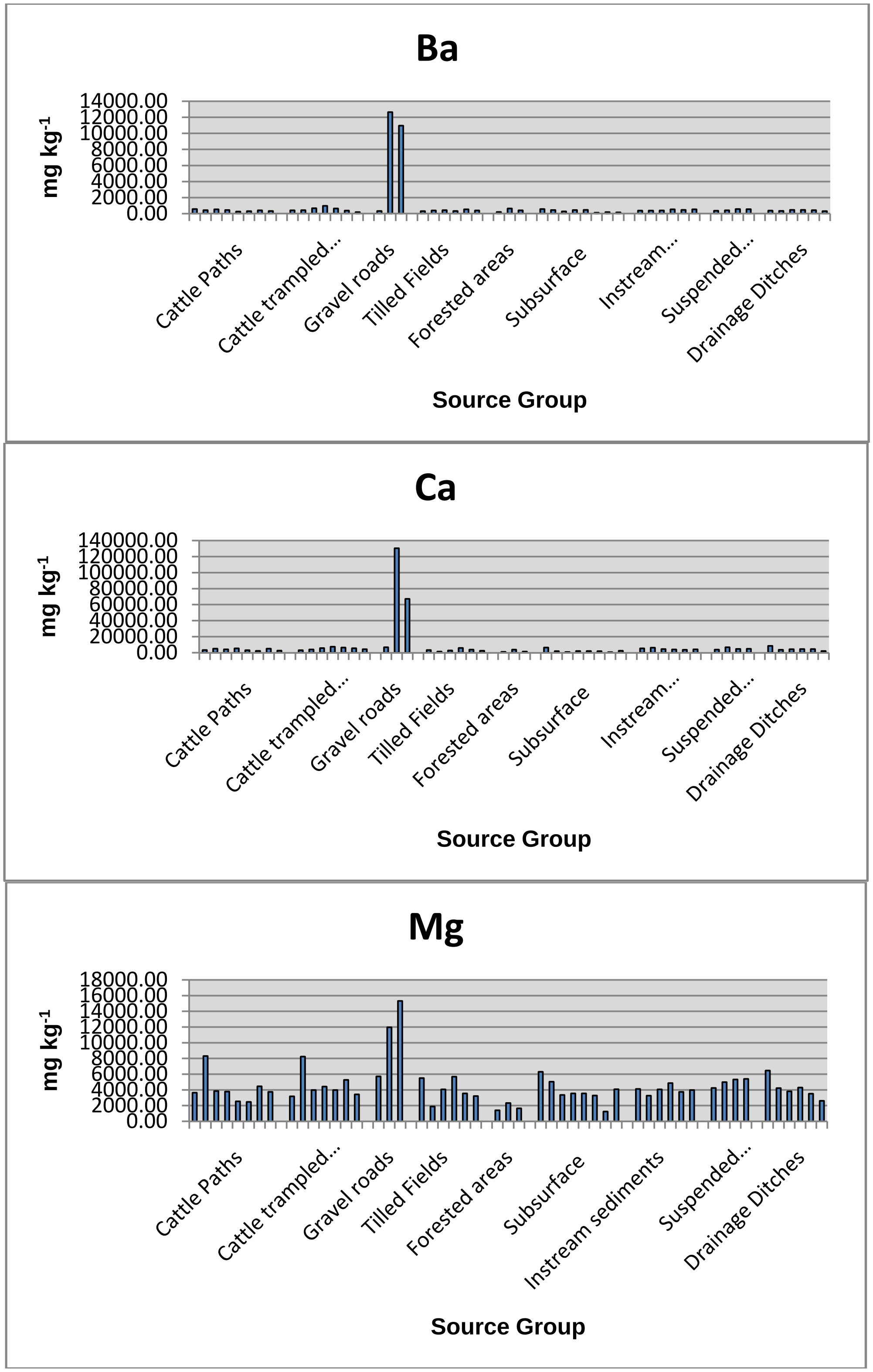


Figure 19. The histograms illustrate the distribution of total barium (Ba), calcium (Ca), and magnesium (Mg) in the Pond Creek watershed samples as a function of group, showing the extreme difference offered by the gravel road samples.

Table 12. Results of the Kruskal-Wallis rank test using total elemental contents and excluding the gravel road samples (8 groups).

Kruskal-Wallis Test			
Element	X^2	DF	Pr>X^2
Al*	14.9057	7	0.0372*
Ba	4.0046	7	0.7792
Ca*	19.2336	7	0.0075*
Cd	9.4193	7	0.2239
Ce	7.6132	7	0.3679
Co	4.1402	7	0.7635
Cr	6.4049	7	0.4933
Cu*	15.9732	7	0.0254*
Fe	10.7495	7	0.1499
K	12.3834	7	0.0886
La	4.4704	7	0.7243
Li	11.2767	7	0.127
Mg	11.9156	7	0.1034
Mn	8.0381	7	0.3293
Na	5.4405	7	0.6064
Nd	1.2004	7	0.9909
Ni	6.2776	7	0.5077
P*	21.7342	7	0.0028*
Rb	9.7814	7	0.2013
Si	8.5333	7	0.2879
Sr	5.7464	7	0.5697
Ti*	19.4772	7	0.0068*
V*	14.293	7	0.0462*
Zn	7.3367	7	0.3947
Zr*	15.9998	7	0.0251*

*Indicates elements that exhibited significant differences among the groups at $P<0.05$.

Table 13. Results of the discriminant function analysis using total elemental contents and excluding the gravel road samples (8 groups).

Discriminant Function Analysis			
Element	R^2	F	Pr>F
Al*	0.4587	4.12	0.0023
Ba	0.128	0.69	0.6781
Ca	0.2352	1.45	0.2194
Cd	0.1847	1.07	0.4053
Ce	0.076	0.39	0.9029
Co	0.08	0.41	0.8892
Cr	0.2337	1.44	0.224
Cu	0.1283	0.69	0.6769
Fe	0.175	1	0.4487
K*	0.4679	4.27	0.0018
La	0.1622	0.91	0.509
Li*	0.3194	2.28	0.0513
Mg	0.2101	1.25	0.303
Mn	0.1705	0.97	0.4694
Na	0.1131	0.6	0.7503
Nd	0.084	0.43	0.8749
Ni	0.2395	1.48	0.2068
P*	0.5447	5.81	0.0002
Rb	0.2204	1.33	0.2663
Si	0.0766	0.39	0.9007
Sr*	0.4004	3.24	0.0096
Ti*	0.4784	4.46	0.0013
V	0.1944	1.14	0.3643
Zn	0.1139	0.61	0.7464
Zr*	0.343	2.54	0.0327

*Indicates elements that provided power for discriminating the groups. Pr>F values must be below 0.15 for an element to be considered to provide discrimination power.

groups (Tables 12 and 14); nor did Fe provide any power to discriminate among these groups (Table 13; Fig. 20). Calcium concentrations were significantly different in at least one of the groups (Tables 12 and 14), but did not provide any power to discriminate among the groups (Table 13; Fig. 21). On the other hand, Li did not exhibit any significant differences among any groups according to the KW test (Table 12; Fig. 22). However, Li concentrations differed according to the SNK test (Table 14) and offered power to discriminate between groups (Table 13). Finally, the Ti concentrations were significantly different among some of the groups (Tables 12 and 14) and also provided power for discriminating among groups (Table 13; Fig. 23). The results of the SNK test (Table 14) showed that the means of the groups exhibited significant differences for eight elements (Ca, Cd, K, Li, Mg, P, Ti, V) and that the between group differences varied with element (Table 14).

Since there were eight initial groups (7 source groups and the suspended sediment group), and only four elements (Al, P, Ti, Zr) were significantly different among the groups (KW test) and had discriminatory power, it was not possible to quantify the sources of suspended sediment using the initial group definitions or the criteria to select the elements for discrimination analysis. Source identification requires that the number of numerical variables used for discriminating the groups be greater than or equal to the number of groups. In this case the criteria were not met. Thus, the next iteration of the stream sediment source identification scheme involved reducing the number of groups to four: surface, subsurface, sediments, and suspended sediments. Soil samples from cattle paths, cattle tramped areas, tilled fields, and forested areas were combined to form the surface group; in-stream sediment and drainage ditch samples were combined to form the sediments group. The subsurface and suspended sediment groups remained unchanged. Using these groups, the statistical analyses were repeated. The results of the analyses showed

Table 14. Results of the Student-Newman-Keuls multiple-range test using total elemental contents and excluding the gravel road samples (8 groups). For each element, groups identified by the same letter are not significantly different at P<0.05.

Student-Newman-Keuls multiple-range test

Aluminum

SNK Group	Mean	N	Groups
A	72727	8	Subsurface
A	72022	6	Tilled fields
A	69737	7	Cattle trampled areas
A	65269	6	Drainage ditches
A	63855	4	Suspended sediment
A	58742	8	Cattle paths
A	47980	6	Instream sediment
A	30747	3	Forested areas

Barium

SNK Group	Mean	N	Groups
A	529.57	7	Cattle trampled areas
A	478.63	4	Suspended sediment
A	449.36	6	Instream sediment
A	418.72	8	Cattle paths
A	418.09	3	Forested areas
A	405.15	6	Tilled fields
A	398.6	6	Drainage ditches
A	333.96	8	Subsurface

Cadmium

SNK Group	Mean	N	Groups
A	4.42	4	Suspended sediment
AB	3.41	7	Cattle trampled areas
AB	3.33	6	Tilled fields
AB	3.29	8	Subsurface
AB	3.1	6	Drainage ditches
AB	2.94	6	Instream sediment
AB	2.92	8	Cattle paths
B	1.66	3	Forested areas

Calcium

SNK Group	Mean	N	Groups
A	5231.7	7	Cattle trampled areas
AB	5060.3	4	Suspended sediment
ABC	4674.5	6	Instream sediment
ABC	4611.6	6	Drainage ditches
ABC	3887.9	8	Cattle paths
ABC	3289.8	6	Tilled fields
BC	2285.3	8	Subsurface
C	2060.5	3	Forested areas

Cerium

SNK Group	Mean	N	Groups
A	88.83	6	Tilled fields
A	88.66	4	Suspended sediment
A	78.97	6	Drainage ditches
A	75.3	8	Cattle paths
A	70.17	7	Cattle trampled areas
A	68.22	8	Subsurface
A	66.07	6	Instream sediment
A	58.75	3	Forested areas

Chromium

SNK Group	Mean	N	Groups
A	572.3	3	Forested areas
A	503.3	7	Cattle trampled areas
A	498.4	8	Subsurface
A	274.7	6	Instream sediment
A	245.2	6	Drainage ditches
A	227.8	8	Cattle paths
A	187.8	6	Tilled fields
A	53.7	4	Suspended sediment

Table 14 continued.

Cobalt

SNK Group	Mean	N	Groups
A	20.03	6	Drainage ditches
A	19.76	6	Instream sediment
A	19.5	4	Suspended sediment
A	18.96	7	Cattle trampled areas
A	17.97	8	Cattle paths
A	17.65	6	Tilled fields
A	16.76	8	Subsurface
A	12.52	3	Forested areas

Copper

SNK Group	Mean	N	Groups
A	176.92	8	Cattle paths
A	173.67	3	Forested areas
A	132.38	6	Instream sediment
A	132.09	8	Subsurface
A	130.2	6	Drainage ditches
A	94.23	7	Cattle trampled areas
A	87.91	6	Tilled fields
A	30.11	4	Suspended sediment

Iron

SNK Group	Mean	N	Groups
A	46549	7	Cattle trampled areas
A	42786	8	Subsurface
A	41705	6	Tilled fields
A	40336	8	Cattle paths
A	38942	6	Drainage ditches
A	34739	4	Suspended sediment
A	32695	6	Instream sediment
A	16935	3	Forested areas

Lanthanum

SNK Group	Mean	N	Groups
A	53.7	3	Forested areas
A	50.56	4	Suspended sediment
A	43.27	6	Tilled fields
A	40.26	7	Cattle trampled areas
A	39.42	6	Drainage ditches
A	36.65	8	Cattle paths
A	35.7	8	Subsurface
A	34.09	6	Instream sediment

Lithium

SNK Group	Mean	N	Groups
A	57.97	6	Tilled fields
AB	56.96	6	Drainage ditches
AB	56.43	8	Subsurface
AB	56.25	4	Suspended sediment
AB	54.61	7	Cattle trampled areas
AB	51.37	8	Cattle paths
AB	49.21	6	Instream sediment
B	32.95	3	Forested areas

Magnesium

SNK Group	Mean	N	Groups
A	4987.9	4	Suspended sediment
A	4640.6	7	Cattle trampled areas
AB	4150.5	6	Drainage ditches
AB	4098.9	8	Cattle paths
AB	4004.2	6	Instream sediment
AB	3985.1	6	Tilled fields
AB	3802.6	8	Subsurface
B	1789	3	Forested areas

Table 14 continued.

Manganese

SNK Group	Mean	N	Groups
A	3048.9	4	Suspended sediment
A	2389.1	3	Forested areas
A	2251.8	6	Instream sediment
A	2110.1	6	Tilled fields
A	1992	8	Cattle paths
A	1720.5	6	Drainage ditches
A	1498.3	8	Subsurface
A	1466.5	7	Cattle trampled areas

Neodymium

SNK Group	Mean	N	Groups
A	39.92	3	Forested areas
A	25.05	4	Suspended sediment
A	24.99	6	Instream sediment
A	24.61	7	Cattle trampled areas
A	24.15	8	Cattle paths
A	22.99	6	Drainage ditches
A	22.12	8	Subsurface
A	22.11	6	Tilled fields

Nickel

SNK Group	Mean	N	Groups
A	329.2	3	Forested areas
A	290.3	7	Cattle trampled areas
A	286.5	8	Subsurface
A	162	6	Instream sediment
A	142.3	6	Drainage ditches
A	125.4	8	Cattle paths
A	106.7	6	Tilled fields
A	32.7	4	Suspended sediment

Phosphorus

SNK Group	Mean	N	Groups
A	2200	7	Cattle trampled areas
AB	1824.1	6	Drainage ditches
AB	1764.3	8	Cattle paths
AB	1412.9	6	Instream sediment
AB	1235.2	4	Suspended sediment
AB	1189.1	6	Tilled fields
B	775.9	8	Subsurface
B	463.1	3	Forested areas

Potassium

SNK Group	Mean	N	Groups
A	13217	4	Suspended sediment
AB	11661	6	Instream sediment
AB	11503	8	Cattle paths
AB	11440	7	Cattle trampled areas
AB	11265	6	Drainage ditches
AB	10239	8	Subsurface
AB	9775	6	Tilled fields
B	6844	3	Forested areas

Rubidium

SNK Group	Mean	N	Groups
A	114.14	7	Cattle trampled areas
A	102.75	8	Subsurface
A	100.81	6	Tilled fields
A	95.75	8	Cattle paths
A	91.75	6	Drainage ditches
A	83.68	4	Suspended sediment
A	80.03	6	Instream sediment
A	38.38	3	Forested areas

Table 14 continued.

Silica

SNK Group	Mean	N	Groups
A	226850	6	Instream sediment
A	217755	4	Suspended sediment
A	214780	3	Forested areas
A	211527	8	Subsurface
A	210849	6	Drainage ditches
A	207225	8	Cattle paths
A	198641	6	Tilled fields
A	193412	7	Cattle trampled areas

Sodium

SNK Group	Mean	N	Groups
A	1061.6	7	Cattle trampled areas
A	1017.4	8	Cattle paths
A	982.7	6	Instream sediment
A	880.9	4	Suspended sediment
A	837	8	Subsurface
A	828.4	6	Drainage ditches
A	807.4	6	Tilled fields
A	785.2	3	Forested areas

Strontium

SNK Group	Mean	N	Groups
A	42.02	7	Cattle trampled areas
A	39.12	8	Cattle paths
A	32.43	6	Instream sediment
A	31.72	6	Drainage ditches
A	30.68	3	Forested areas
A	30.21	8	Subsurface
A	30.17	6	Tilled fields
A	29.98	4	Suspended sediment

Titanium

SNK Group	Mean	N	Groups
A	2916.3	6	Tilled fields
AB	2446.4	6	Drainage ditches
AB	2303.3	7	Cattle trampled areas
AB	2261.2	8	Cattle paths
B	2177.7	4	Suspended sediment
B	2075.3	8	Subsurface
B	1775.1	3	Forested areas
B	1728.2	6	Instream sediment

Vanadium

SNK Group	Mean	N	Groups
A	98.07	6	Tilled fields
AB	92.38	8	Subsurface
AB	86.96	7	Cattle trampled areas
AB	81.5	6	Drainage ditches
AB	77.57	8	Cattle paths
AB	73.82	4	Suspended sediment
AB	61.33	6	Instream sediment
B	45.02	3	Forested areas

Zinc

SNK Group	Mean	N	Groups
A	201.98	7	Cattle trampled areas
A	181.81	4	Suspended sediment
A	179.85	6	Drainage ditches
A	149.8	3	Forested areas
A	146.6	6	Tilled fields
A	137.01	8	Cattle paths
A	135.63	8	Subsurface
A	124.36	6	Instream sediment

Table 14 continued.

Zirconium			
SNK Group	Mean	N	Groups
A	134.08	7	Cattle trampled areas
A	128.65	6	Tilled fields
A	128.41	8	Cattle paths
A	118.93	8	Subsurface
A	112.35	6	Drainage ditches
A	111.84	6	Instream sediment
A	93.48	3	Forested areas
A	90.33	4	Suspended sediment

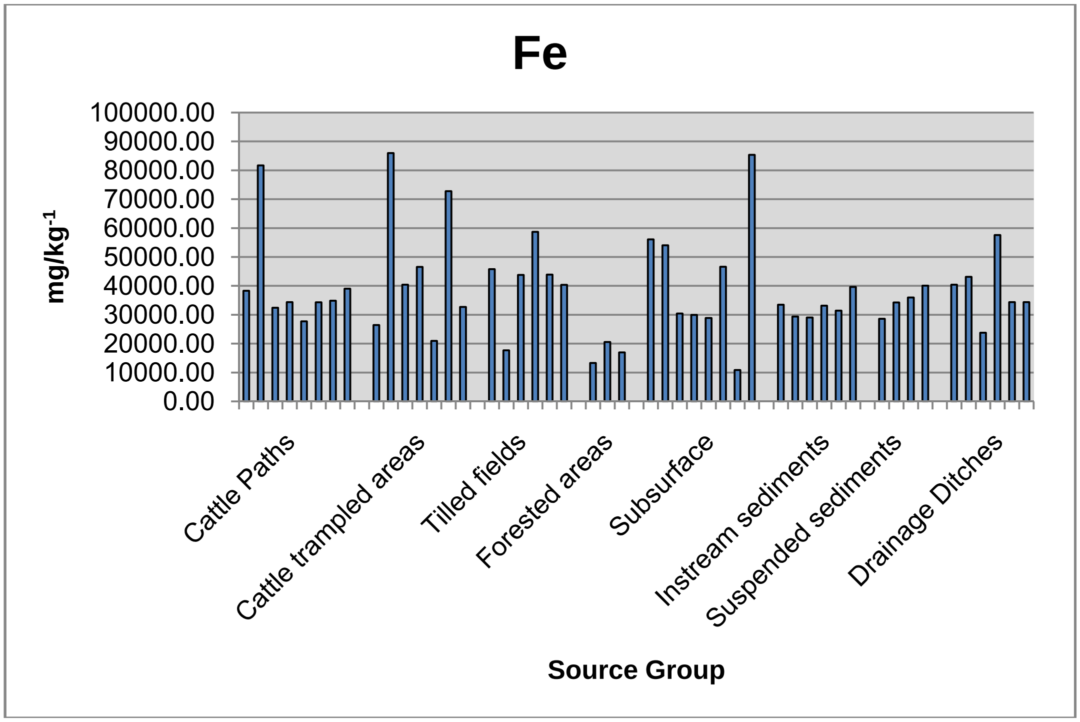


Figure 20. A histogram illustrating the distribution of total iron (Fe). Iron concentrations did not differ significantly among the groups (Tables 12 and 14) and did not provide discriminatory power (Table 13).

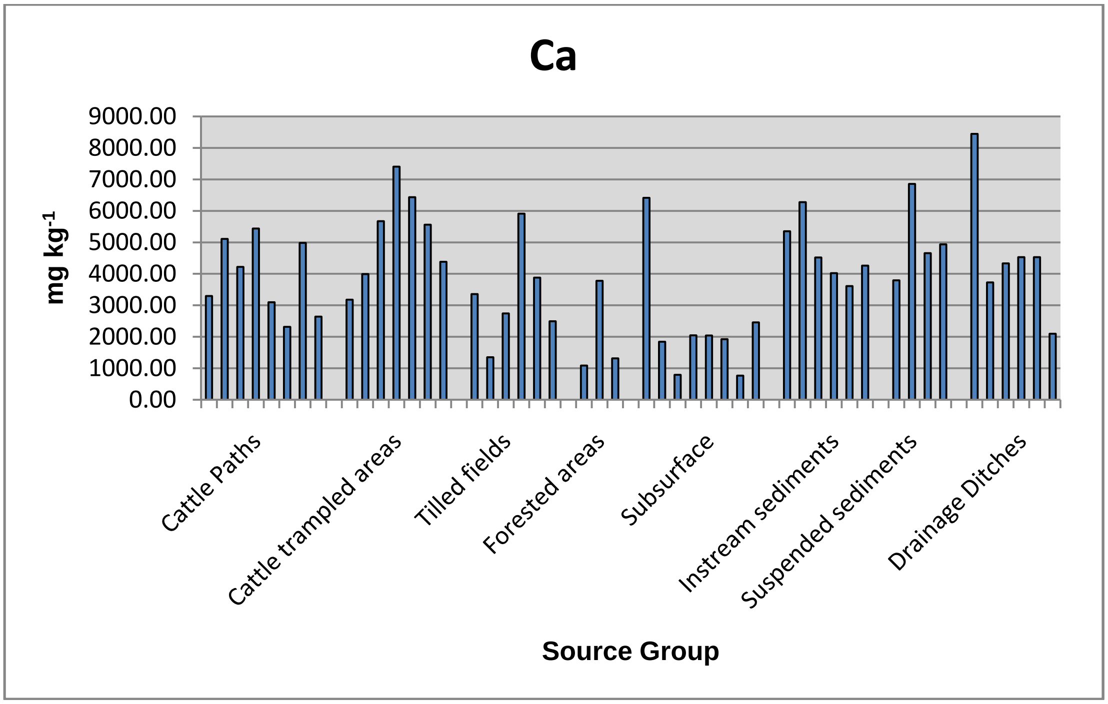


Figure 21. A histogram illustrating the distribution of total calcium (Ca). Calcium concentrations differed significantly among the groups (Tables 12 and 14) but did not provide discriminatory power (Table 14).

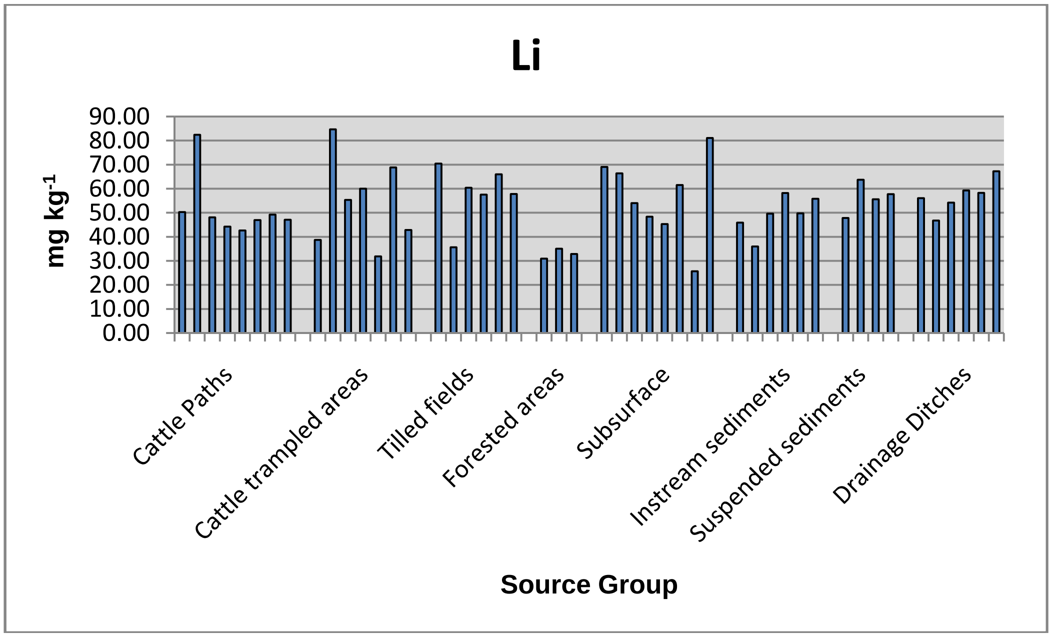


Figure 22. A histogram illustrating the distribution of total lithium (Li). Lithium concentrations did not differ significantly among the groups according to the KW test (Table 12), but did significantly differ significantly according to the SNK test (Table 14) and did offer discriminatory power (Table 13).

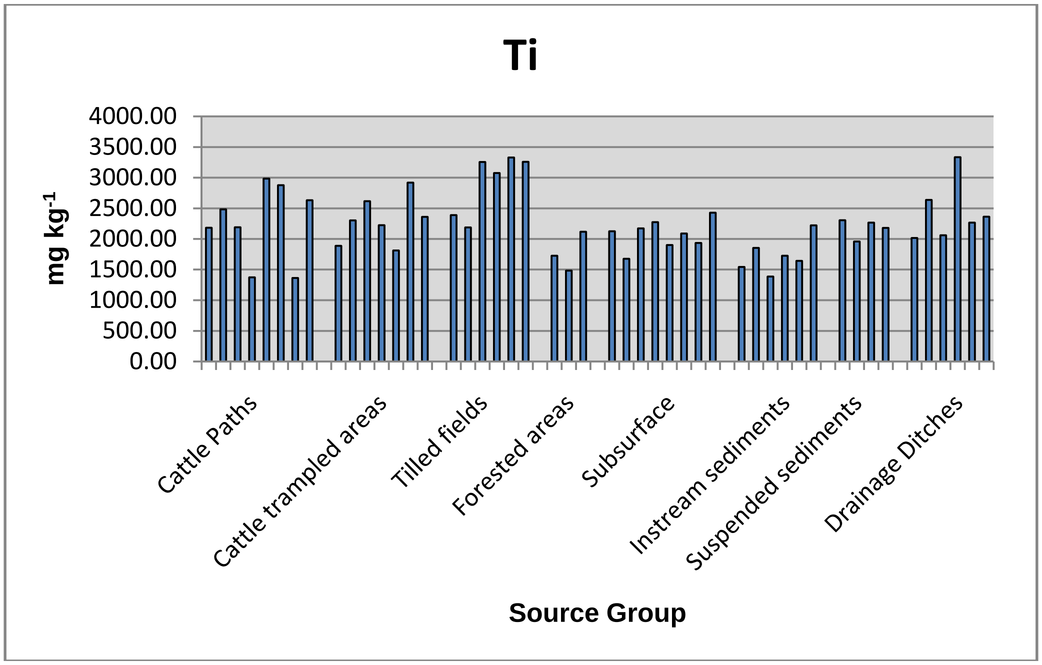


Figure 23. A histogram illustrating the distribution of total titanium (Ti).Titanium concentrations differed significantly among the groups (Tables 12 and 14) and provided discriminatory power (Table 13).

that only three elements (Ca, Cu, and Zr) exhibited significant differences among the groups according to the KW test (Table 15), and seven elements(Al, Ca, Cd, K, Rb, Ti, Zr) had the ability to discriminate the groups (Table 16). However, only two elements (Ca and Zr) had both properties, which is less than the number of defined groups. The results of the SNK test (Table 17) showed that the means of the groups exhibited significant differences for three elements (Ca, Mn, Zr). Again, the number of variables that were both significantly different among the groups and could be used to discriminate the groups, was less than the number of groups.

The statistical approach was again modified to allow the elemental data to identify a statistically-viable set of potential sediment source groups. This was accomplished using cluster analysis and canonical discriminant analysis (CDA) and all elemental information. The cluster analysis provides a mechanism for evaluating whether or not the selected number of groups (clusters) to be created is realistic for the data set, while CDA produces canonical variables that have the highest possible multiple correlations within groupings of samples. When determining the number of population clusters applicable to a particular data set, no individual method is completely satisfactory (Everitt, 1979). However, it has been suggested that metrics generated during cluster analysis may be used to select the number of clusters. These criteria include the cubic clustering criterion (CCC) (Sarle, 1983), the pseudo F statistic (PSF) (Calinski and Harabasz, 1974), and the pseudo t^2 statistic (PST2) (Duda and Hart, 1973). Specifically, increases in the CCC value and PSF, value coupled with a corresponding decrease in the PST2 value with an increase in cluster number indicates the number of clusters (SAS Institute, 2005). For example, increasing the number of clusters from three to four results in an increase in CCC (0.15 to 4.07) and PSF (45.6 to 63.6), and a decrease in PST2 (81.4 to 55.5) (Table 18). This would suggest that four clusters are adequate to describe the population. Similarly, increases in

Table 15. Results of the Kruskal-Wallis rank test using four groups (surface, subsurface, sediment, suspended sediment) and total concentrations.

Kruskal-Wallis Test			
Element	X^2	DF	Pr>X^2
Al	2.1302	3	0.5458
Ba	3.7013	3	0.2956
Ca	9.6802	3	0.0215*
Cd	0.9775	3	0.8067
Ce	4.087	3	0.2522
Co	2.0099	3	0.5704
Cr	1.1178	3	0.7728
Cu	11.8107	3	0.0081*
Fe	0.358	3	0.9488
K	6.1071	3	0.1065
La	2.4513	3	0.4842
Li	0.8263	3	0.8432
Mg	5.1717	3	0.1596
Mn	6.1358	3	0.1052
Na	1.3069	3	0.7275
Nd	0.7882	3	0.8523
Ni	1.7458	3	0.6268
P	6.6037	3	0.0857
Rb	0.2249	3	0.9735
Si	3.5501	3	0.3143
Sr	3.8289	3	0.2805
Ti	2.9683	3	0.3965
V	1.5064	3	0.6806
Zn	1.1711	3	0.7599
Zr	8.9747	3	0.0296*

*Indicates elements that exhibited significant differences among the groups at $P<0.05$.

Table 16. Results of the discriminant function analysis using four groups (surface, subsurface, sediment, suspended sediment) and total concentrations.

Discriminant Function Analysis			
Element	R^2	F	Pr>F
Al	0.2055	3.28	0.0313*
Ba	0.1153	1.61	0.2041
Ca	0.1347	1.97	0.1345*
Cd	0.1697	2.59	0.0671*
Ce	0.0601	0.79	0.5078
Co	0.0495	0.64	0.5925
Cr	0.0282	0.36	0.7837
Cu	0.0309	0.39	0.7586
Fe	0.0146	0.18	0.9072
K	0.3229	6.04	0.0018*
La	0.0859	1.16	0.3385
Li	0.0842	1.13	0.348
Mg	0.0512	0.66	0.5789
Mn	0.0542	0.71	0.554
Na	0.1117	1.55	0.2177
Nd	0.0581	0.76	0.5235
Ni	0.0288	0.37	0.7777
P	0.0787	1.05	0.3805
Rb	0.1547	2.32	0.0910*
Si	0.0546	0.71	0.5513
Sr	0.088	1.19	0.3267
Ti	0.2607	4.47	0.0088*
V	0.0191	0.24	0.8677
Zn	0.0744	0.99	0.4074
Zr	0.1577	2.37	0.0856*

*Indicates elements that provided power for discriminating the groups. Pr>F values must be below 0.15 for an element to be considered to provide discrimination power.

Table 17. Results of the Student-Newman-Keuls multiple-range test using four groups (surface, subsurface, sediment, suspended sediment) and total concentrations. For each element, groups identified by the same letter are not significantly different at P<0.05.

Student-Newman-Keuls multiple-range test

Aluminum

SNK Group	Mean	N	Groups
A	71221	9	Subsurface
A	63855	4	Suspended sediment
A	61883	23	Surface
A	56624	12	Sediments

Barium

SNK Group	Mean	N	Groups
A	478.63	4	Suspended sediment
A	458.67	23	Surface
A	423.98	12	Sediments
A	318.24	9	Subsurface

Cadmium

SNK Group	Mean	N	Groups
A	4.42	4	Suspended sediment
A	3.23	9	Subsurface
A	3.02	12	Sediments
A	3.02	23	Surface

Calcium

SNK Group	Mean	N	Groups
A	5060.3	4	Suspended sediment
A	4643.1	12	Sediments
AB	3881.1	23	Surface
B	2518.1	9	Subsurface

Cerium

SNK Group	Mean	N	Groups
A	88.66	4	Suspended sediment
A	75.73	23	Surface
A	72.52	12	Sediments
A	67.43	9	Subsurface

Chromium

SNK Group	Mean	N	Groups
A	457.2	9	Subsurface
A	350.5	23	Surface
A	259.9	12	Sediments
A	53.7	4	Suspended sediment

Cobalt

SNK Group	Mean	N	Groups
A	19.9	12	Sediments
A	19.5	4	Suspended sediment
A	17.81	23	Surface
A	16.03	9	Subsurface

Copper

SNK Group	Mean	N	Groups
A	133.05	23	Surface
A	131.29	12	Sediments
A	124.44	9	Subsurface
A	30.11	4	Suspended sediment

Table 17 continued.

Iron

SNK Group	Mean	N	Groups
A	41665	9	Subsurface
A	39864	23	Surface
A	35818	12	Sediments
A	34739	4	Suspended sediment

Lanthanum

SNK Group	Mean	N	Groups
A	50.56	4	Suspended sediment
A	42.39	23	Surface
A	36.76	12	Sediments
A	34.05	9	Subsurface

Lithium

SNK Group	Mean	N	Groups
A	56.25	4	Suspended sediment
A	54.92	9	Subsurface
A	53.09	12	Sediments
A	52.04	23	Surface

Magnesium

SNK Group	Mean	N	Groups
A	4987.9	4	Suspended sediment
A	4077.3	12	Sediments
A	3961.8	23	Surface
A	3761.7	9	Subsurface

Manganese

SNK Group	Mean	N	Groups
A	3048.9	4	Suspended sediment
AB	1986.1	12	Sediments
AB	1963.4	23	Surface
B	1428.5	9	Subsurface

Neodymium

SNK Group	Mean	N	Groups
A	26.46	23	Surface
A	25.05	4	Suspended sediment
A	23.99	12	Sediments
A	20.7	9	Subsurface

Nickel

SNK Group	Mean	N	Groups
A	262.6	9	Subsurface
A	199.6	23	Surface
A	152.2	12	Sediments
A	32.7	4	Suspended sediment

Phosphorus

SNK Group	Mean	N	Groups
A	1618.5	12	Sediments
A	1590.4	23	Surface
A	1235.2	4	Suspended sediment
A	851.7	9	Subsurface

Potassium

SNK Group	Mean	N	Groups
A	13217	4	Suspended sediment
A	11463	12	Sediments
A	10605	23	Surface
A	9921	9	Subsurface

Rubidium

SNK Group	Mean	N	Groups
A	100.16	9	Subsurface
A	95.89	23	Surface
A	85.89	12	Sediments
A	83.68	4	Suspended sediment

Table 17 continued.

Silica

SNK Group	Mean	N	Groups
A	218850	12	Sediments
A	217755	4	Suspended sediment
A	209571	9	Subsurface
A	202345	23	Surface

Sodium

SNK Group	Mean	N	Groups
A	959.6	23	Surface
A	905.5	12	Sediments
A	880.9	4	Suspended sediment
A	821.8	9	Subsurface

Strontium

SNK Group	Mean	N	Groups
A	37.24	23	Surface
A	32.07	12	Sediments
A	29.98	4	Suspended sediment
A	29.47	9	Subsurface

Titanium

SNK Group	Mean	N	Groups
A	2377.2	23	Surface
A	2177.7	4	Suspended sediment
A	2106.9	9	Subsurface
A	2087.3	12	Sediments

Vanadium

SNK Group	Mean	N	Groups
A	91.42	9	Subsurface
A	81.26	23	Surface
A	73.82	4	Suspended sediment
A	71.41	12	Sediments

Zinc

SNK Group	Mean	N	Groups
A	181.81	4	Suspended sediment
A	160.55	23	Surface
A	152.1	12	Sediments
A	136.81	9	Subsurface

Zirconium

SNK Group	Mean	N	Groups
A	126.37	23	Surface
AB	118.12	9	Subsurface
AB	112.1	12	Sediments
B	90.33	4	Suspended sediment

Table 18. Results of the cluster analysis when five clusters and total elemental concentrations were used.

5 Defined Clusters			
Cluster	CCC	PSF	PST2
10	_	121	_
9	9.45	104	12.4
8	10.2	113	3.9
7	10.1	111	11.3
6	10.8	120	6
5	11.4	128	7.3
4	4.07	63.6	55.5
3	0.15	45.6	81.4
2	-0.95	44.2	22.1
1	0	_	44.2

CCC (4.07 to 11.4) and PSF (63.6 to 128), and a decrease in PST2 (55.5 to 7.3) indicate that the population may also be described by five clusters. Cluster analysis suggested that five was a satisfactory number of clusters for this elemental data set; however, it also indicated that four clusters may also be acceptable for the data set (Table 18). The clustering of the samples can be displayed in the form of a dendrogram derived using divisive hierarchical cluster analysis (Fig. 24). Similarities between samples are more pronounced as the r-squared value increases.

Using the canonical variables, CDA generated five statistically similar groups using the elemental data (Fig. 25). The first canonical variable accounts for approximately 70% of the elemental variation of the samples, while the second and third account for 15% and 10% of the variation. Overall, the first three canonical variables account for approximately 95% of the elemental variation. The effect that each element has on the separation of the individual samples (vector magnitude and direction) is shown in the inset in Fig. 25. Interestingly, in the first dimension almost all of the elements separate the samples along the x-axis (canonical variable

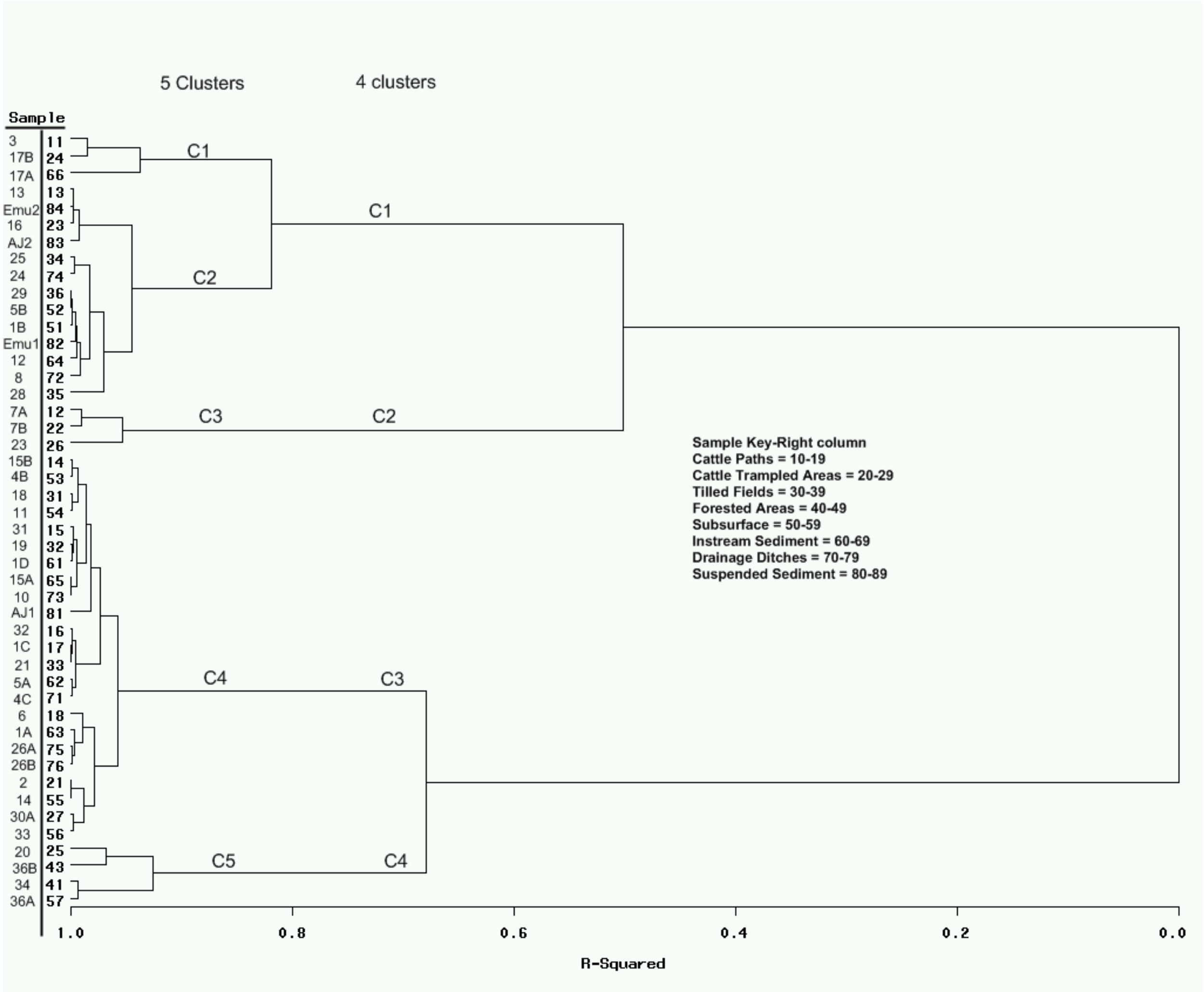


Figure 24. Dendrogram created by divisive hierarchical cluster analysis using the total concentrations of all elements. Sample numbers in the right column correspond with sample type (group) and are indicated in the key. Sample numbers in the left column correspond with sample location (Table 3).

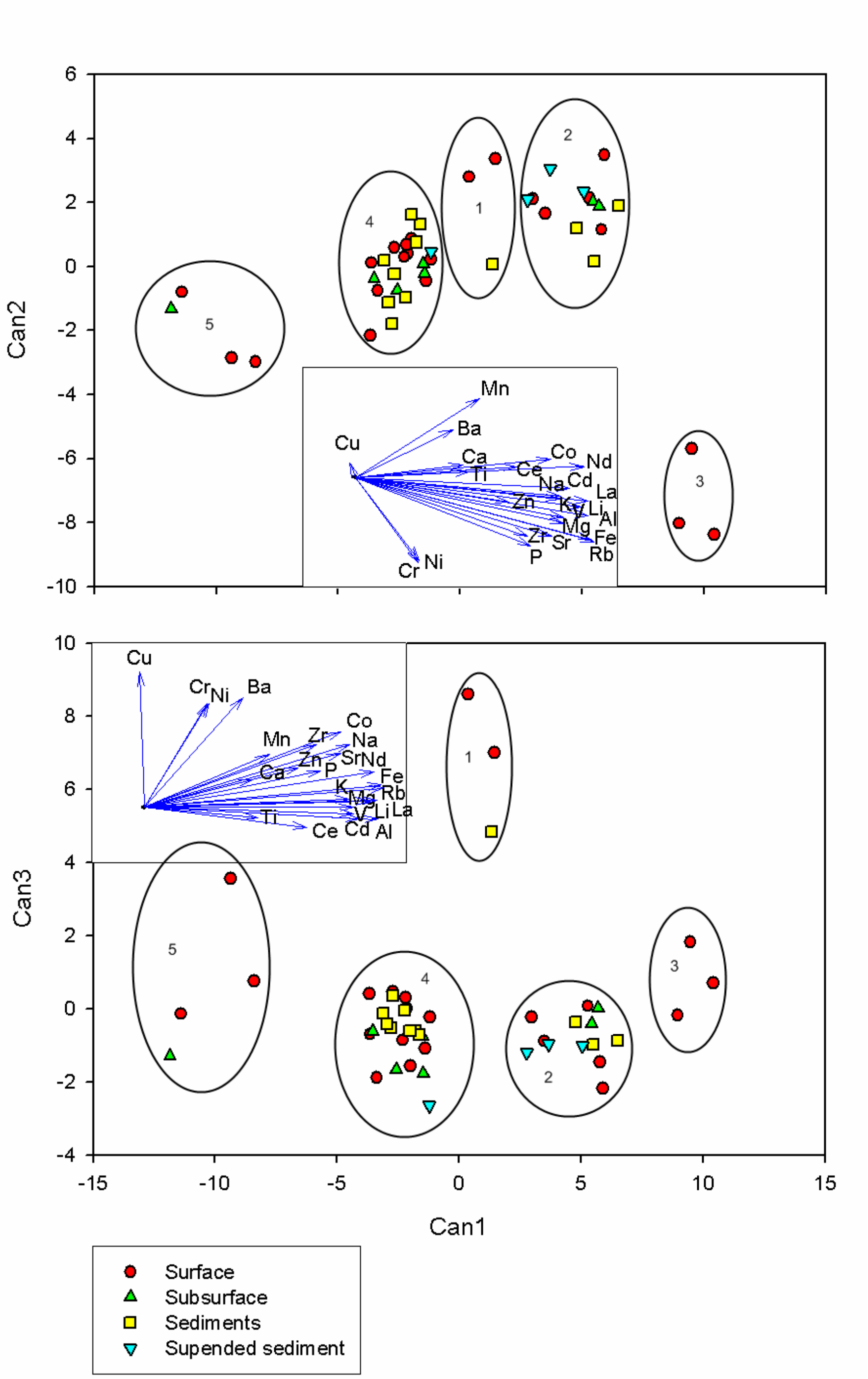


Figure 25. Canonical discriminant analysis of the Pond Creek watershed samples using the total dissolution data to produce five clusters. The plots show the first three canonical variables. The data points represent the individual soil or sediment samples and the arrows in the inset illustrate the impact that each element has on the separation of the samples. The ellipses enclose statistically unique groups, while sample type is represented by both color and shape. Numbers are for reference purposes.

1). Relative to the other elements, Cu provides very little separation power in the canonical variable 1 and 2 dimension. Manganese and Ba separate the samples slightly in the positive direction along the y-axis (canonical variable 2), while Ni and Cr separate the samples slightly in the negative direction along the y-axis. Furthermore, Cr and Ni have similar vectors, suggesting that only one of the pair is necessary for separating the samples in the first dimension (one is redundant to the other). This is the case with many of the elements in Fig. 25. The fact that most of the elements separate the samples in the same direction indicates that it may be possible to obtain the same clusters using a much smaller set of elemental concentration data. When elements overlap both in the magnitude and direction of their effects on separating the data, it follows that all of the overlapping elements are not necessary to separate the samples. The effects of each element in the canonical variable 1 and 3 dimension are similar to those in the variable 1 and 2 dimension. Most of the elements separate the samples along the x-axis (canonical variable 1) in the positive direction, and many of the elements have a similar effect on separating the groups. Copper, however, separates the samples in the positive direction along the y-axis (canonical variable 3). Chromium, Ni, and Ba also separate the samples along the canonical variable 3 axis. Again, Ni and Cr have nearly identical vectors, suggesting that they are both not necessary for creating the clusters. This is likely the case for other elements because many of them overlap in the magnitude and direction in which they separate the samples in the canonical variable 1,2, and 3 dimensions.

Three of the four suspended sediment samples are in the cluster with the second largest number of samples, and the fourth is found in the cluster with the largest number, suggesting that there is an association between the suspended sediment samples and the other samples in these clusters. Also, it may be seen in Fig. 25 that the clusters do not correspond to the initially defined source groups (Table 4). This suggests that either the source of elemental variation that leads to the creation of these groups is something other than the initially defined sample type, or that all of the samples are too similar to effectively separate using this procedure.

Cluster C1 contains only three samples, two of which were collected from proximate locations. One of these was collected from an area heavily trampled by cattle along the bank and in the floodplain of Pond Creek, while the other was collected from an adjacent in-stream sediment bar. However, the third sample in C1was collected from a cattle path at the headwaters of Pond Creek, approximately 6.3 km from the location where the other two samples were collected. Relative to other clusters, the samples in C1 had high levels of Cu, Ni, and Cr. Cluster C3 also contains three samples. Once again, two of the three were collected from approximately the same location. One of them was collected from a cattle path within a trampled area, and the other from within the same trampled area but to the side of the path. The third sample in C3 was collected from a heavily trampled loafing area just outside a milking barn. These samples had particularly high levels of Mg, Ni, La, P, Li, Na, K, Rb, Cd, Cr, and Al relative to samples in other clusters. In cluster C5, there are four samples consisting of two forest samples, a road cut bank sample, and a sample from a cattle trampled area. The road cut bank sample was collected just downslope of one of the forest samples, and likely had been influenced by soil moving down from the forested area. The other sample in cluster C5 was collected from a cattle feeding area along a road near Pond Creek. The elemental composition of this sample may have been influenced by organic matter that was incorporated from the material lost during feeding operations, or from manure additions, and thus its properties were similar to those of the forest soils. The samples in C5 had particularly low levels of almost all of the elements analyzed relative to the other clusters.

The reasons for the grouping seen in clusters C2 and C4, which are each composed of a larger number of samples, were somewhat difficult to identify because of the many different types and locations of samples incorporated into these groups. Cluster C2 contains 13 samples collected from a cattle path, a cattle trampled area, three tilled fields, two stream banks, an in-stream sediment deposit, two drainage ditch samples, and three suspended sediment samples. Initially, five of these samples were considered to be surface samples (cattle path, cattle trampled area, and tilled fields). However, three of these samples were from tilled fields, meaning that the surficial material had been mixed with subsurface material, likely over a period of many years. This would cause the tilled samples to have similarities with other subsurface samples. Also, the cattle path and cattle trampled area samples may represent surface or subsurface material, depending on the degree to which these areas had been eroded. All of the other samples in C2 are either subsurface material or sediments (deposited and suspended). This would suggest that all of the samples in C2 tend to be representative of subsurface material, but C4 also contains a similar variety of sample types. One other important feature is that C2 contains three of the four suspended sediment samples; the fourth suspended sediment sample is contained in C4.

Cluster C4 contains 23 samples consisting of five cattle path samples, two cattle trampled areas, three tilled fields, four subsurface samples, four in-stream bar samples, four drainage ditch samples, and one suspended sediment sample. Clusters C2 and C4 are similar in the types of samples they contain. Again, the C4 samples that were initially considered to be surface material may have actually been subsurface material if the cattle paths and trampled areas were significantly eroded. Likewise, samples taken from tilled areas may also contain subsurface material due to the mixing involved in tillage. This suggests that these two clusters are actually quite similar, and additionally, that all of the samples in C2 and C4 may be representative of subsurface material. This is likely the case, as the only truly undisturbed surface samples collected were those from forested areas, which were contained in C5.

Clusters C2 and C4 contain the suspended sediment samples. Thus, the suspended materials collected from Pond Creek have elemental chemistries that are similar to the majority of the potential source samples collected from the watershed. This finding may be an artifact of the sampling scheme. The collection of potential sediment materials throughout the watershed was not random. Instead, sampling was directed to obtain materials from locations that would likely contribute to the suspended sediment material in Pond Creek. Since sources likely to be contributing were sampled, and most of these “likely sources” cluster together with the suspended sediment, it follows that the sampling procedure effectively obtained the sources of the suspended sediment.

As previously indicated, four clusters could also be used to describe the soil sample population in Pond Creek. In the results of the cluster analysis as the number of clusters is increased from three to four both the CCC and PSF increase along with a corresponding decrease in the PST2 value (Table 19). Canonical discriminant analysis was repeated in order to generate four statistical groups using the elemental data (Fig. 26). The first canonical variable explains approximately 75% of the elemental variation in the data set. The second explains approximately 18.5% of the variation, and the third 6% of the variation. In this analysis, these three variables account for 100% of the variation. The results of the four group CDA are presented in Fig. 26. These results are similar to those presented in Fig. 25. Hence, the effect that each element has on the separation of the samples is also similar. Once again, the majority of the samples separate the samples along the x-axis in both dimensions, with the exception of a few elements previously discussed. Three of the four generated clusters contain the same samples as when five clusters

Table 19. Results of the cluster analysis when four clusters and total elemental concentrations were used.

4 Defined Clusters			
Cluster	CCC	PSF	PST2
10	_	123	3.6
9	10.5	126	5.3
8	10	119	13.4
7	10.2	122	6.7
6	9.76	117	13.3
5	10.7	130	5.4
4	9.6	148	57.9
3	1.86	61.2	89.5
2	-0.31	51.2	90.4
1	0	_	51.2

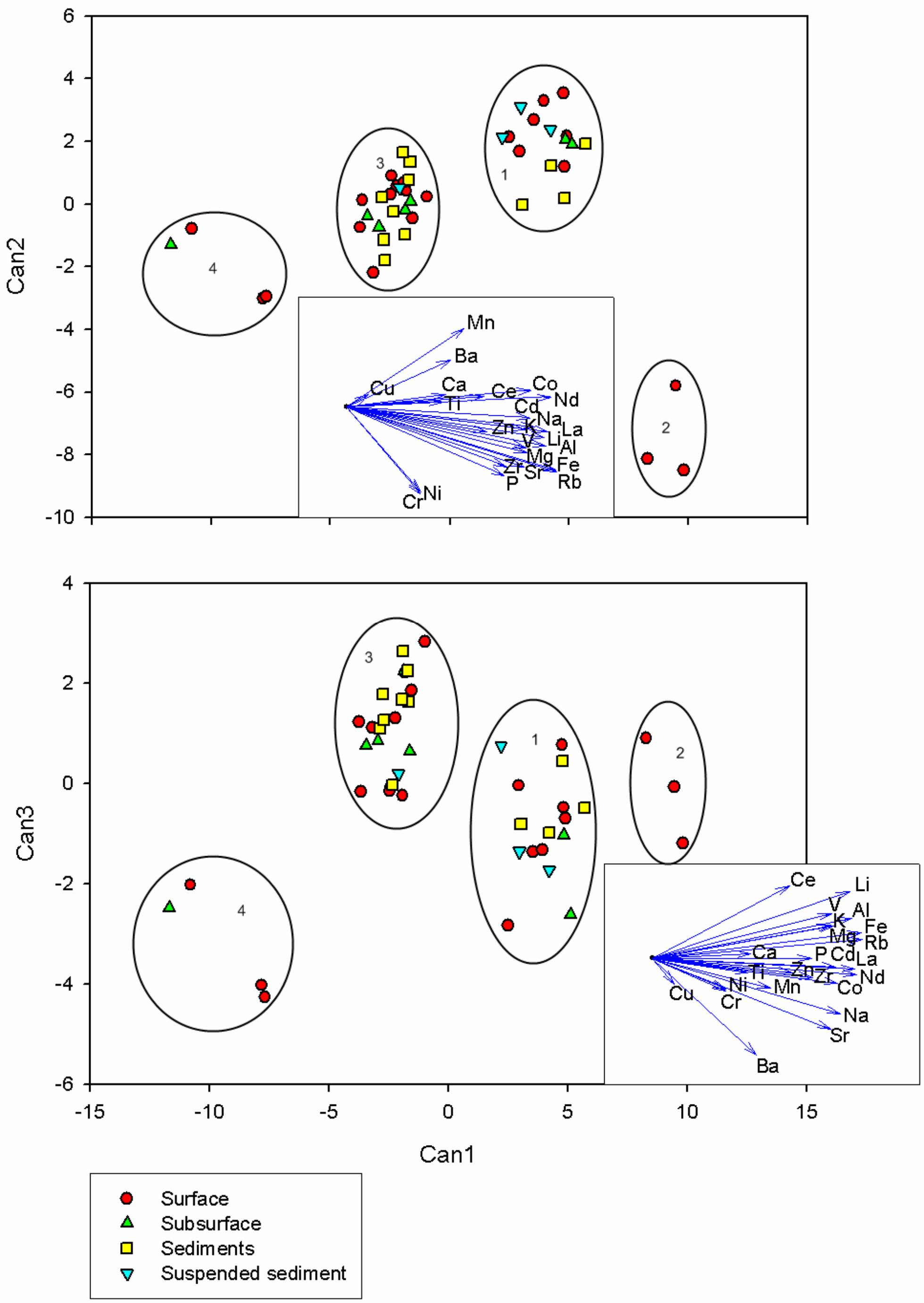


Figure 26. Canonical discriminant analysis of the Pond Creek watershed samples using the total dissolution data to produce four clusters. The data points represent the individual soil or sediment samples and the arrows in the inset illustrate the impact that each element has on the separation of the samples. The ellipses enclose statistically unique groups, while sample type is represented by both color and shape. Numbers are for reference purposes.

were created. The only difference is that C1 and C2 (Figure 25) become a single cluster represented by C1 in Fig. 26. This is expected, since clusters C1 and C2 in Fig. 25 were the most similar in canonical space. The similarities of C1 and C2 (5 clusters) are also seen in Fig. 24, as they are the closest together with respect to their r-squared values. As the branches of the dendrogram become smaller the samples they contain are more similar in their elemental make-up. The three samples at the top of the dendrogram (Fig. 24) (3, 17B, 17A) form a unique cluster (C1, Fig. 25) when the defined number of clusters in five; yet, when four clusters are created these three samples are incorporated into one cluster made up by the top 16 sample in the dendrogram and represented by C1 in Fig. 26. The other three clusters remain the same and make up the lower three branches in Fig. 24. This strengthens the point that the directed sampling protocol was too focused on obtaining sediment sources. It appears that the directed sampling did capture most of the important sources of sediment, since all of the suspended sediment samples are found in the two large clusters which contain 85% of the samples.

Nitric Acid Extraction Data

Descriptive Statistics

Of the 29 elements analyzed, 26 were above detectable concentrations in all of the Pond Creek HNO_3 extracts (Table 20). Based on the coefficient of variation (%CV, 100 times the std. deviation divided by the mean), there is considerable heterogeneity in the elemental data. As previously indicated, %CV values can be used to describe the heterogeneity of a soil property. Soil elemental data that are described by %CV values that are <15% are identified as having little variability. Elemental data with moderate variability have %CV values between 16 and 35%, and highly variable data has %CV values >36%. Hence, the higher the %CV value, the

Table 20. Descriptive statistics of the nitric acid extraction data.

Element	N	Mean	Median	Std. Deviation	Variance	Min	Max	CV	X^2
				g kg^{-1}					
Al	46	33.28	31.48	12.79	163538.5	13.53	67.91	38.42	0.081*
Ca	44	3.59	3.49	1.87	3481.88	0.39	8.43	51.96	0.65
Fe	46	33.52	32.11	13.29	176543.4	9.08	65.16	39.63	0.288
K	46	2.79	2.51	1.21	1459.65	0.64	5.56	43.29	0.6
Mg	44	2.27	2.15	0.89	787.51	0.81	4.81	39.1	0.082*
Mn	46	1.89	1.64	1.15	1317.37	0.26	5.12	60.76	0.024*
				mg kg^{-1}					
Ba	43	293.43	295.43	146.94	21591.27	38.58	601.22	50.08	0.061*
Cd	46	1.86	1.67	0.78	0.6	0.6	3.87	41.72	0.017*
Ce	44	73.67	70.84	28.46	810.01	22.18	134.65	38.63	0.55
Co	46	16.78	17.88	6.36	40.44	4.83	31.04	37.91	0.316
Cr	45	27.79	25.79	9.41	88.47	8.73	52.19	33.85	<.001*
Cu	46	95.7	87.79	48.35	2337.52	7.32	202.07	50.52	0.145
Hf	44	3.42	3.13	1.33	1.77	1.08	7.11	38.93	0.492
La	44	21.84	21.72	7.49	56.14	7.6	40.71	34.32	0.191
Li	45	21.48	21	6.65	44.19	9.08	37.51	30.95	0.388
Mo	46	0.75	0.69	0.3	0.09	0.21	1.6	40.04	0.05*
Nd	45	16.2	17.66	6.72	45.2	2.58	28.64	41.51	0.142
Ni	46	23.16	22.7	7.25	52.58	6.56	39.01	31.31	0.637
P	46	1205.47	1038.81	762.41	581268	148.33	3058.53	63.25	0.018*
Rb	46	75.51	72.51	30.37	922.57	18.9	145.58	40.22	0.572
S	45	487.71	400.7	371	137641.8	123.68	1843.86	76.07	<.001*
Sr	43	13.28	11.24	8.12	65.88	2.97	37.36	61.14	0.018*
Ti	44	484.52	454.07	240.74	57957.2	139.68	995.7	49.69	0.05*
V	45	46.87	43.52	15.93	253.64	19.97	83.19	33.98	0.858
Zn	46	128.37	112.59	54.43	2962.1	48.4	267.91	42.4	0.14
Zr	46	7.75	7.6	2.94	8.67	2.48	15.2	38	0.56

*Elemental data are not normally distributed at P<0.1

more heterogeneous the data for a particular element. The %CV values range from 31.0% (Li) to 76.1% (S). For the elements Cr, La, Li, Ni, and V, the %CV values are between 16-35%, indicating that these populations have moderate variability. The other elements (Al, Ba, Ca, Cd, Ce, Co, Cu, Fe, Hf, K, Mg, Mn, Mo, Nd, P Rb, S, Sr, Ti, Zn, and Zr) all have %CV values that are >36%, indicating that their populations are highly variable (Mulla and McBratney, 2000). Although %CV values are only one criteria for evaluating the heterogeneity of soil elemental content, these values suggest that more than one population, or sediment source groups, of soil samples may exist in the watershed.

The chi-square distribution coefficient values (X^2) show that a number of the elements are not normally distributed in the watershed (Table 20). This also indicates that the elemental content of soils may be used for discriminating sediment source groups. In general, elements that are normally distributed, such as Fe and Li (Fig. 27), are also less variable in the watershed. Sulfur and Sr are highly variable, and their distributions are both highly skewed (Fig. 28). Ba and Ti also do not fit a normal distribution. These two elements can be described as having several modes (Fig. 29). The multimodal distributions suggest that the data contain more than one population. Thus, these elements may provide significant power for discriminating the various types of sediment samples collected in the watershed because an element or variable that has discrimination power is defined as having the ability to differentiate between groups within a population.

Sediment Source Discrimination

The elemental content of each soil sample obtained by HNO_3 extraction is unique and can be described as a fingerprint. Two examples of soil sample fingerprints are illustrated for a forested area and a subsurface sample (Fig 30). In order to differentiate the various potential

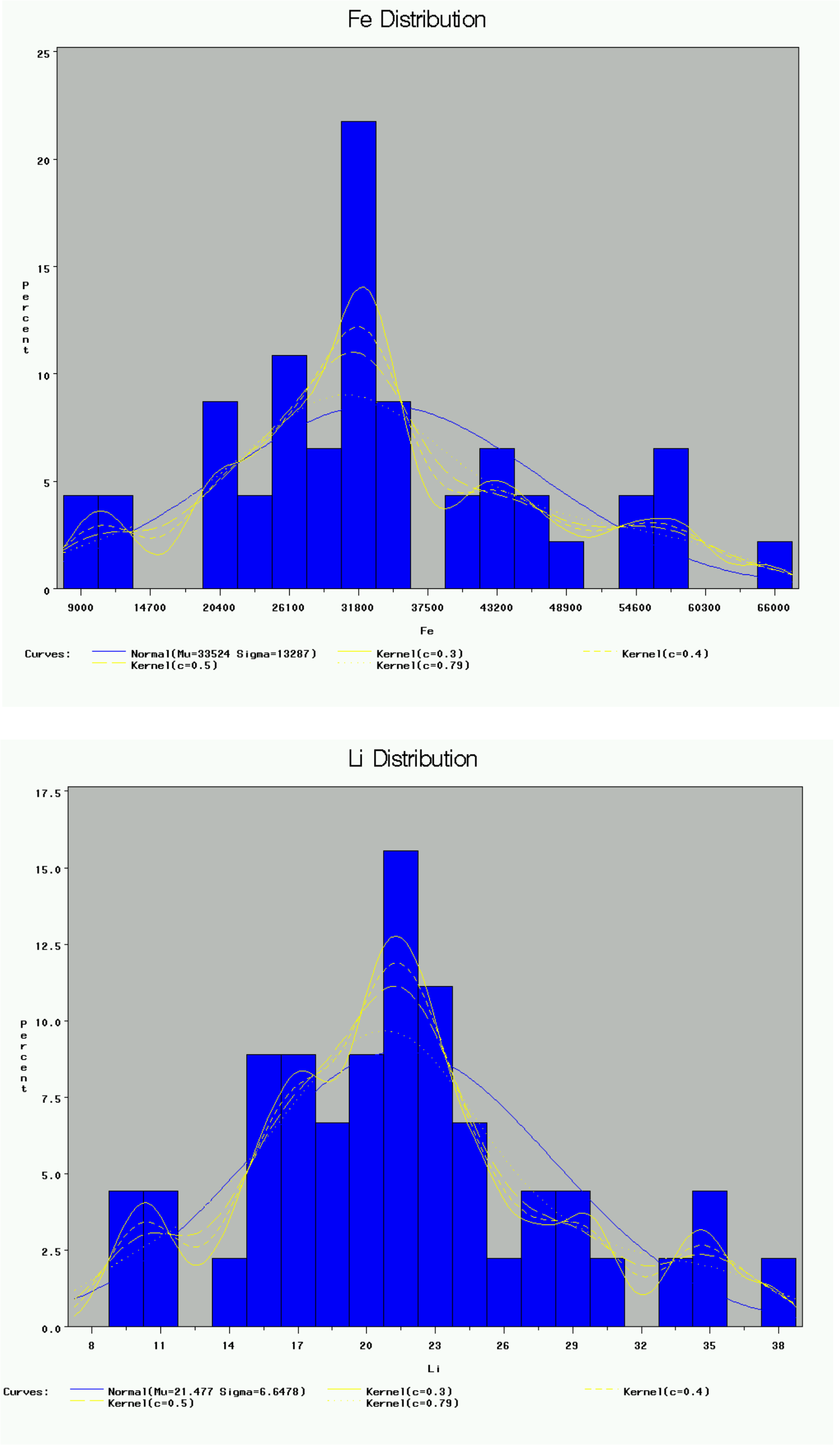


Figure 27. Frequency distributions for HNO_3-extractable Fe and Li. These two elements are described by a normal distribution.

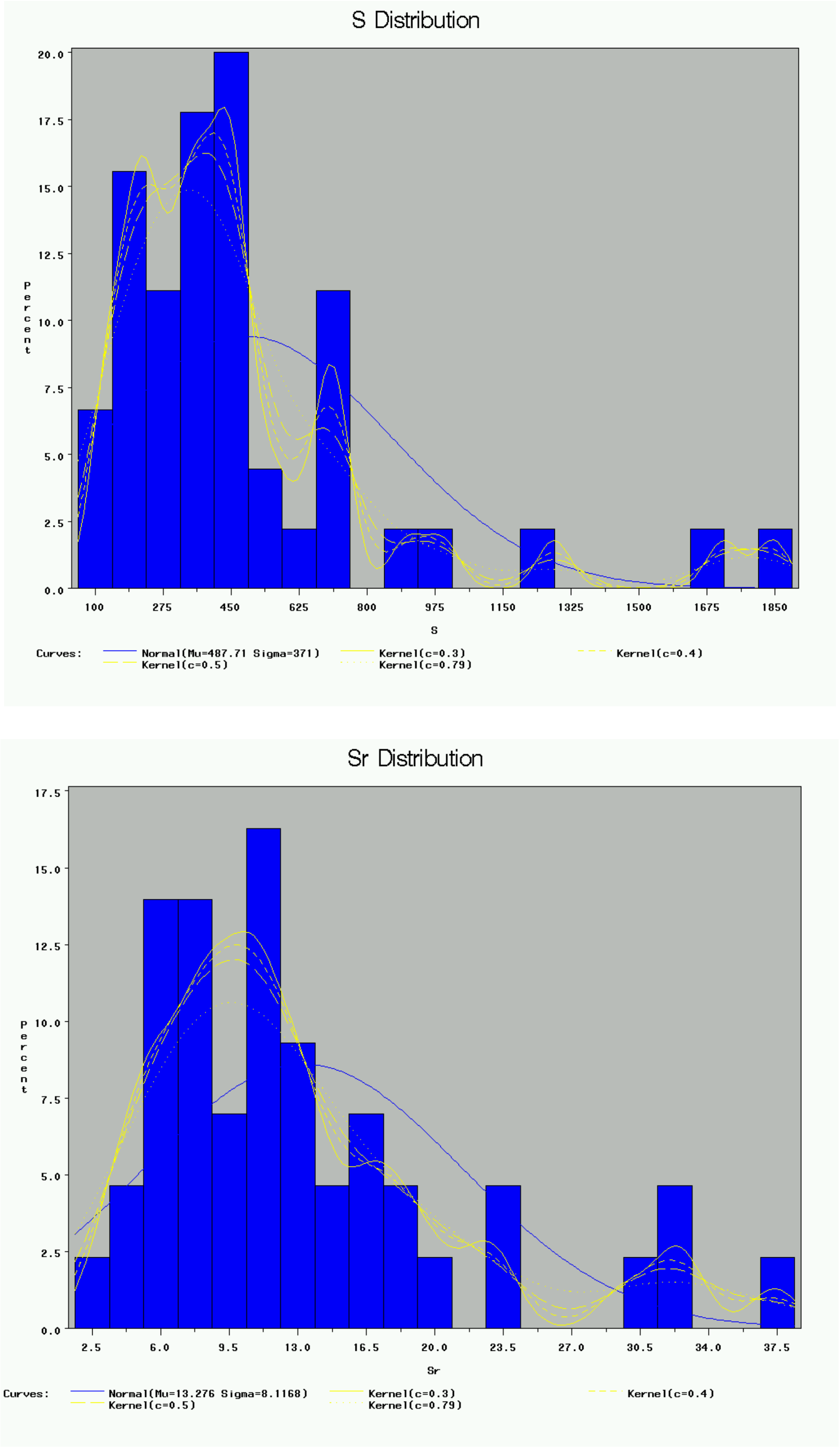
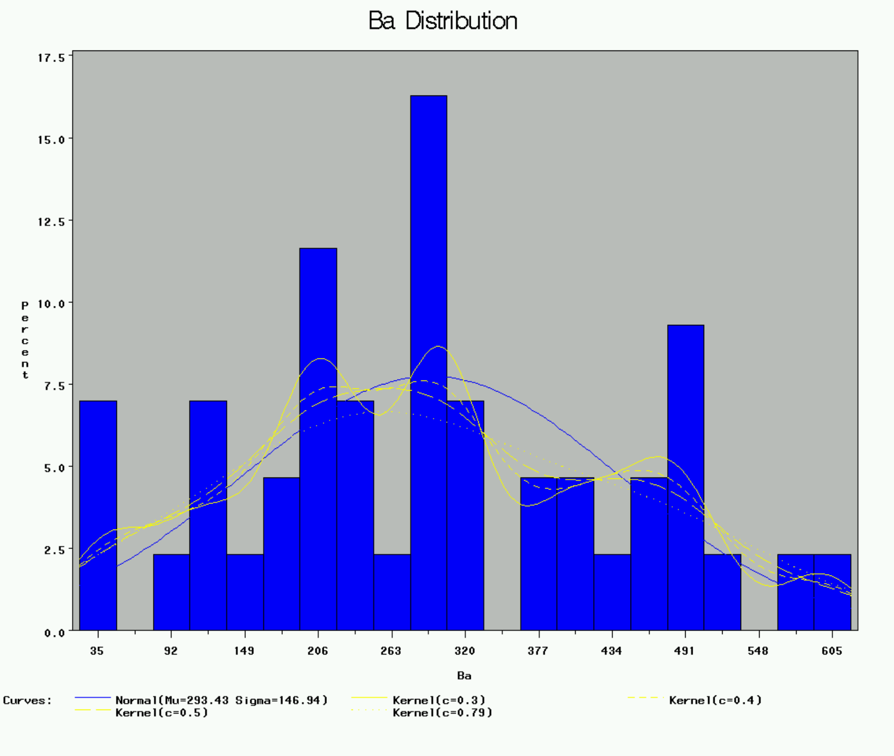


Figure 28. Frequency distributions for HNO_3-extractable S and Sr. These two elements are not described by a normal distribution and their distributions are highly skewed.



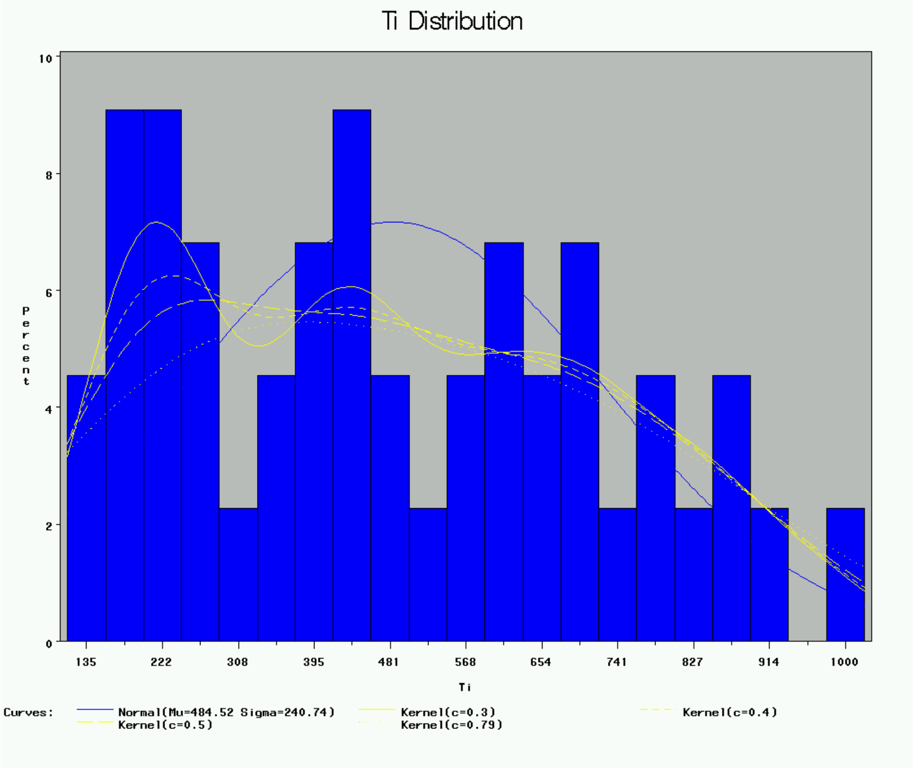
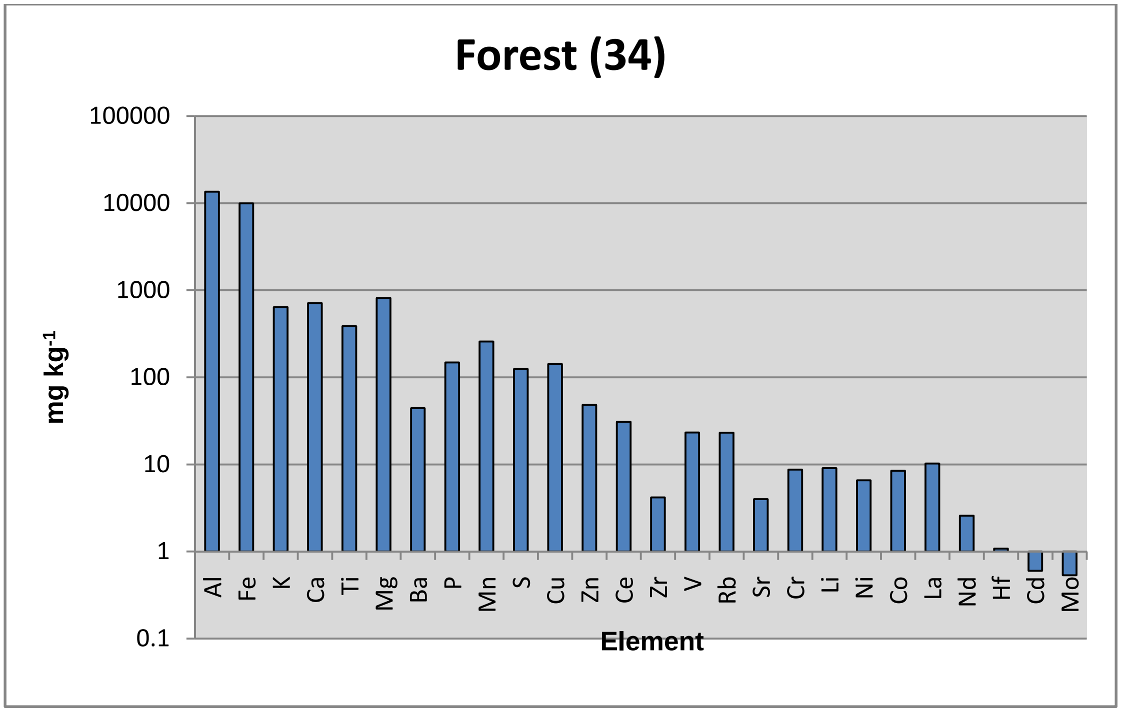


Figure 29. Frequency distributions for HNO_3-extractable Ba and Ti. These two elements are not described by a normal distribution, and their distribution is characterized as containing several modes.



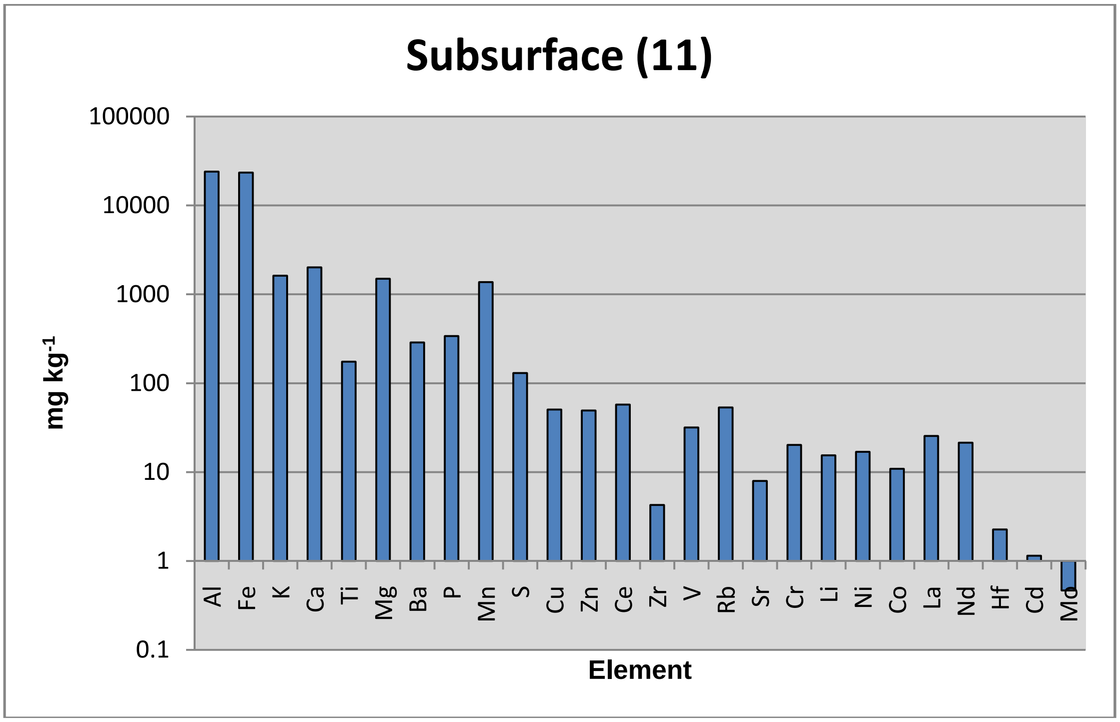


Figure 30. The histograms illustrate the HNO_3-extractable elemental composition (fingerprint) of a forested area and a subsurface sample.

stream sediment sources using the elemental fingerprint data, the following stipulations were assumed:

(1) Potential stream sediment source samples could be placed into source groups based on the current and past management, location in the landscape, or depth of the soil sample.

(2) A group of elements could be identified as having significantly different concentrations among the defined source groups.

(3) A group of elements could be identified as having significant power to discriminate the defined source groups.

To test for significant differences in the concentrations of each element among eight of the initially defined groups (suspended sediment and sources) (Table 4, excluding gravel roads) both a Kruskal-Wallis (KW) rank test with $P < 0.05$ and a Student-Newman-Keuls (SNK) multiple-range test with $P < 0.05$ were used. The former is a non-parametric test, while the latter is parametric. Secondly, a stepwise discriminant analysis was used to identify those elements that were useful for discriminating among the source groups. Using the eight initially defined groups, 14 elements (Al, Ba, Ca, Cd, Co, Cu, K, Li, Mg, P, S, Sr, V, Zr) exhibited significant differences among the groups according to the KW test (Table 21), and nine elements (K, Li, Cd, Cr, Ba, Zr, Cu, Zn, V) provided power for discriminating between the groups (Table 22). Seven elements (Ba, Cd, Cu, K, Li, V, Zr) had both characteristics. For example, consider the concentrations of Fe, Co, Cr, Zr in the Pond Creek materials. Iron concentrations did not significantly differ between any of the groups according to the KW test (Table 21; Fig. 31); nor did Fe provide any power to discriminate between the groups (Table 22). However, the mean Fe concentration of the forested area samples did significantly differ from all of the other groups according to the SNK

Table 21. Results of the Kruskal-Wallis rank test using HNO_3-extractable elemental data (8 groups, Table 4).

Kruskal-Wallis Test

Element	X^2	DF	Pr>X^2
Al*	18.2863	7	0.0107
Ba*	14.1433	7	0.0487
Ca*	20.1171	7	0.0053
Cd*	17.2727	7	0.0157
Ce	10.1467	7	0.1804
Co*	14.5116	7	0.0428
Cr	13.9469	7	0.0521
Cu*	16.33	7	0.0223
Fe	11.3805	7	0.1229
Hf	12.6247	7	0.0818
K*	23.349	7	0.0015
La	8.4395	7	0.2954
Li*	17.4947	7	0.0145
Mg*	21.7888	7	0.0028
Mn	9.3264	7	0.2301
Mo	2.9794	7	0.8869
Nd	6.2283	7	0.5134
Ni	8.0939	7	0.3244
P*	24.8182	7	0.0008
Rb	10.8975	7	0.1432
S*	23.4226	7	0.0014
Sr*	16.205	7	0.0233
Ti	10.0845	7	0.1838
V*	16.0973	7	0.0242
Zn	13.6733	7	0.0573
Zr*	22.6084	7	0.02

*Indicates elements that exhibited significant differences among the groups at $P<0.05$.

Table 22. Results of the discriminant function analysis using HNO_3-extractable elemental data (8 groups, Table 4).

Discriminant Function Analysis			
Element	R^2	F	Pr>F
Al	0.2433	1.19	0.3406
Ba*	0.3663	2.23	0.0633
Ca	0.2148	1.02	0.4433
Cd*	0.5802	5.33	0.0006
Ce	0.0871	0.35	0.9203
Co	0.1669	0.74	0.6374
Cr*	0.6532	7.26	<.0001
Cu*	0.4499	3.15	0.0144
Fe	0.1822	0.83	0.5739
Hf	0.0725	0.29	0.9519
K*	0.4831	3.6	0.0072
La	0.2292	1.1	0.3895
Li*	0.6203	6.3	0.0002
Mg	0.263	1.33	0.2782
Mn	0.2766	1.42	0.2396
Mo	0.0933	0.38	0.9043
Nd	0.1657	0.74	0.6424
Ni	0.1648	0.73	0.646
P	0.2058	0.96	0.4783
Rb	0.1653	0.74	0.6439
S	0.2107	0.99	0.459
Sr	0.0727	0.29	0.9513
Ti	0.1444	0.63	0.7293
V*	0.3662	2.23	0.0634
Zn*	0.3798	2.36	0.0509
Zr*	0.5702	5.12	0.0009

*Indicates elements that provided power for discriminating the groups Pr>F values must be below 0.15 for an element to be considered to provide discrimination power.

test (Table 23). Cobalt concentrations were significantly different in at least one of the groups (Tables 21 and 23; Fig. 32), but did not provide any power to discriminate between the groups (Table 22). Alternatively, Cr concentrations did not exhibit any significant differences between groups according to the KW test (Table 21; Fig. 33), and did offer power to discriminate between groups (Table 22). Yet, according to the SNK test the mean Cr concentrations of the suspended sediment and forested area groups were significantly different (Table 23). Finally, the Zr concentrations were significantly different between some of the groups (Table 21 and 23; Fig. 34), and also provided power for discriminating between the groups (Table 22). The results of the SNK test (Table 23) indicated that significant differences existed between the means of some groups for Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hf, K, Li, Mg, Mn, Ni, P, Rb, Sr, Ti, V, and Zr, and that the between group differences varied with element.

Since there were eight initial groups (suspended sediment and seven sources), and only seven elements (Ba, Cd, Cu, K, Li, V, Zr) were significantly different (KW test) among the groups and had discriminatory power, it was not possible to quantify the sources of suspended sediment using the initial group definitions or the criteria used to select the elements for discrimination analysis. Source identification requires that the number of numerical variables used for discriminating the source groups be greater than or equal to the number of groups. Again, in this case the criteria were not met. Thus, the next iteration of the stream sediment source identification scheme involved reducing the number of groups to four: surface, subsurface, sediment, and suspended sediment. Soil samples from cattle paths, cattle tramped areas, tilled fields, and forested areas were combined to form the surface group; in-stream sediment and drainage ditch samples were combined to form the sediments group. The subsurface and suspended sediment groups remained unchanged. Using these groups the

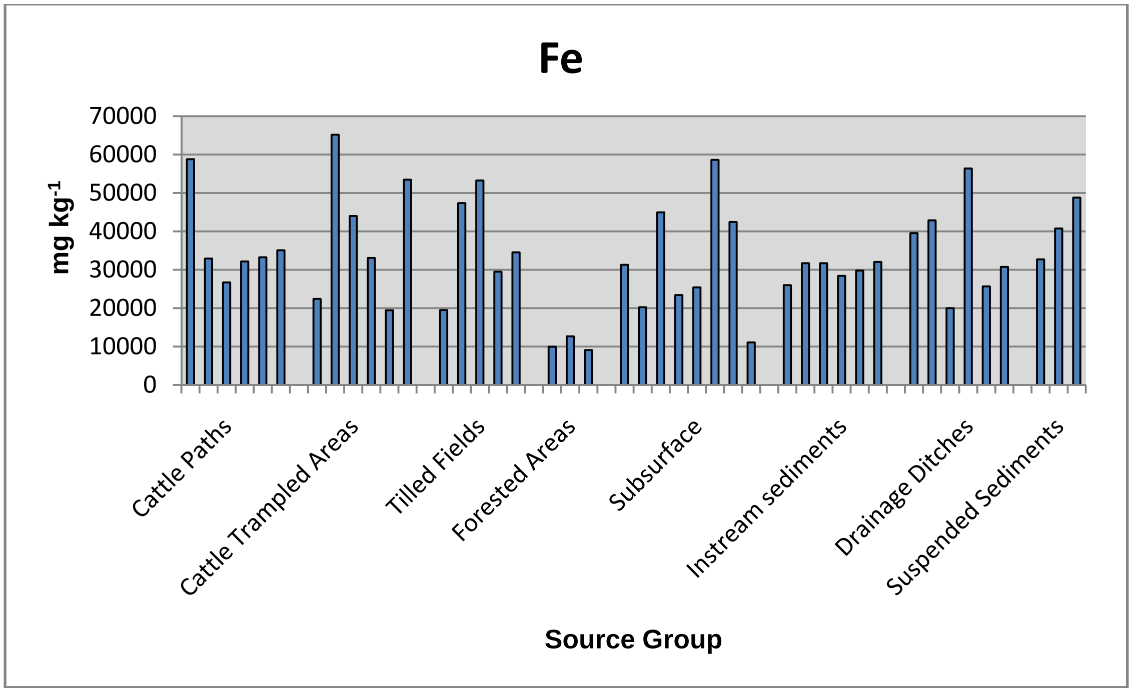


Figure 31. A histogram illustrating the distribution of HNO_3-extractable iron (Fe). Iron concentrations did not differ significantly among the groups according to the KW test (Table 21), but did significantly differ according to the SNK test (Table 23) and did not provide discriminatory power (Table 22).

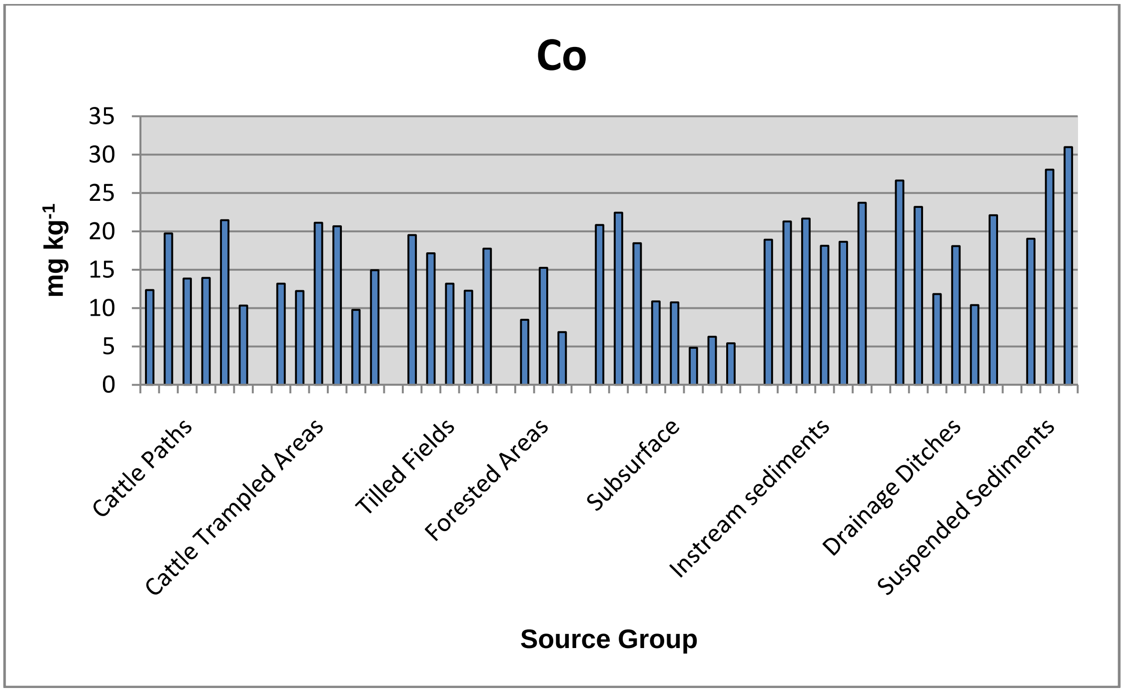


Figure 32. A histogram illustrating the distribution of HNO_3-extractable cobalt (Co). Cobalt concentrations differed significantly among the groups (Tables 21 and 23) but did not provide discriminatory power (Table 22).

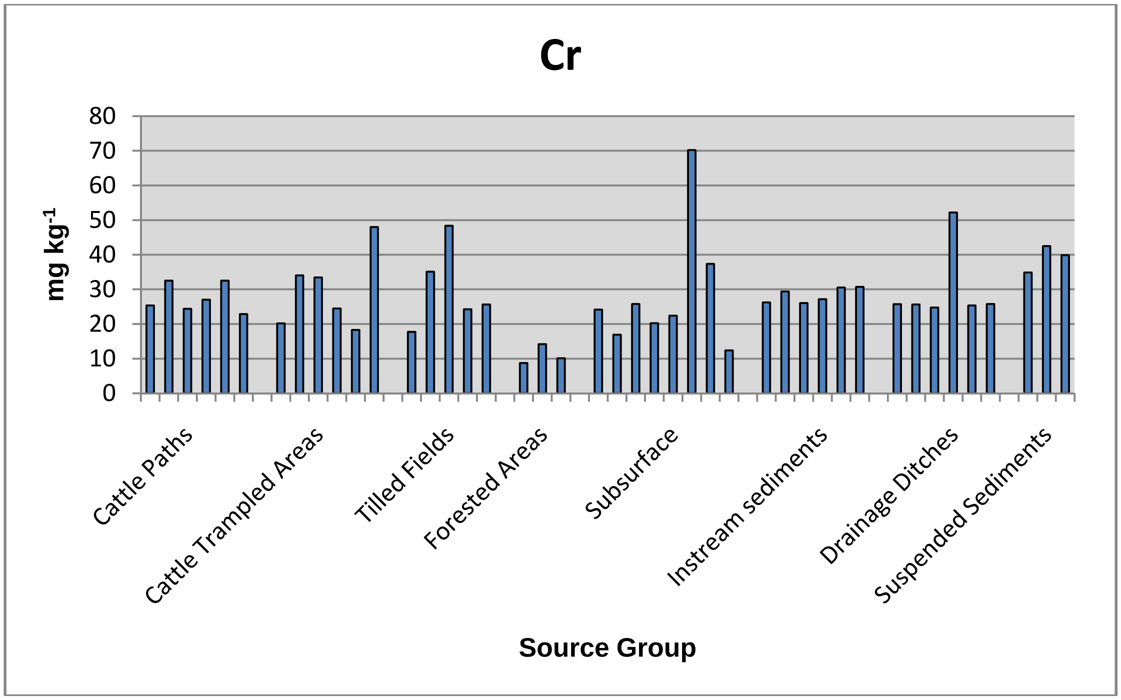


Figure 33. A histogram illustrating the distribution of HNO_3-extractable chromium (Cr). Chromium concentrations did not differ significantly among the groups according to the KW test (Table 21), but did differ significantly according to the SNK test (Table 23), and did offer discriminatory power (Table 22).

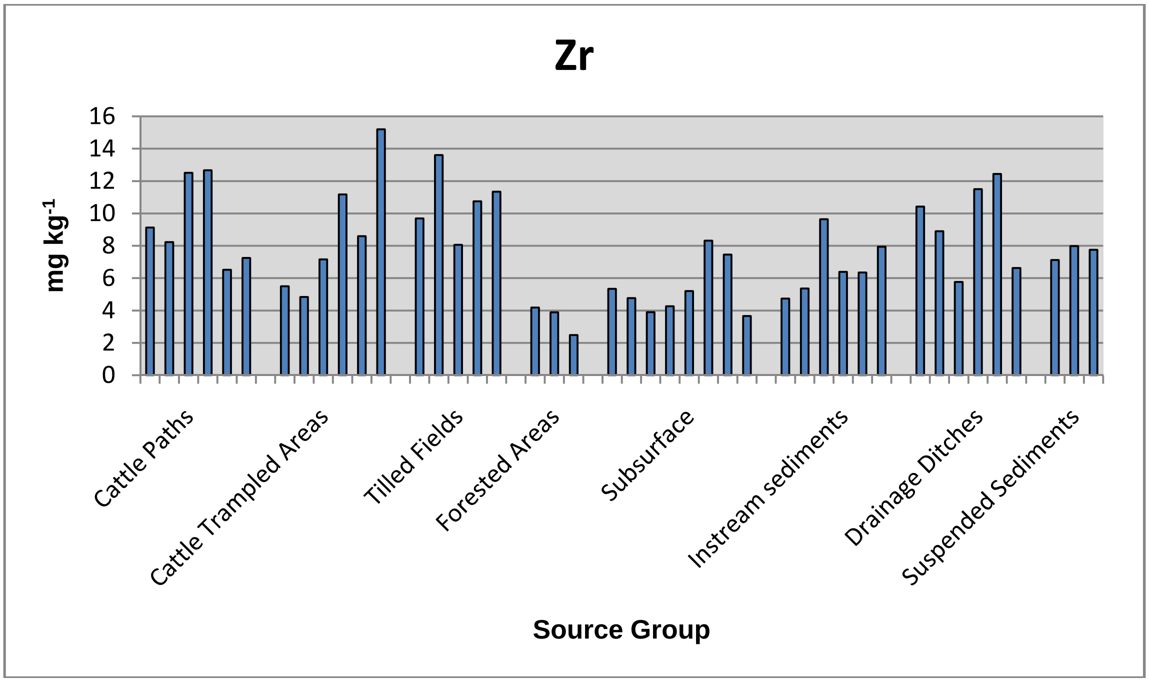


Figure 34. A histogram illustrating the distribution of HNO_3-extractable titanium (Ti). Titanium concetrations differed significantly among the groups (Tables 21 and 23) and provided discriminatory power (Table 22).

Table 23. Results of the Student-Newman-Keuls multiple-range test for HNO$_3$-extractable elements (8 groups, Table 4). For each element, groups identified by the same letter are not significantly different at P<0.05.

Student-Newman-Keuls multiple-range test

Aluminum				Barium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	43056	5	Tilled fields	A	793	6	Cattle trampled areas
A	42052	3	Suspended sediment	AB	412.4	3	Suspended sediment
AB	39025	6	Cattle trampled areas	AB	373.2	6	Instream sediment
AB	38951	6	Drainage ditches	AB	371.3	6	Drainage ditches
AB	33246	6	Cattle paths	B	250.2	5	Tilled fields
AB	31340	8	Subsurface	B	234	6	Cattle paths
AB	25122	6	Instream sediment	B	212	3	Forested areas
B	17351	3	Forested areas	B	201.5	8	Subsurface
Calcium				Cadmium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	4995.3	3	Suspended sediment	A	2.4351	5	Tilled fields
A	4975.2	6	Cattle trampled areas	A	2.292	6	Cattle trampled areas
AB	4362.4	6	Drainage ditches	AB	2.0728	6	Drainage ditches
AB	4242.1	6	Instream sediment	AB	2.0429	6	Cattle paths
AB	3418.7	6	Cattle paths	AB	1.8532	3	Suspended sediment
AB	2894	5	Tilled fields	AB	1.7606	8	Subsurface
B	1845.3	8	Subsurface	AB	1.3803	6	Instream sediment
B	1643	3	Forested areas	B	0.8237	3	Forested areas
Cerium				Cobalt			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	104.89	5	Tilled fields	A	26.023	3	Suspended sediment
A	99.51	3	Suspended sediment	AB	20.4	6	Instream sediment
A	90.75	6	Drainage ditches	AB	18.712	6	Drainage ditches
A	81.3	6	Cattle paths	B	15.973	5	Tilled fields
A	70.25	6	Instream sediment	B	15.32	6	Cattle trampled areas
A	67.18	3	Forested areas	B	15.279	6	Cattle paths
A	64.13	8	Subsurface	B	12.484	8	Subsurface
A	61.55	6	Cattle trampled areas	B	10.2	3	Forested areas

Table 23 continued.

Chromium				Copper			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	39.08	3	Suspended sediment	A	138.89	3	Forested area
AB	30.211	5	Tilled fields	A	119.46	6	Instream sediment
AB	29.921	6	Drainage ditches	A	117.64	6	Drainage ditches
AB	29.739	6	Cattle trampled areas	A	107.37	8	Subsurface
AB	28.648	8	Subsurface	A	102.44	6	Cattle paths
AB	28.353	6	Instream sediment	AB	78.92	6	Cattle trampled areas
AB	27.441	6	Cattle paths	AB	66.86	5	Tilled fields
B	11.012	3	Forested areas	B	13.79	3	Suspended sediment

Hafnium				Iron			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	4.8205	6	Cattle trampled areas	A	40763	3	Suspended sediment
AB	3.7388	6	Cattle paths	A	39597	6	Cattle trampled areas
AB	3.7255	6	Drainage ditches	A	36839	5	Tilled fields
AB	3.4407	5	Tilled fields	A	36479	6	Cattle paths
AB	3.1786	3	Suspended sediment	A	35864	6	Drainage ditches
AB	3.0519	8	Subsurface	A	32186	8	Subsurface
AB	2.943	6	Instream sediment	A	29946	6	Instream sediment
B	1.5875	3	Forested areas	B	10561	3	Forested areas

Lanthanum				Lithium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	40.586	3	Forested areas	A	39.612	3	Suspended sediment
A	35.055	3	Suspended sediment	B	25.454	6	Drainage ditches
A	29.907	5	Tilled fields	B	24.126	6	Cattle trampled areas
A	24.766	6	Drainage ditches	B	22.371	5	Tilled fields
A	23.657	6	Instream sediment	B	21.311	6	Instream sediment
A	21.567	6	Cattle trampled areas	B	20.792	6	Cattle paths
A	20.734	6	Cattle paths	B	18.802	8	Subsurface
A	18.291	8	Subsurface	C	9.998	3	Forested areas

Table 23 continued.

Magnesium

SNK Group	Mean	N	Groups
A	3775.4	3	Suspended sediment
B	2571.9	6	Cattle trampled areas
B	2492.3	6	Drainage ditches
B	2393.1	6	Cattle paths
BC	2250.8	6	Instream sediment
BC	2007.2	5	Tilled fields
BC	1583.5	8	Subsurface
C	1172.5	3	Forested areas

Manganese

SNK Group	Mean	N	Groups
A	3810.2	3	Suspended sediment
AB	2389	5	Tilled fields
AB	2195.2	6	Instream sediment
AB	2042.1	3	Forested areas
B	1697.1	6	Drainage ditches
B	1531.9	6	Cattle paths
B	1388.2	6	Cattle trampled areas
B	1282.8	8	Subsurface

Molybdenum

SNK Group	Mean	N	Groups
A	0.9424	3	Suspended sediment
A	0.8642	6	Drainage ditches
A	0.7517	8	Subsurface
A	7300	5	Tilled fields
A	0.7085	6	Cattle paths
A	0.6807	6	Cattle trampled areas
A	0.6785	6	Instream sediment
A	0.5773	3	Forested areas

Neodymium

SNK Group	Mean	N	Groups
A	31.261	3	Forested areas
A	24.63	3	Suspended sediment
A	18.934	6	Instream sediment
A	18.11	6	Cattle trampled areas
A	17.711	6	Drainage ditches
A	17.335	5	Tilled fields
A	14.148	6	Cattle paths
A	14.123	8	Subsurface

Nickel

SNK Group	Mean	N	Groups
A	32.66	3	Suspended sediment
AB	26.085	6	Cattle trampled area
AB	25.279	6	Drainage ditches
AB	23.57	5	Tilled fields
AB	21.892	8	Subsurface
AB	21.329	6	Cattle paths
AB	20.894	6	Instream sediment
B	15.725	3	Forested areas

Phosphorus

SNK Group	Mean	N	Groups
A	2024.1	6	Cattle trampled areas
AB	1672.5	6	Drainage ditches
ABC	1542.5	6	Cattle paths
ABC	1280.3	6	Instream sediment
ABC	1170.3	3	Suspended sediment
ABC	1021.9	5	Tilled fields
BC	589.3	8	Subsurface
C	369.9	3	Forested areas

Table 23 continued.

Potassium

SNK Group	Mean	N	Groups
A	4146.3	6	Cattle trampled areas
AB	3632.9	3	Suspended sediment
AB	3538.3	6	Cattle paths
AB	3257	6	Drainage ditches
AB	2641.1	6	Instream sediment
BC	2194.3	5	Tilled fields
BC	2019.5	8	Subsurface
C	804.1	3	Forested areas

Rubidium

SNK Group	Mean	N	Groups
A	90.05	3	Suspended sediment
A	90.05	6	Cattle trampled areas
A	82.67	5	Tilled fields
A	82.39	6	Cattle paths
A	81.11	6	Drainage ditches
A	73.23	8	Subsurface
A	66.53	6	Instream sediment
B	22.7	3	Forested areas

Sulfur

SNK Group	Mean	N	Groups
A	745.2	6	Cattle trampled areas
A	667.7	6	Instream sediment
A	533.4	6	Drainage ditches
A	491.7	3	Suspended sediment
A	461.9	6	Cattle paths
A	317.7	3	Forested areas
A	267.7	5	Tilled fields
A	206.4	8	Subsurface

Strontium

SNK Group	Mean	N	Groups
A	28.615	6	Cattle trampled areas
B	15.8	6	Cattle paths
B	14.181	6	Drainage ditches
B	13.253	3	Suspended sediment
B	12.784	6	Instream sediment
B	9.139	8	Subsurface
B	8.883	3	Forested areas
B	8.015	5	Tilled fields

Titanium

SNK Group	Mean	N	Groups
A	1044.2	3	Suspended sediment
AB	687.1	6	Drainage ditches
AB	620.3	5	Tilled fields
AB	545.6	6	Cattle paths
B	432.4	6	Cattle trampled areas
B	420.1	3	Forested areas
B	409.5	6	Instream sediment
B	355.9	8	Subsurface

Vanadium

SNK Group	Mean	N	Groups
A	62.04	5	Tilled fields
AB	53.75	6	Drainage ditches
AB	52.07	3	Suspended sediment
AB	51.72	6	Cattle paths
AB	51.69	8	Subsurface
AB	48.61	6	Cattle trampled areas
AB	36	6	Instream sediment
B	23.17	3	Forested areas

Table 23 continued.

Zinc				Zirconium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	182.11	6	Cattle trampled areas	A	10.689	5	Tilled fields
A	158.07	6	Drainage ditches	AB	9.382	6	Cattle paths
A	143.7	3	Suspended sediment	AB	9.276	6	Drainage ditches
A	130.24	3	Forested areas	AB	8.745	6	Cattle trampled areas
A	112.68	6	Instream sediment	ABC	7.616	3	Suspended sediment
A	108.86	6	Cattle paths	ABC	6.737	6	Instream sediment
A	103.63	5	Tilled fields	BC	5.365	8	Subsurface
A	94.1	8	Subsurface	C	3.515	3	Forested areas

statistical analyses were repeated. The results of the analyses showed that eight elements (Ba, Ca, Co, Cu, Li, Mg, P, S) had significant differences among the groups according to the KW test (Table 24) and seven elements(Ca, Cd, Cr, Cu, Li, P, Sr, Zn) had the ability to discriminate between groups (Table 25). However, only three elements (Cu, Ca, Li) had both characteristics, which is less than the number of defined groups. The results of the SNK test (Table 26) showed that the means of the groups exhibited significant differences for eight elements (Ca, Co, Cu, Li, Mg, Mn, Ni, Ti). Again, the number of variables that are both significantly different among the groups and may be used to discriminate the groups, are less than the number of groups.

The statistical approach was again modified to allow the HNO_3-extractable elemental data to identify a statistically-viable set of potential sediment source groups. This was accomplished using cluster analysis and canonical discriminant analysis (CDA) and all the elemental information. The cluster analysis provides a mechanism for evaluating whether or not the selected number of groups (clusters) to be created is realistic for the data set, while the CDA produces canonical variables that have the highest possible multiple correlations within groupings of samples. As previously indicated the CCC, PSF, and PST2 are three metrics generated during cluster analysis that may be used for determining the number of population clusters that are applicable to a particular data set. The results of the cluster analysis suggest that five clusters was an adequate number of clusters for this elemental data set (Table 27). Increasing the number of clusters from four to five results in an increase in CCC (13.2 to 23.9) and PSF (104 to 287), and a decrease in PST2 (94.6 to 10.6). Two of the three criteria (CCC and PSF) for evaluating the number of clusters also indicate that four may be an acceptable number of clusters for the data set. The CCC and PSF both increase as the number of clusters increased from three to four, although, the PST2 also increased. The clustering of the samples into five groups can be

Table 24. Results of the Kruskal-Wallis rank test using four groups (surface, subsurface, sediment, and suspended sediment) and HNO_3-extractable elemental data.

Kruskal-Wallis Test			
Element	X^2	DF	Pr>X^2
Al	3.4627	3	0.3256
Ba*	7.8478	3	0.0493
Ca*	12.8919	3	0.0049
Cd	2.8317	3	0.4183
Ce	5.2432	3	0.1548
Co*	12.4003	3	0.0061
Cr	7.0415	3	0.0706
Cu*	11.0378	3	0.0115
Fe	1.8091	3	0.6129
Hf	1.2563	3	0.7395
K	6.4691	3	0.0909
La	7.4075	3	0.06
Li*	9.9814	3	0.0187
Mg*	13.133	3	0.0044
Mn	6.5988	3	0.0858
Mo	0.6295	3	0.8896
Nd	4.4411	3	0.2176
Ni	5.0747	3	0.1664
P*	10.4556	3	0.0151
Rb	1.3758	3	0.7112
S*	12.6929	3	0.0054
Sr	4.4874	3	0.2134
Ti	6.3609	3	0.0953
V	1.3809	3	0.71
Zn	4.2214	3	0.2385
Zr	7.3589	3	0.0613

*Indicates elements that exhibited significant differences among the groups at $P<0.05$.

Table 25. Results of the discriminant function analysis using four groups (surface, subsurface, sediment, and suspended sediment) and HNO_3-extractable elemental data.

	Discriminant Function Analysis		
Element	R^2	F	Pr>F
Al	0.0196	0.21	0.8866
Ba	0.1368	1.69	0.1887
Ca	0.1346	1.66	0.1953
Cd*	0.5772	15.02	<.0001
Ce	0.0235	0.26	0.8561
Co	0.0617	0.7	0.5584
Cr*	0.4223	8.04	0.0004
Cu*	0.2526	3.72	0.0208
Fe	0.0258	0.28	0.8379
Hf	0.034	0.37	0.7717
K	0.0841	0.98	0.4148
La	0.0593	0.67	0.5756
Li*	0.6745	22.79	<.0001
Mg	0.0938	1.1	0.362
Mn	0.1074	1.28	0.2966
Mo	0.0986	1.17	0.3375
Nd	0.0528	0.6	0.6228
Ni	0.0633	0.72	0.5467
P*	0.4642	9.53	0.0001
Rb*	0.1838	2.48	0.0786
S	0.0142	0.15	0.9267
Sr*	0.2081	2.89	0.0501
Ti	0.1154	1.39	0.2632
V	0.0449	0.5	0.6837
Zn	0.0825	0.96	0.4239
Zr	0.0677	0.77	0.517

*Indicates elements that provided power for discriminating the groups Pr>F values must be below 0.15 for an element to be considered to provide discrimination power.

Table 26. Results of the Student-Newman-Keuls multiple-range test using four groups (surface, subsurface, sediment, suspended sediment) and HNO_3-extractable elements. For each element, groups identified by the same letter are not significantly different at $P<0.05$.

Student-Newman-Keuls multiple-range test

Aluminum

SNK Group	Mean	N	Groups
A	42052	3	Suspended sediment
A	35048	20	Surface
A	32036	12	Sediment
A	31340	8	Subsurface

Barium

SNK Group	Mean	N	Groups
A	412.4	3	Suspended sediment
A	402.4	20	Surface
A	372.3	12	Sediment
A	201.5	8	Subsurface

Calcium

SNK Group	Mean	N	Groups
A	4995.3	3	Suspended sediment
A	4302.3	12	Sediment
AB	3488.1	20	Surface
B	1845.3	8	Subsurface

Cadmium

SNK Group	Mean	N	Groups
A	2.0328	20	Surface
A	1.8532	3	Suspended sediment
A	1.7606	8	Subsurface
A	1.7266	12	Sediment

Cerium

SNK Group	Mean	N	Groups
A	99.51	3	Suspended sediment
A	80.5	12	Sediment
A	79.15	20	Surface
A	64.13	8	Subsurface

Cobalt

SNK Group	Mean	N	Groups
A	26.023	3	Suspended sediment
B	19.556	12	Sediment
BC	14.703	20	Surface
C	12.484	8	Subsurface

Chromium

SNK Group	Mean	N	Groups
A	39.08	3	Suspended sediment
A	29.137	12	Sediment
A	28.684	8	Subsurface
A	26.359	20	Surface

Copper

SNK Group	Mean	N	Groups
A	118.55	12	Sediment
A	107.37	8	Subsurface
A	91.96	20	Surface
B	13.79	3	Suspended sediment

Table 26 continued.

Hafnium				Iron			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	3.6661	20	Surface	A	40763	3	Suspended sediment
A	3.3343	12	Sediment	A	33617	20	Surface
A	3.1786	3	Suspended sediment	A	32905	12	Sediment
A	3.0519	8	Subsurface	A	32186	8	Subsurface
Lanthanum				Lithium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	35.055	3	Suspended sediment	A	39.612	3	Suspended sediment
A	26.255	20	Surface	B	23.383	12	Sediment
A	24.211	12	Sediment	B	20.568	20	Surface
A	18.291	8	Subsurface	B	18.802	8	Subsurface
Magnesium				Manganese			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	3775.4	3	Suspended sediment	A	3810.2	3	Suspended sediment
B	2371.5	12	Sediment	B	1946.2	12	Sediment
B	2167.2	20	Surface	B	1779.6	20	Surface
B	1583.5	8	Subsurface	B	1282.8	8	Subsurface
Molybdenum				Neodymium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	0.9424	3	Suspended sediment	A	24.63	3	Suspended sediment
A	0.7714	12	Sediment	A	18.7	20	Surface
A	0.7517	8	Subsurface	A	18.323	12	Sediment
A	0.6859	20	Surface	A	14.123	8	Subsurface
Nickel				Phosphorus			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	32.66	3	Suspended sediment	A	1476.4	12	Sediment
B	23.086	12	Sediment	A	1380.9	20	Surface
B	22.475	20	Surface	A	1170.3	3	Suspended sediment
B	21.892	8	Subsurface	A	589.3	8	Subsurface

Table 26 continued.

Potassium

SNK Group	Mean	N	Groups
A	3632.9	3	Suspended sediment
A	2974.6	20	Surface
A	2949	12	Sediment
A	2019.5	8	Subsurface

Rubidium

SNK Group	Mean	N	Groups
A	90.05	3	Suspended sediment
A	75.8	20	Surface
A	73.82	12	Sediment
A	73.23	8	Subsurface

Sulfur

SNK Group	Mean	N	Groups
A	600.6	12	Sediment
A	491.7	3	Suspended sediment
A	476.7	20	Surface
A	206.4	8	Subsurface

Strontium

SNK Group	Mean	N	Groups
A	16.661	20	Surface
A	13.482	12	Sediment
A	13.253	3	Suspended sediment
A	9.139	8	Subsurface

Titanium

SNK Group	Mean	N	Groups
A	1044.2	3	Suspended sediment
B	548.3	12	Sediment
B	511.5	20	Surface
B	355.9	8	Subsurface

Vanadium

SNK Group	Mean	N	Groups
A	52.07	3	Suspended sediment
A	51.69	8	Subsurface
A	49.08	20	Surface
A	44.87	12	Sediment

Zinc

SNK Group	Mean	N	Groups
A	143.7	3	Suspended sediment
A	135.38	12	Sediment
A	132.74	20	Surface
A	94.1	8	Subsurface

Zirconium

SNK Group	Mean	N	Groups
A	8.638	20	Surface
A	8.007	12	Sediment
A	7.616	3	Suspended sediment
A	5.365	8	Subsurface

Table 27. Results of the cluster analysis when five clusters and HNO_3-extractable elemental data were used.

5 Defined Clusters			
Cluster	CCC	PSF	PST2
10	_	230	7.5
9	_	235	9.4
8	19.9	231	6.3
7	20.7	240	5.5
6	22.1	262	4.2
5	23.9	287	10.6
4	13.2	104	94.6
3	1.86	37.7	75.5
2	-2.1	17.7	40
1	0	_	17.7

displayed in the form of a dendrogram derived using divisive hierarchical cluster analysis (Fig. 35). Similarities between samples are more pronounced as the r-squared value increases.

Using the canonical variables, CDA generated five statistically similar groups using the HNO_3-extractation elemental data (Fig. 36). The first canonical variable explains approximately 52% of the variability of the HNO_3-extractable elemental data, while the second and third account for 34.5% and 11.5% of the variability. Overall, the first three canonical variables account for 98% of the variability of the HNO_3-extractable elemental data. The effect that each element has on the separation of the individual samples (vector magnitude and direction) is shown in the inset in Fig. 36. In the first dimension (canonical variable 1 and 2) all of the elements separate the samples primarily along the x-axis (canonical variable 1). Relative to the other elements, Cu has an opposite, but very weak effect on the separation of the samples along the x-axis. The vectors of Ca, Mg, and Ti lie directly on the x-axis in the first dimension and have no effect on the separation of the samples along the y-axis (canonical variable 2), while Ba, Ce, Co, La, Mn, and Nd separate the samples slightly in the negative direction along the y-axis.

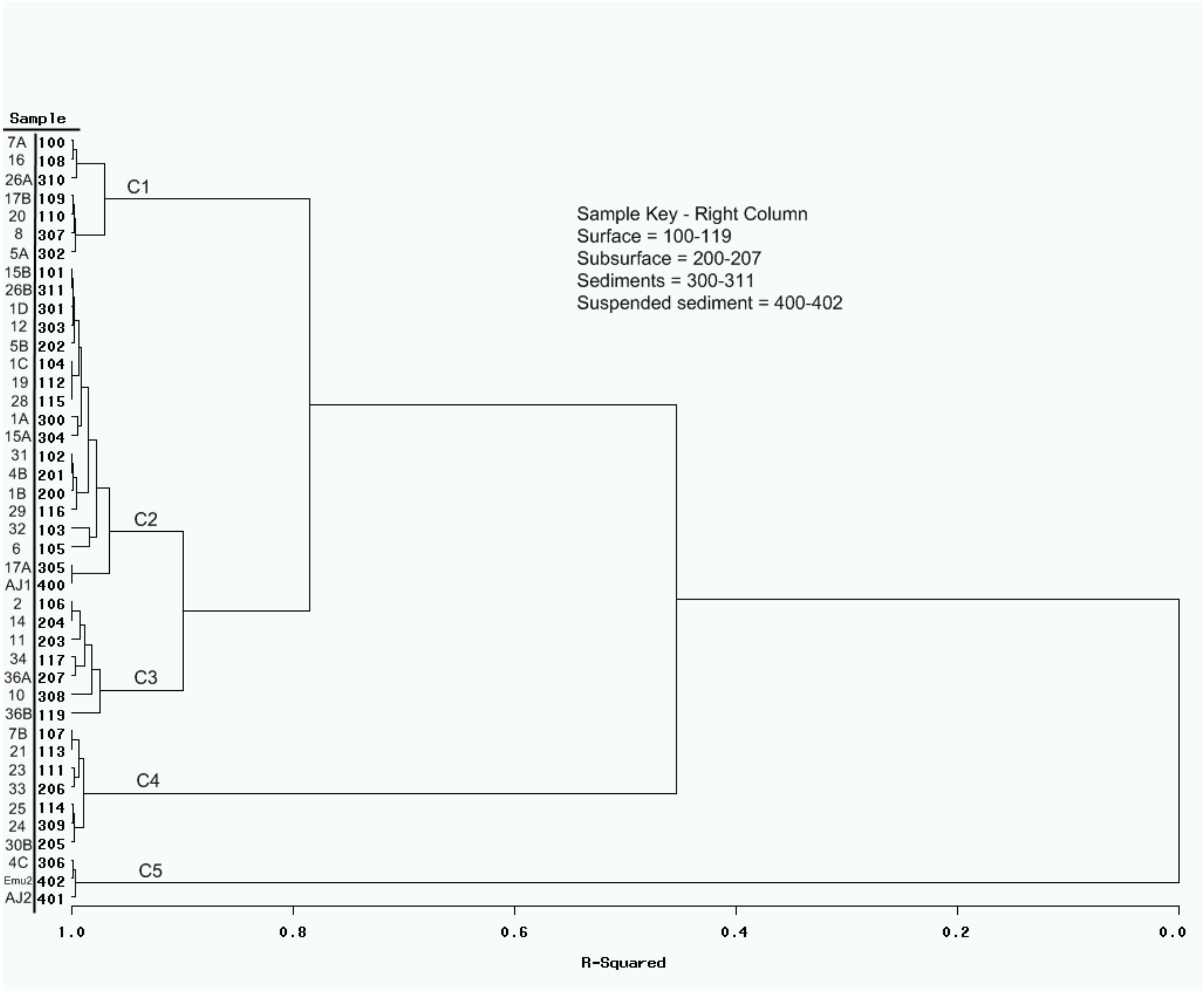


Figure 35. Dendrogram created by divisive hierarchical cluster analysis using the HNO_3-extraction data for all the elements. Sample numbers in the right column correspond with sample type (group) and are indicated in the key. Sample numbers in the left column correspond with sample location (Table 3).

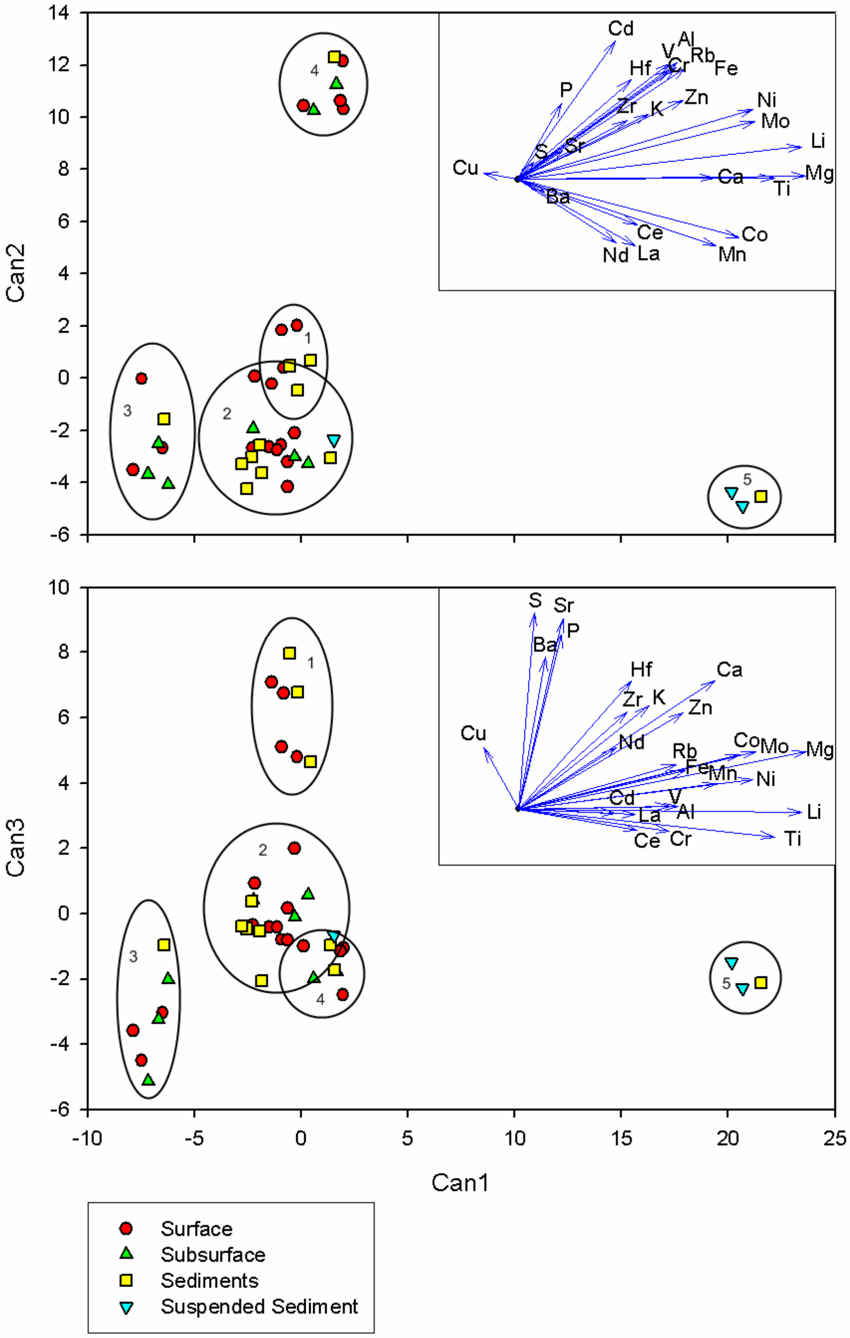


Figure 36. Canonical discriminant analysis of the Pond Creek watershed samples using the nitric acid extraction data to produce five clusters. The plots show the first three canonical variables. The data points represent the individual soil or sediment samples and the arrows in the inset illustrate the impact that each element has on the separation of the samples. The ellipses enclose statistically unique groups, while sample type is represented by both color and shape. Numbers are for reference purposes.

The rest of the elements separate the samples in a slightly positive direction along the y-axis in the canonical variable 1 and 2 dimension. In the second dimension (canonical variable 1 and 3) the power that most of the elements provide for separating the samples is in the positive direction along the x-axis (canonical variable 1). However, Ba, P, S, and Sr separate the samples solely along the y-axis (canonical variable 3). Copper separates the samples along the y-axis, but also has an effect in the negative direction along the x-axis. While the vectors of many elements overlap in each dimension, no two elements have identical vectors in both dimensions, suggesting that all of the elements have some utility for separating the groups.

Interestingly, in the analysis of the HNO_3-extraction data, two of the three suspended sediment samples and a sediment sample taken from a drainage ditch form a unique cluster C5. The two suspended sediment samples were collected on the same day at different locations, indicating that the characteristics of the suspended sediment were very similar over a 5 km section of the stream. The sediment sample from the drainage ditch was collected approximately 4.3 km upstream from one suspended sediment sampling site and 9 km upstream from the other. Furthermore, it was collected from a location adjacent to a gravel road, which may have had major impacts on the chemical characteristics of this sample. These samples cluster together because they have high extractable concentrations of Ba, Ca, Ce, Co, La, Li, Mg, Mn, Nd, Ni, and Ti relative to samples in other clusters.

Cluster C1 consists of a cattle path sample, three cattle trampled area samples, an in-stream sediment bar sample, and two drainage ditch samples. All of these samples had very high levels of P relative to the other samples. One reason for the high P levels in these samples is that all of them were collected from areas that had been heavily trampled and manured by cattle. Manure deposition and incorporation into the soil is a likely cause of high P levels in the samples because extended manure applications can lead to high levels of P in soils. The cattle path and cattle trampled area samples in C1 were all collected from unvegetated areas that were directly affected by cattle. The sediment bar sample was from within Pond Creek in a location where cattle had direct access to the stream, and it too had been heavily trampled by cattle. One of the drainage ditch samples (sample 8) was collected in a drainage ditch behind a manure storage pit just below where liquid manure was pumped from the pit. The other drainage ditch sample was collected from the surface layers of material in a drainage ditch that appeared visually to contain manure carried by runoff from a nearby dairy. Thus, all of the samples appear to be similar in the fact that they all had been influenced by manure.

Cluster C2 is the largest and most diverse cluster generated by this analysis, and a central theme linking all of its samples is more difficult to establish. It contains five samples from cattle paths, three from tilled fields, three from subsurface materials, five in-stream sediment samples, a drainage ditch sample, and the other suspended sediment sample. Four of the samples in this cluster were collected proximate to one another. Two of these were from an in-stream bar, one was from a cattle path, and one was from a stream bank. The HNO_3-extractable elemental concentrations of the samples in C2 show no discernible pattern relative to other clusters. This cluster is near the origin in both the first and second canonical dimensions of Fig 36. In general, it seems that the samples in this group represent subsurface materials, although only three samples in C2 were collected from true subsurface materials (stream banks). However, three samples were from tilled fields, which may contain subsurface material due to the mixing involved with tillage. Also, the five cattle path samples may have contained subsurface material due to the degree to which they had been eroded. All of the other samples in C2 are either deposited or suspended sediments, which suggests that subsurface material is contributing a significant portion of the sediment reaching Pond Creek.

Cluster C3 contains two forest samples, a cattle trampled area sample, three subsurface samples, and a sample from a drainage ditch. One of the subsurface samples was from a road cut bank, and was collected just downslope from where one of the forest samples was collected. This sample may have been influenced by the migration of the forest soil downslope. The other two subsurface samples in C3 were from the banks of Pond Creek. Also, the drainage ditch sample was collected very close to where one of these stream bank samples was collected. In general, all of the samples in this cluster had low concentrations of Al, Fe, Hf, Li, Ni, P, Rb, V, and Zr relative to the samples in other clusters, although there does not appear to be a clear explanation for their grouping based on sample type and location.

Cluster C4 contains two cattle trampled area samples, two tilled field samples, two subsurface samples, and a sample from a drainage ditch. Relative to the other clusters, the samples in this group have particularly high levels of Al, Cd, Cr, Fe, Rb, and V. The two cattle trampled area samples were collected in a sloping area that had been heavily affected by cattle. Also, the drainage ditch sample was collected just down slope from one of the cattle trampled samples. One of samples considered to be subsurface was collected from a mass of material removed when a barn was constructed. This material was located just outside the barn where it may have been affected by manure from cattle. It is also important to note that the true origin of this material is unknown and may have been affected by cattle prior to the construction of the barn. The other subsurface sample was collected very close to the same barn from a surface routinely scraped as manure was pushed out of the barn. The two tilled samples, although not directly affected by manure applications, may have been affected by the application of biosolids from the local wastewater treatment plant. It is known that one of the tilled samples was from a location where biosolids had been applied. Although it is unknown whether biosolids had been applied at the location where the other tilled sample was collected, it seems possible since these two samples have such similar HNO_3-extractable elemental chemistry. However, the samples in C4 are found in many different clusters when the total dissolution data are used to group the samples. One explanation for the high concentrations of metals in all of the samples in C4 (Fig. 36) is that the metals had built up due to the continuous application of manure or biosolids, but this does not explain why these samples do not cluster together using the totals data.

As previously indicated, four clusters may also be acceptable for describing the soil sample population in Pond Creek. Cluster analysis and CDA were repeated in order to generate four statistical groups using the elemental data (Table 28). The clustering of the samples into four groups is displayed as a dendrogram derived using divisive hierarchical cluster analysis (Fig. 37). The contents of these clusters differ slightly from those presented in Fig. 35. The results of the four group CDA are presented in Fig. 38. The first canonical variable explains approximately 73% of the elemental variation in the data set. The second explains approximately 24.5%, and the third 2.3% of the variation. In this analysis, these three variables account for 100% of the variation. Once again, the clusters created when four groups was designated contain similar samples to the five clusters previously created. However, the effects that each element has on the separation of the samples are different from the five cluster CDA. In this analysis the power that most of the elements provide for separating the samples in the first dimension (canonical variable 1 and 2) is along the y-axis (canonical variable 2). However, Ba, Ce, Co, La, Mn, and Nd separate the samples mostly along the x-axis (canonical variable 1). In the second dimension (canonical variable 1 and 3) the elements provide power for separating the samples

Table 28. Results of the cluster analysis when five clusters and the HNO_3-extractable elemental data were used.

4 Defined Clusters			
Cluster	CCC	PSF	PST2
10	_	406	11.2
9	_	439	2.3
8	16.6	430	7.5
7	17.3	469	3
6	17.3	471	8.5
5	14.8	530	4.1
4	15.7	606	7.3
3	4.49	190	152
2	-3	41.9	168
1	0	_	41.9

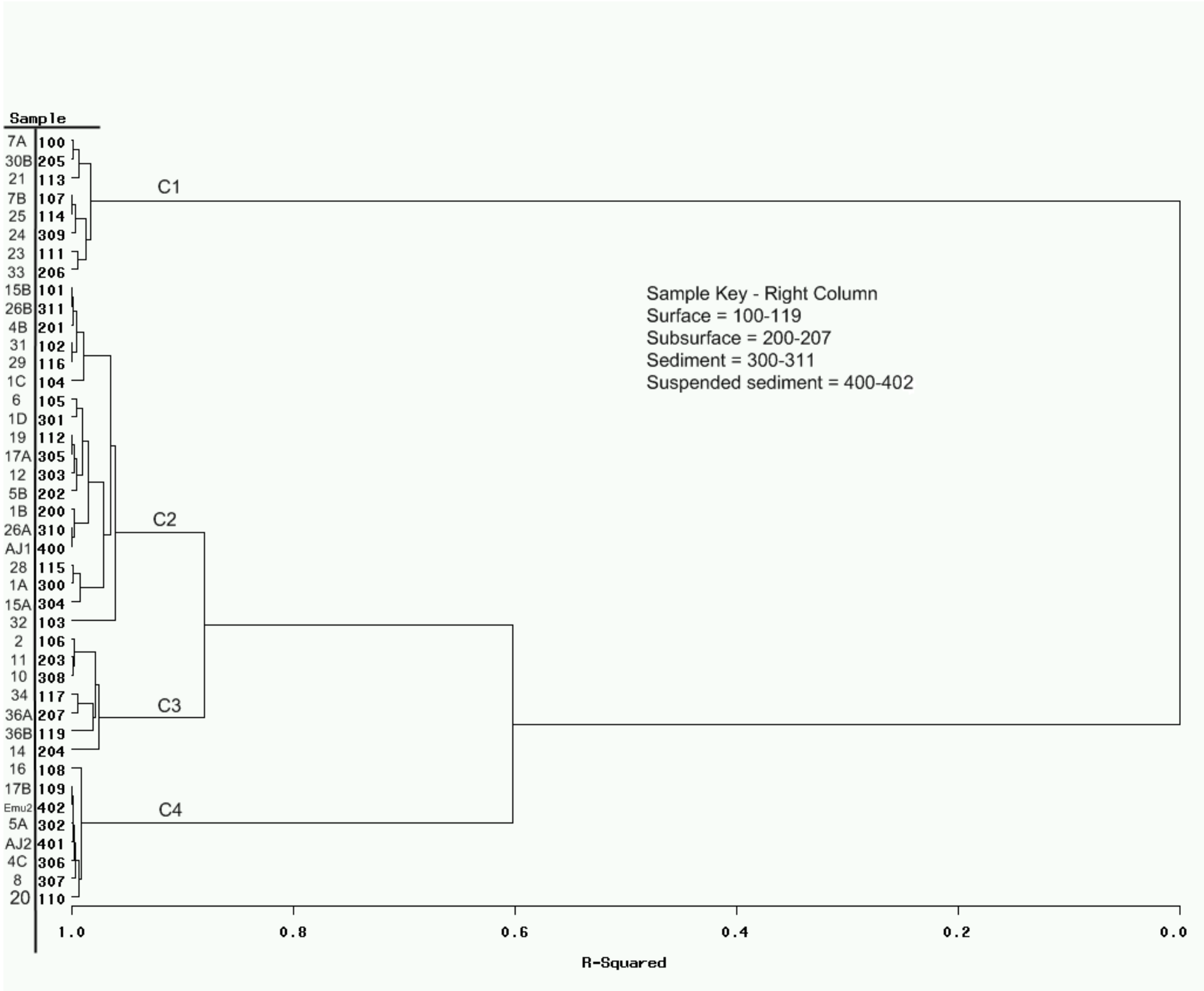


Figure 37. Dendrogram created by divisive hierarchical cluster analysis using all the HNO_3-extractable elements. Sample numbers in the right column correspond with sample type (group) and are indicated in the key. Sample numbers in the left column correspond with sample location (Table 3).

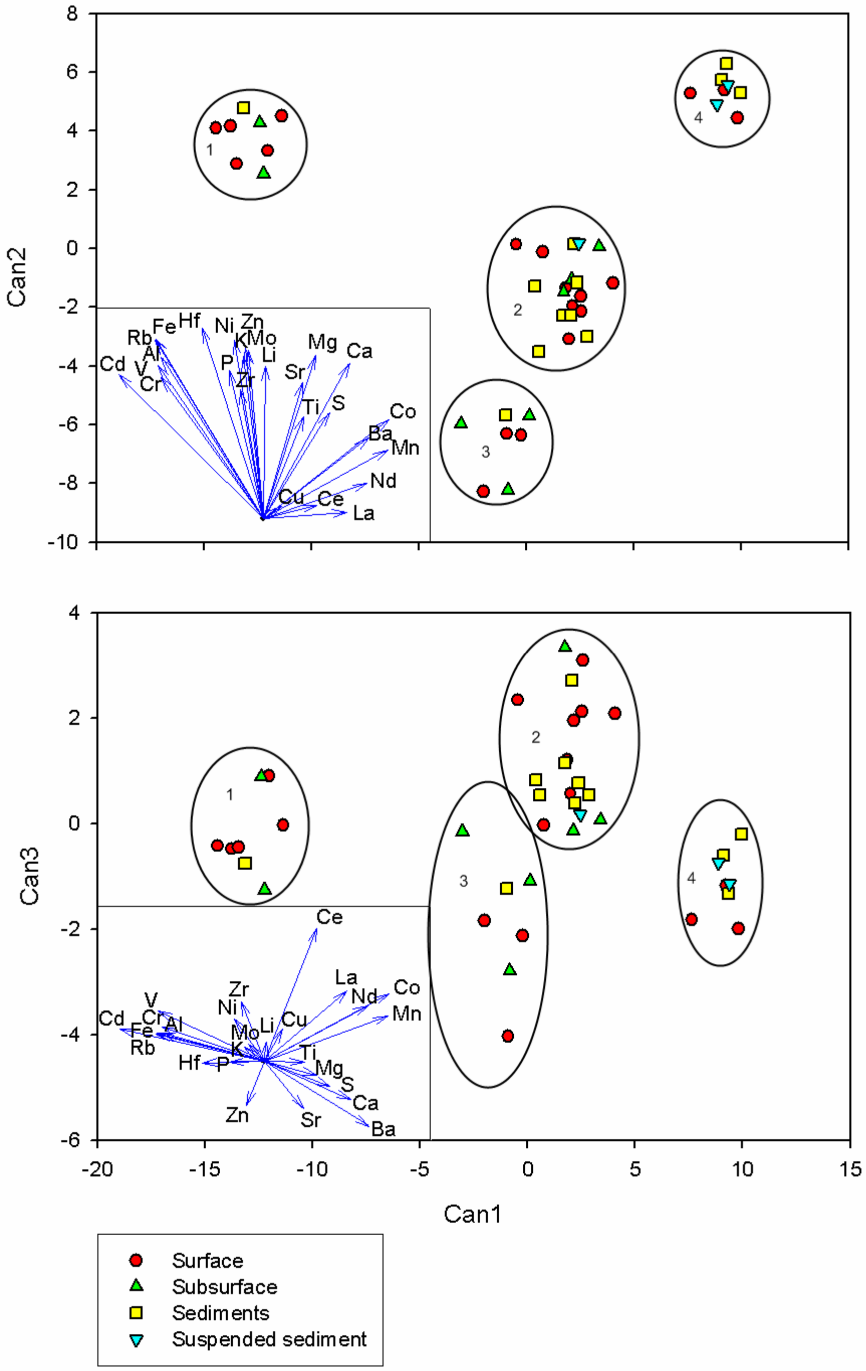


Figure 38. Canonical discriminant analysis of the Pond Creek watershed samples using the nitric acid extraction data to produce four clusters. The data points represent the individual soil or sediment samples and the arrows in the inset illustrate the impact that each element has on the separation of the samples. The ellipses enclose statistically unique groups, while sample type is represented by both color and shape. Numbers are for reference purposes.

along both axes. The vectors of the elements that separate the samples along the x-axis (canonical variable 1) are larger in magnitude than the vectors of the elements that separate the samples along the y-axis (canonical variable 3). Thus, the elements associated with the x-axis provide greater power for separating the samples than those associated with the y-axis. For this reason the groups appear to be aligned along the x-axis in the variable 1 and 3 dimension. Also, the vectors of Fe and Rb overlap almost exactly in both dimensions, which indicates that only one of them is necessary for separating the groups.

In general, the clusters contain the same samples as in the previous analyses of the HNO_3-extractable elements. Cluster C3 in Figs. 36 and 38 both contain the exact same samples, all of which had low concentrations of Al, Fe, Hf, Li, Ni, P, Rb, V, and Zr relative to all the other samples. The other clusters in Fig. 38 are slightly altered from those in Fig. 36. Cluster C1 in Fig. 38 is the same as cluster C4 in Fig. 36, except that it contains an extra cattle path sample (7A) that was collected adjacent to one of the cattle trampled area samples (7B) already in this cluster. This is a reasonable inclusion since both of these samples were collected at the same location, and also clustered together when the total dissolution data was used to group the samples. Once again, the samples in this group tend to have particularly high levels of Al, Cd, Cr, Fe, Rb, and V, which may have accumulated as a result of both the application of biosolids (tilled fields) and manure.

Cluster C2 in Fig. 38 contains the same samples as C2 in Fig. 36, except for an additional sample from a drainage ditch. This particular drainage ditch sample (26A) was collected from the surface layers of deposition in the drainage ditch, while one of the other samples in this cluster was collected from the subsurface layers of deposited material in the ditch. Thus, the addition of this sample to this cluster seems reasonable. Cluster C2 contains the largest number of samples of all the clusters in Fig. 36. As stated above, this cluster contains one of the three suspended sediment samples (AJ1).

Cluster C4 Fig. 38, was formed from a combination of C1 and C5 in Fig. 36. The samples contained in C4 (Fig. 38) consist of three cattle trampled area samples, an in-stream bar sample, two drainage ditch samples, and two suspended sediment samples. In general, all of these samples had higher concentrations of Ba, Ca, Co, P, and Zn than other clusters. Also, all of them had been affected by cattle and manure in some manner. Two of the cattle trampled samples in C4 were collected on the bank of Pond Creek proximate to where one of the suspended sediment samples (AJ2) was collected, and only one sample in this cluster was collected downstream of the AJ2 sampling location. Also interesting is the fact that the two suspended sediment samples collected on the same day but at different locations cluster together, as they did when using the totals data. This indicates that the chemical properties of the suspended sediment were very similar over a 5 km length of the stream on the second suspended sediment sampling date.

Reasonable explanations can be made for the clusters that were created using the nitric acid extraction data along with cluster analysis and CDA. Similar to when the total dissolution data was used, the samples form a number of clusters that appear rather similar based on the type of samples they contain and their location in canonical space relative to one another. This fact suggests that the chemistry of all of the samples is actually quite similar, and strengthens the point that these similarities are likely a result of the directed sampling protocol. Samples collected were from sources that appeared particularly susceptible to erosion and likely to be contributing to the suspended sediment found in Pond Creek. However, unlike the results of the analyses of the total dissolution data, all of the suspended sediment samples do not cluster together; nor do they all cluster in the larger groups. Furthermore, the clusters created when using the HNO_3 extractable data differ greatly from those created using the totals data for both scenarios (four and five groups).

Mehlich 3 Extraction Data

Descriptive Statistics

Of the 29 elements analyzed, 21 were above detectable concentrations in all of the Pond Creek Mehlich 3-extracts (Table 29). Based on the coefficient of variation (%CV, 100 times the std. deviation divided by the mean) values, there is considerable heterogeneity in the elemental data. As previously indicated, %CV values can be used to describe the heterogeneity of a soil property. Soil elemental data that are described by %CV values <15% are identified as having little variability. Elemental data with moderate variability have %CV values between 16 and 35%, and highly variable data have %CV values >36%. Hence, the higher the %CV value, the more heterogeneous the data for a particular element. The %CV values range from 30.9% (Hf) to 120% (Nd). With the exception of Hf, which has a moderately variable population, the %CV values for all of the elements are >36%, which indicates that their populations are highly variable (Mulla and McBratney, 2000). Although the %CV values are only one criteria for evaluating the heterogeneity of the soil elemental content, these values suggest that more than one population, or sediment source groups, of soil samples may exist in the watershed.

The chi-square distribution coefficient values (X^2) show that a majority of the elements are not normally distributed in the watershed (Table 29). This also indicates that the M3-extractable elemental content of soils may be used for discriminating sediment source groups. In general, elements that are normally distributed, such as Ca and Sr (Fig. 39), are also less variable in the watershed. Potassium and P are highly variable, and their distributions are both highly

Table 29. Descriptive statistics of the Mehlich 3 extraction data.

Element	N	Mean	Median	Std. Deviation	Variance	Min	Max	CV	X^2
				mg kg^{-1}					
Ba	51	91.97	100.85	49.41	2440.94	12.06	218.03	53.72	<.001*
Ca	49	2903.34	2855.11	1329.66	1768002.47	324.78	7054.06	45.80	0.562
Cd	50	0.11	0.11	0.05	0.00	0.04	0.31	43.12	<.001*
Ce	51	0.99	0.79	0.74	0.55	0.04	3.97	74.95	<.001*
Co	51	4.70	4.14	2.53	6.41	0.67	10.36	53.84	0.036*
Cr	51	0.46	0.39	0.29	0.08	0.14	1.49	62.39	<.001*
Cu	51	47.12	32.35	46.63	2174.31	0.47	211.16	98.96	<.001*
Fe	51	287.20	297.10	158.00	24963.42	37.11	811.18	55.01	<.001*
Hf	49	0.53	0.53	0.16	0.03	0.17	0.96	30.91	0.468
K	51	479.95	251.80	440.73	194245.44	80.04	1741.96	91.83	<.001*
Mg	51	520.11	419.80	312.18	97458.39	68.90	1377.23	60.02	0.054*
Mn	49	865.84	766.09	462.99	214357.83	147.54	2040.75	53.47	0.576
Nd	50	2.59	1.03	3.11	9.66	0.08	11.08	119.87	<.001*
Ni	50	0.97	0.80	0.53	0.28	0.26	2.49	54.44	0.008*
P	50	110.10	51.02	123.47	15246.04	3.81	458.23	112.15	<.001*
Rb	49	0.64	0.69	0.36	0.13	0.05	1.35	55.23	0.148
S	50	75.88	72.66	36.97	1366.65	21.69	196.50	48.72	<.001*
Sr	50	5.06	4.46	2.16	4.69	1.27	11.12	42.77	0.707
V	51	1.41	1.23	1.22	1.49	0.14	5.53	86.40	<.001*
Zn	50	22.44	18.31	15.40	237.26	2.49	71.36	68.65	<.001*
Zr	51	3.07	2.81	1.39	1.93	0.22	6.03	45.29	0.062*

*Elemental data are not normally distributed at P<0.1

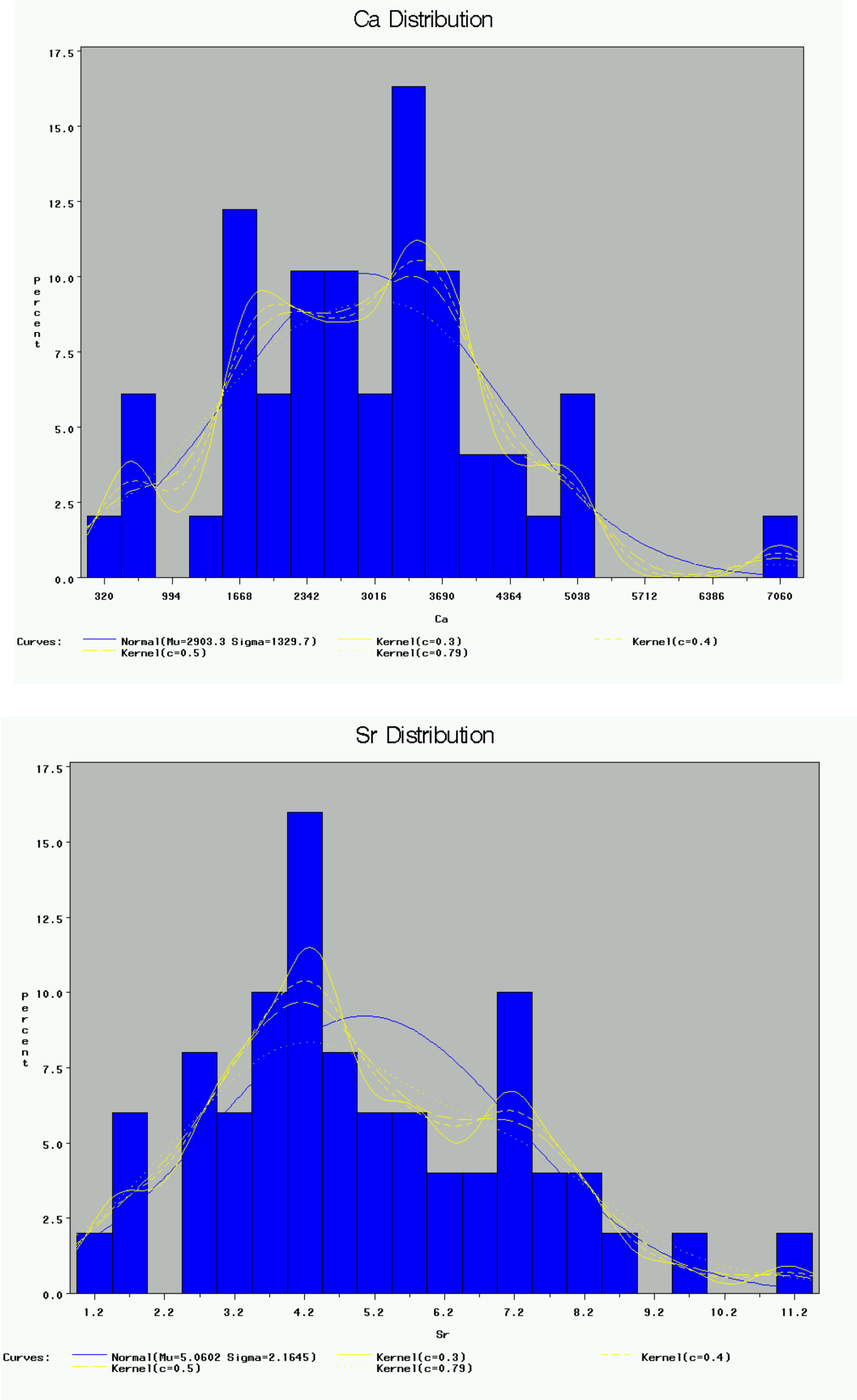


Figure 39. Frequency distributions for Mehlich 3-extractable Ca and Sr. These two elements are described by a normal distribution.

skewed (Fig. 40). Two other elements that do not fit a normal distribution are Ba and Fe. These two elements can be described as having several modes (Fig. 41). The multi-modal distributions suggest that the data contain more than one population. Thus, the elements with multi-modal distributions may provide significant power for discriminating the various types of sediment samples collected in the watershed because an element or variable that has discrimination power is defined as having the ability to differentiate between groups within a population.

Sediment Source Discrimination

The Mehlich 3 extractions, although less powerful than the total dissolution or nitric acid extraction procedures for extracting elements from soil, provide elemental concentration data for each soil sample. Although the Mehlich 3 extraction does not dissolve the mineral structure of soil, it does extract many of the commonly measured cations, and should provide a good indication of the availability of many elements in the soil samples that are exchangeable. Since the extractability of elements is dependent upon the management of a soil, the elemental composition data from the Mehlich 3 extraction may be more variable than total and HNO_3-extractable. Two examples of soil sample fingerprints are illustrated for an in-stream sediment bar sample and a cattle path sample (Fig. 42). These two samples were collected proximate to one another, but their fingerprints are different. To differentiate the various potential stream sediment sources using the elemental fingerprint data, the following stipulations were assumed:

(1) Potential stream sediment source samples could be placed into source groups based on the current and past management, location in the landscape, or depth of the soil sample.

(2) A group of elements could be identified as having significant differences among the defined source groups.

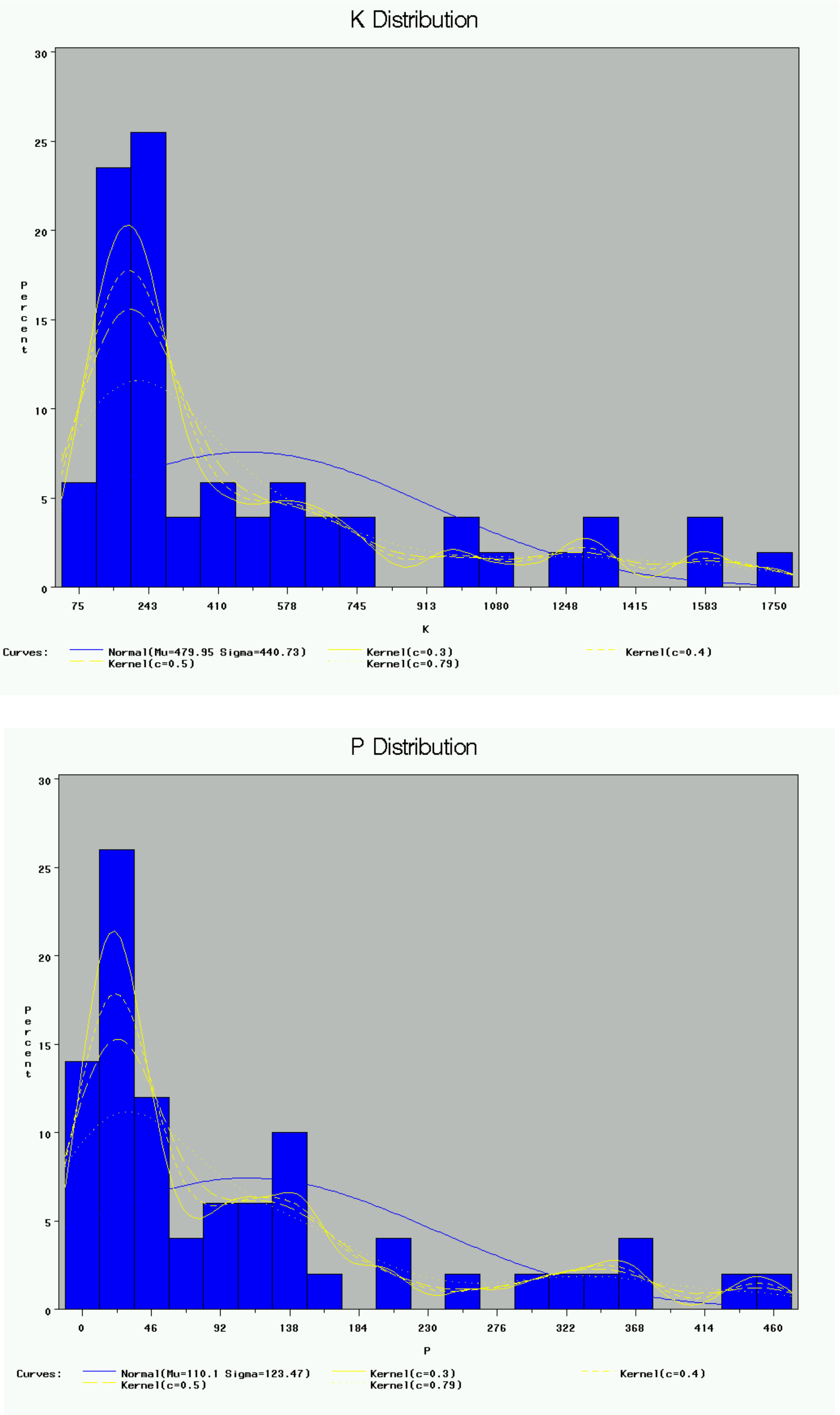


Figure 40. Frequency distributions for Mehlich 3-extractable K and P. These two elements are not described by a normal distribution and their distributions are highly skewed.

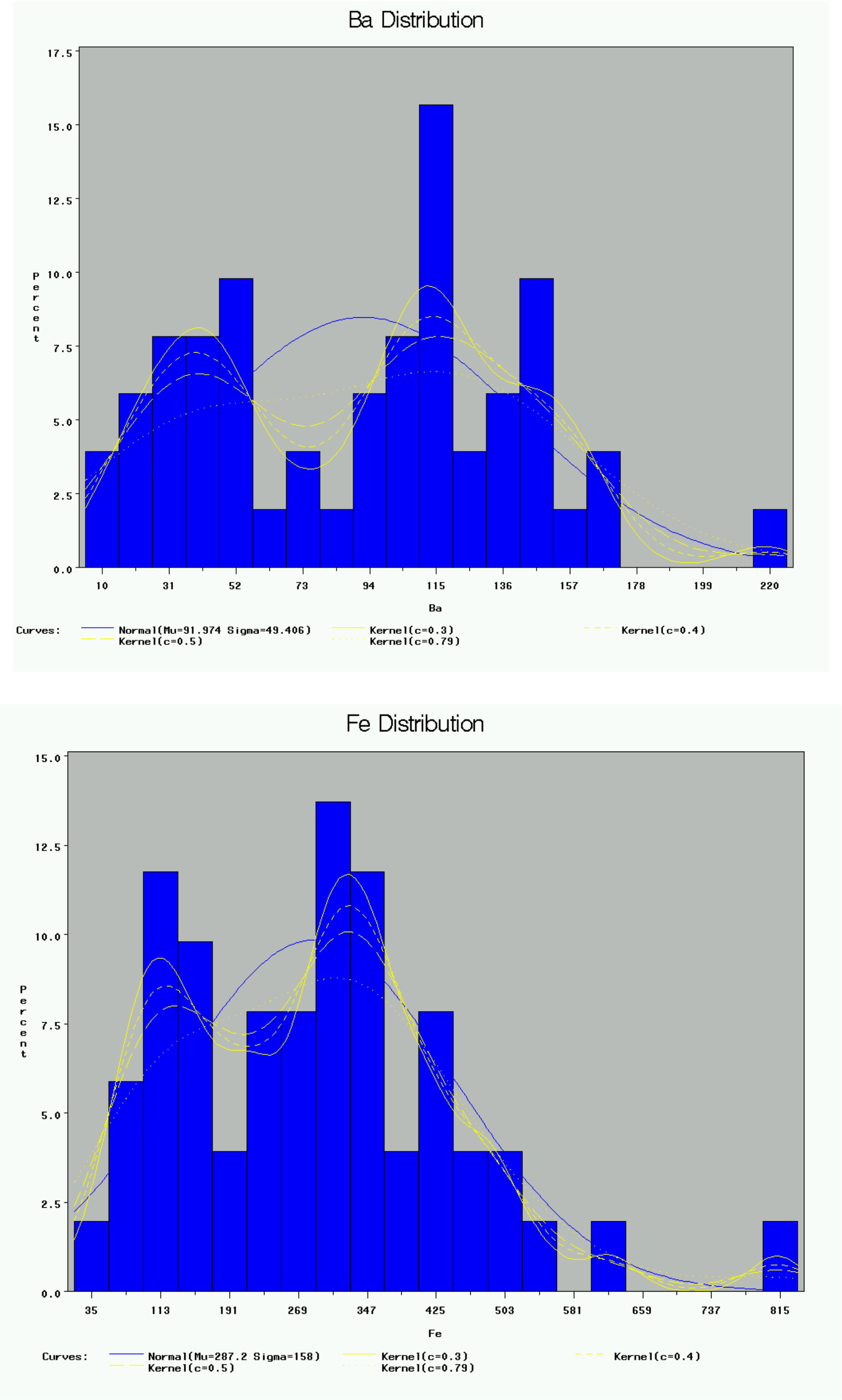
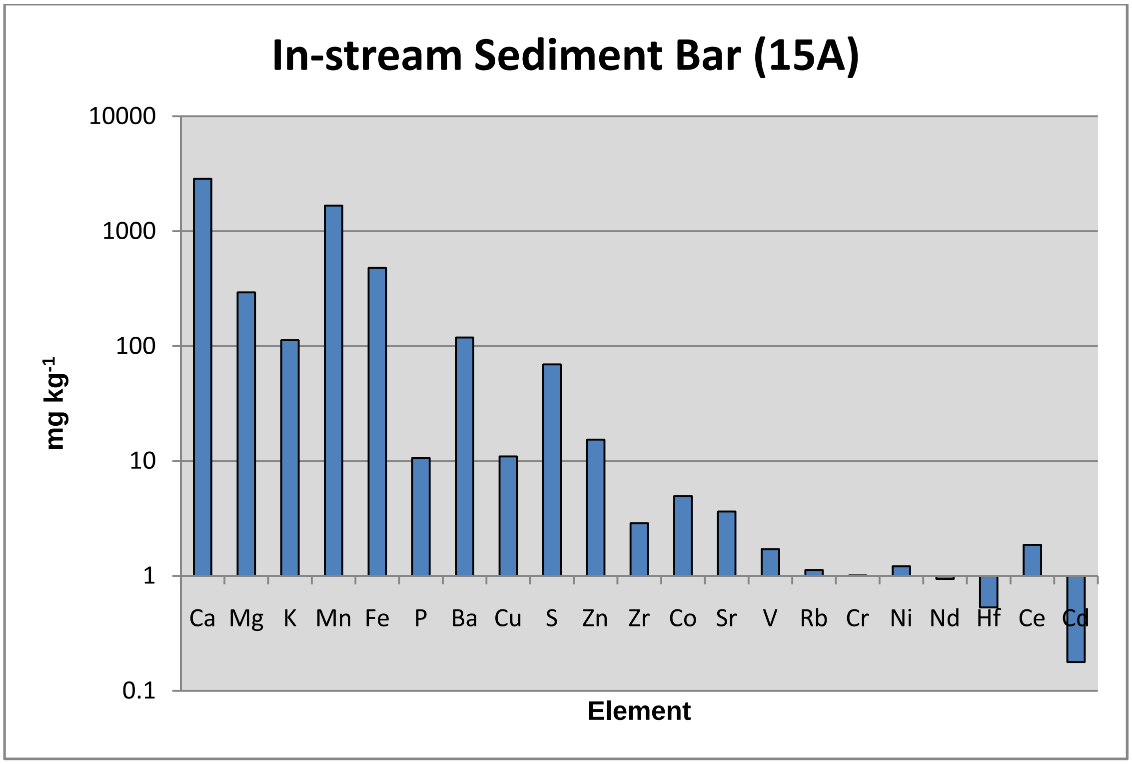


Figure 41. Frequency distributions for Mehlich 3-extractable Ba and Fe. These two elements are not described by a normal distribution, and their distribution is characterized as containing several modes.



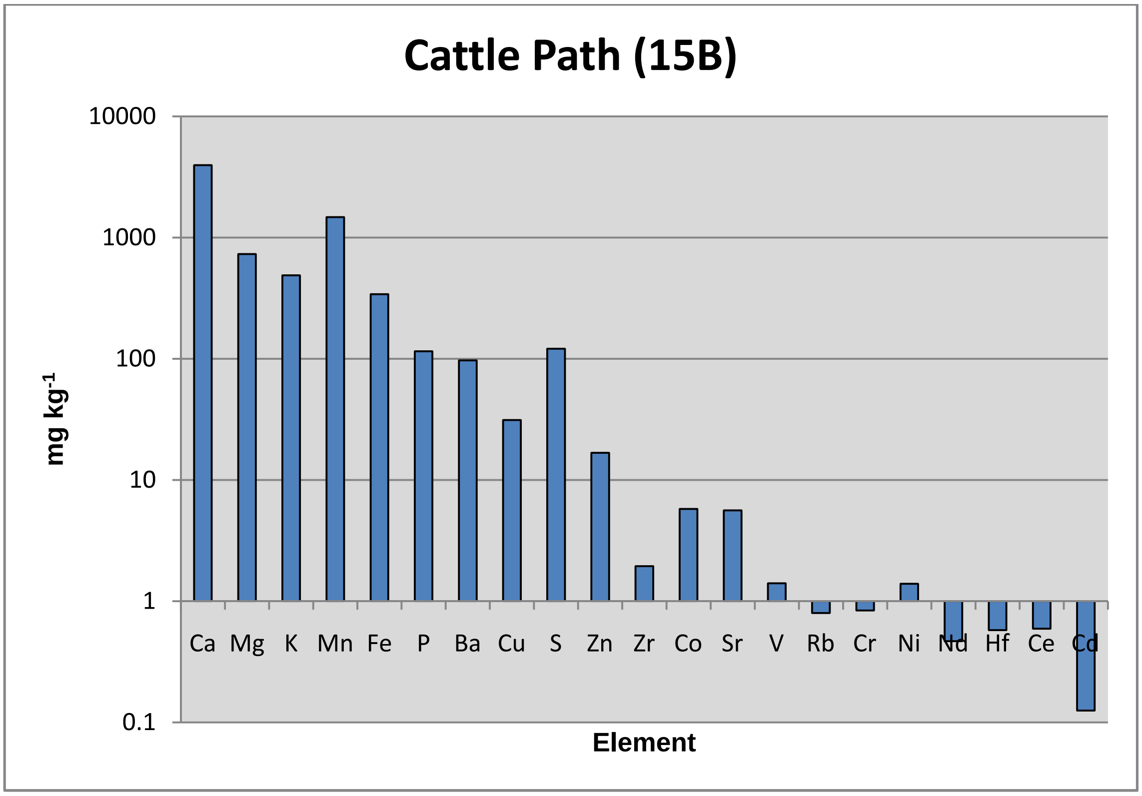


Figure 42. The histograms illustrate the Mehlich 3-extractable elemental composition (fingerprint) of an in-stream sediment bar and a cattle path sample.

(3) A group of elements could be identified as having significant power to discriminate the defined source groups.

To test for significant differences in the concentrations of each element among the defined groups (suspended sediment and sources) (Table 4, excluding gravel roads) both a Kruskal-Wallis (KW) rank test with $P < 0.05$ and a Student-Newman-Keuls (SNK) with $P < 0.05$ were used. The former is a non-parametric test and the latter is parametric. Secondly, a stepwise discriminant analysis was used to identify those elements that were capable of discriminating among the source groups. Using the eight initially defined groups (Table 4, excluding gravel roads), 16 elements (Ca, Cd, Ce, Co, Cu, Fe, K, Mg, Nd, Ni, P, Rb, Sr, V, Zn, Zr) exhibited significant differences among the groups according to the KW test (Table 30), and nine elements (Ca, Fe, K, Co, Ni, Ce, Zn, S, Zr) provided power for discriminating among the groups (Table 31). Eight elements (Ca, Ce, Co, Fe, K, Ni, Zn, Zr) had both properties. For example, consider the concentrations of Ba, Mg, S, and K in the Pond Creek materials. Mehlich 3-extractable Ba concentrations did not significantly differ between any of the groups (Tables 30 and 32; Fig. 43); nor did Ba provide any power to discriminate among these groups (Table 31). Mehlich 3-extractable Mg concentrations were significantly different in at least one of the groups (Tables 30 and 32; Fig. 44), but did not provide any power to discriminate among the groups (Table 31). Alternatively, Mehlich 3-extractable S concentrations did not exhibit significant differences between any of the groups (Tables 30 and 32; Fig. 45), but did offer power to discriminate between groups (Table 31). Finally, Mehlich 3-extractable K concentrations were significantly different among some of the groups (Tables 30 and 32; Fig. 46), and also provided power for discriminating among groups (Table 31). The SNK test (Table 32) showed that the means of the groups exhibited significant differences for nine elements (Ca, Cu, Fe, K, Mg, Nd, P, Rb, Zr).

Table 30. Results of the Kruskal-Wallis rank test using Mehlich 3-extractable elemental data (8 groups, Table 4).

Kruskal-Wallis Test			
Element	X^2	DF	Pr>X^2
Ba	6.7721	7	0.453
Ca*	22.0504	7	0.0025
Cd*	16.3601	7	0.022
Ce*	20.7172	7	0.0042
Co*	17.3211	7	0.0154
Cr	13.3403	7	0.0642
Cu*	21.119	7	0.0036
Fe*	26.6384	7	0.0004
Hf	13.4885	7	0.0611
K*	20.6287	7	0.0044
Mg*	17.6172	7	0.0138
Mn	13.0436	7	0.0711
Nd*	18.6732	7	0.0093
Ni*	17.4435	7	0.0147
P*	25.1373	7	0.0007
Rb*	25.2807	7	0.0007
S	13.943	7	0.0522
Sr*	15.7764	7	0.0272
V*	18.7324	7	0.0091
Zn*	18.5778	7	0.0096
Zr*	16.1398	7	0.0239

*Indicates elements that exhibited significant differences among the groups at $P<0.05$.

Table 31. Results of the discriminant function analysis using Mehlich 3-extractable elemental data (8 groups, Table 4).

Discriminant Function Analysis			
Element	R^2	F	Pr>F
Ba	0.0471	0.22	0.9782
Ca*	0.6433	8.24	<.0001
Cd	0.2543	1.51	0.2005
Ce*	0.3859	2.87	0.0191
Co*	0.5055	4.67	0.0011
Cr	0.2126	1.2	0.3343
Cu	0.2721	1.66	0.1571
Fe*	0.5042	4.65	0.0011
Hf	0.1716	0.92	0.5065
K*	0.3252	2.2	0.0605
Mg	0.2484	1.46	0.2166
Mn	0.1746	0.94	0.4927
Nd	0.1012	0.5	0.8284
Ni*	0.5348	5.26	0.0005
P	0.0575	0.27	0.9609
Rb	0.1418	0.73	0.6466
S*	0.4408	3.6	0.0057
Sr	0.1762	0.95	0.4857
V	0.2077	1.16	0.3529
Zn*	0.4241	3.37	0.0084
Zr*	0.3926	2.96	0.0166

*Indicates elements that provided power for discriminating the groups Pr>F values must be below 0.15 for an element to be considered to provide discrimination power.

Table 32. Results of the Student-Newman-Keuls multiple-range test using Mehlich 3-extractable elemental data (8 groups, Table 4). For each element, groups identified by the same letter are not significantly different at P<0.05.

Student-Newman-Keuls multiple-range test

Barium

SNK Group	Mean	N	Groups
A	146.31	4	Suspended sediment
A	111.76	6	Instream sediment
A	100.28	6	Tilled fields
A	84.95	3	Forested areas
A	84.8	6	Drainage ditches
A	79.49	8	Cattle paths
A	73.69	7	Cattle trampled areas
A	68.53	8	Subsurface

Calcium

SNK Group	Mean	N	Groups
A	4744.1	4	Suspended sediment
AB	3739	7	Cattle trampled areas
ABC	3378.7	6	Drainage ditches
ABC	3349.7	6	Instream sediment
BCD	2631.2	8	Cattle paths
BCD	2555	6	Tilled fields
CD	1673.1	8	Subsurface
D	1210	3	Forested areas

Cadmium

SNK Group	Mean	N	Groups
A	1.0798	4	Suspended sediment
A	0.1536	6	Instream sediment
A	0.1479	6	Tilled fields
A	0.1198	6	Drainage ditches
A	0.116	7	Cattle trampled areas
A	0.1097	8	Cattle paths
A	0.1038	3	Forested areas
A	0.0684	8	Subsurface

Cerium

SNK Group	Mean	N	Groups
A	1.4121	8	Subsurface
A	1.2643	6	Tilled fields
A	1.1565	6	Drainage ditches
A	1.12	6	Instream sediment
A	0.739	4	Suspended sediment
A	0.6975	8	Cattle paths
A	0.5596	3	Forested areas
A	0.3025	7	Cattle trampled areas

Cobalt

SNK Group	Mean	N	Groups
A	5.962	8	Cattle paths
A	5.838	6	Instream sediment
A	5.479	6	Drainage ditches
A	4.679	7	Cattle trampled areas
A	4.452	6	Tilled fields
A	3.264	8	Subsurface
A	2.898	3	Forested areas
A	1.915	4	Suspended sediment

Chromium

SNK Group	Mean	N	Groups
A	0.8113	6	Instream sediment
A	0.5704	8	Cattle paths
A	0.5261	6	Drainage ditches
A	0.4153	6	Tilled fields
A	0.3676	4	Suspended sediment
A	0.3644	7	Cattle trampled areas
A	0.3102	8	Subsurface
A	0.2957	3	Forested areas

Table 32 continued.

Copper

SNK Group	Mean	N	Groups
A	113.88	3	Forested areas
AB	62.99	8	Subsurface
AB	54.95	8	Cattle paths
AB	46.28	6	Tilled fields
AB	44.49	6	Drainage ditches
B	24.72	7	Cattle trampled areas
B	24.26	6	Instream sediment
B	5.57	4	Suspended sediment

Hafnium

SNK Group	Mean	N	Groups
A	0.6288	4	Suspended sediment
A	0.6183	7	Cattle trampled areas
A	0.5925	6	Drainage ditches
A	0.5653	6	Instream sediment
A	0.5547	8	Cattle paths
A	0.4845	3	Forested areas
A	0.416	8	Susbsurface
A	0.4132	6	Tilled fields

Iron

SNK Group	Mean	N	Groups
A	450.64	6	Instream sediment
AB	376.3	6	Drainage ditches
AB	365.08	7	Cattle trampled areas
ABC	347.01	4	Suspended sediment
ABC	334.28	8	Cattle paths
BC	194.09	8	Subsurface
C	145.91	3	Forested areas
C	142.66	6	Tilled fields

Magnesium

SNK Group	Mean	N	Groups
A	943.8	4	Suspended sediment
AB	736.2	7	Cattle trampled areas
ABC	579.3	8	Cattle paths
ABC	547.8	6	Drainage ditches
BC	418.6	6	Tilled fields
BC	405.7	6	Instreams sediment
BC	352.3	8	Susbsurface
C	166.2	3	Forested areas

Manganese

SNK Group	Mean	N	Groups
A	1453.4	6	Instream sediment
A	1210.8	8	Cattle paths
A	1108.5	6	Drainage ditches
A	870.2	6	Tilled fields
A	793.8	7	Cattle trampled areas
A	722.5	4	Suspended sediment
A	665.3	3	Forested areas
A	515.4	8	Susbsurface

Neodymium

SNK Group	Mean	N	Groups
A	7.716	3	Forested areas
AB	5.562	6	Tilled fields
AB	5.146	8	Subsurface
B	1.82	6	Drainage ditches
B	1.558	8	Cattle paths
B	1.237	7	Cattle trampled areas
B	0.979	4	Suspended sediment
B	0.616	6	Instream sediment

Table 32 continued.

Nickel				Phosphorus			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	1.5622	4	Suspended sediment	A	262.92	7	Cattle trampled areas
A	1.4093	6	Instream sediment	AB	193.25	6	Drainage ditches
A	1.2318	3	Forested areas	AB	175.43	8	Cattle paths
A	1.0944	8	Cattle paths	AB	108.07	6	Tilled fields
A	0.9933	6	Drainage ditches	AB	91.23	6	Instream sediment
A	0.9128	7	Cattle trampled areas	B	34.84	8	Subsurface
A	0.7742	8	Susbsurface	B	20.78	3	Forested areas
A	0.5432	6	Tilled fields	B	16.56	4	Suspended sediment

Potassium				Rubidium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	972.6	7	Cattle trampled areas	A	1.0711	6	Instream sediment
AB	700.1	6	Drainage ditches	AB	0.9235	4	Suspended sediment
AB	676.5	8	Cattle paths	AB	0.9144	7	Cattle trampled areas
AB	374.2	8	Subsurface	AB	0.8993	6	Drainage ditches
B	283.3	6	Tilled fields	ABC	0.7944	8	Cattle paths
B	263.8	4	Suspended sediment	BC	0.4658	8	Subsurface
B	199.1	6	Instream sediment	C	0.3201	3	Forested areas
B	187.3	3	Forested areas	C	0.2947	6	Tilled fields

Sulfur				Strontium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	110.36	6	Instream sediment	A	6.963	4	Suspended sediment
A	104.81	4	Suspended sediment	A	6.493	7	Cattle trampled area
A	89.3	6	Drainage ditches	A	5.546	6	Drainage ditches
A	78.93	7	Cattle trampled areas	A	5.081	6	Instream sediment
A	76.17	8	Cattle paths	A	4.984	3	Forested areas
A	73.01	8	Susbsurface	A	4.872	8	Cattle paths
A	47.99	6	Tilled fields	A	3.631	6	Tilled fields
A	41.07	3	Forested areas	A	3.459	8	Susbsurface

Table 32 continued.

Vanadium

SNK Group	Mean	N	Groups
A	2.2556	8	Cattle paths
A	1.8511	7	Cattle trampled areas
A	1.6969	6	Drainage ditches
A	1.589	6	Instream sediment
A	1.559	8	Subsurface
A	0.6053	6	Tilled fields
A	0.6002	4	Suspended sediment
A	0.4704	3	Forested areas

Zinc

SNK Group	Mean	N	Groups
A	50.27	4	Suspended sediment
A	36.4	6	Drainage ditches
A	33.52	7	Cattle trampled areas
A	26.03	3	Forested areas
A	24.9	6	Instream sediment
A	22.16	8	Cattle paths
A	14.86	6	Tilled fields
A	8.77	8	Subsurface

Zirconium

SNK Group	Mean	N	Groups
A	4.3412	8	Subsurface
AB	3.6891	6	Tilled fields
AB	3.226	8	Cattle paths
AB	3.114	6	Drainage ditches
AB	2.7813	7	Cattle trampled areas
AB	2.4305	4	Suspended sediment
B	1.9478	6	Instream sediment
B	1.8306	3	Forested areas

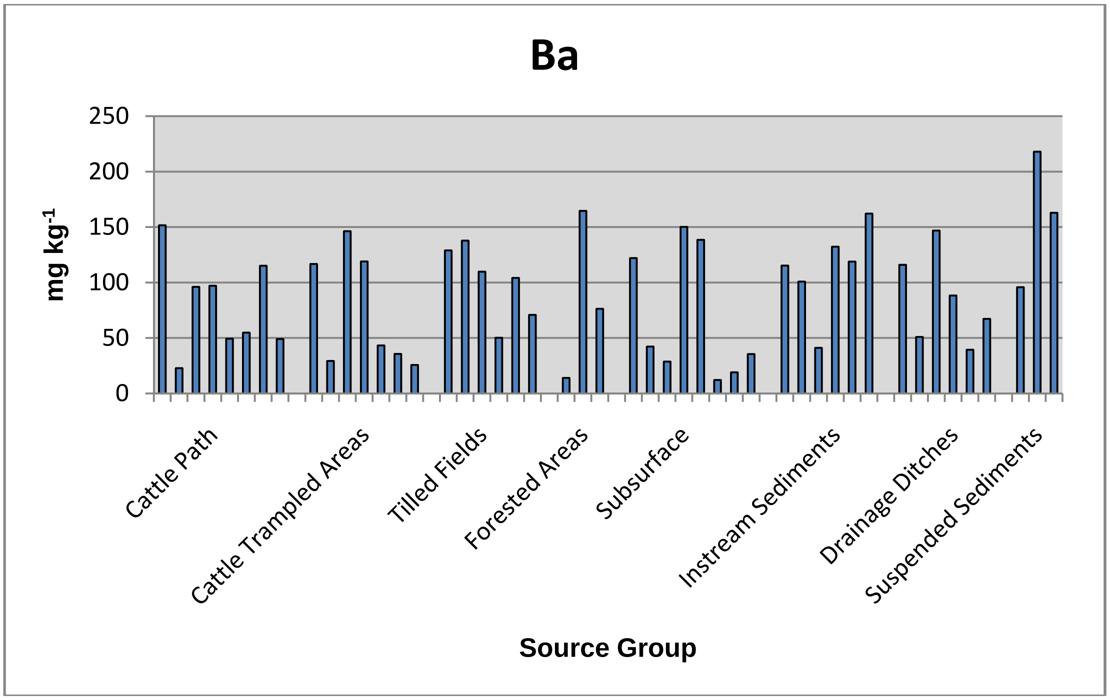


Figure 43. A histogram illustrating the distribution of Mehlich 3-extractable Ba. Barium concentrations did not differ significantly among the eight groups (Tables 30 and 32) and did not provide discrimnatory power (Table 31).

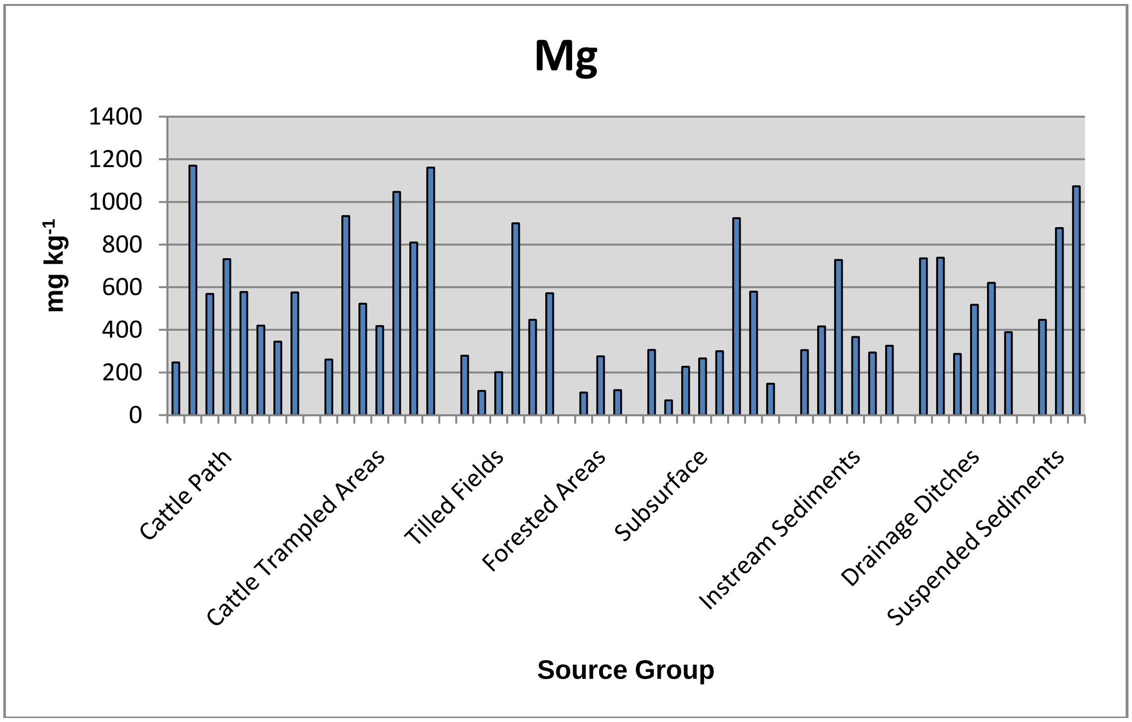


Figure 44. A histogram illustrating the distribution of Mehlich 3-extractable Mg. Magnesium concentrations differed significantly among the eight groups (Tables 30 and 32) but did not provide discriminatory power (Table 31).

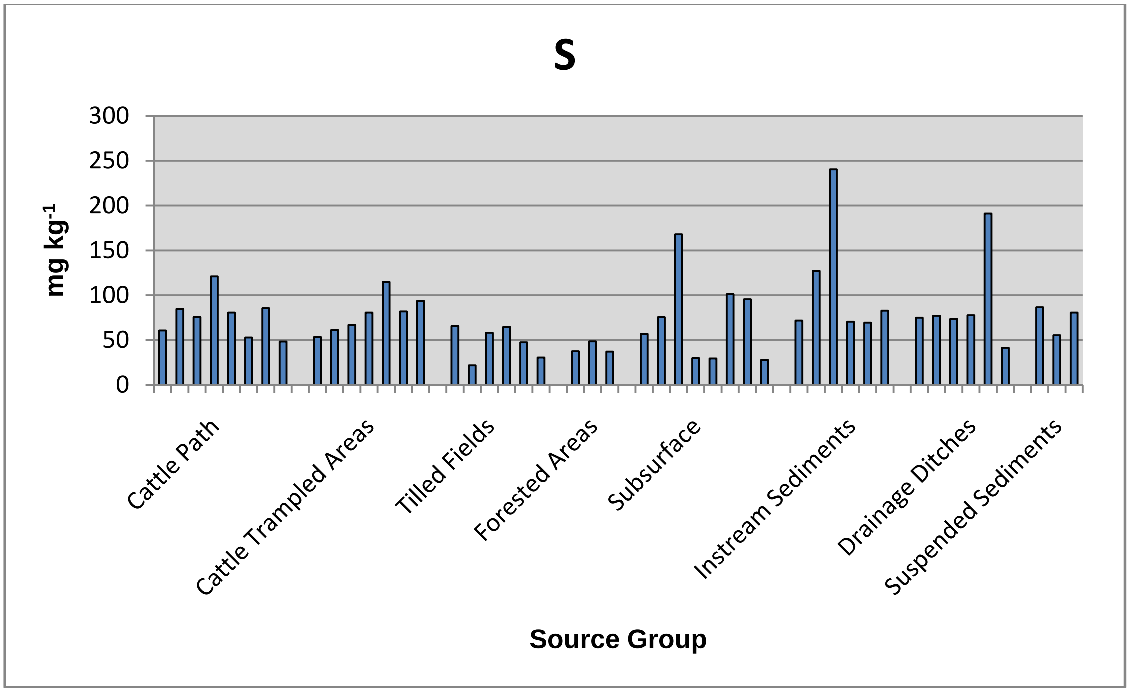


Figure 45. A histogram illustrating the distribution of Mehlich 3-extractable S. Sulfur concetrations did not differ significantly among the eight groups (Tables 30 and 32) but did provide discriminatory power (Table 31).

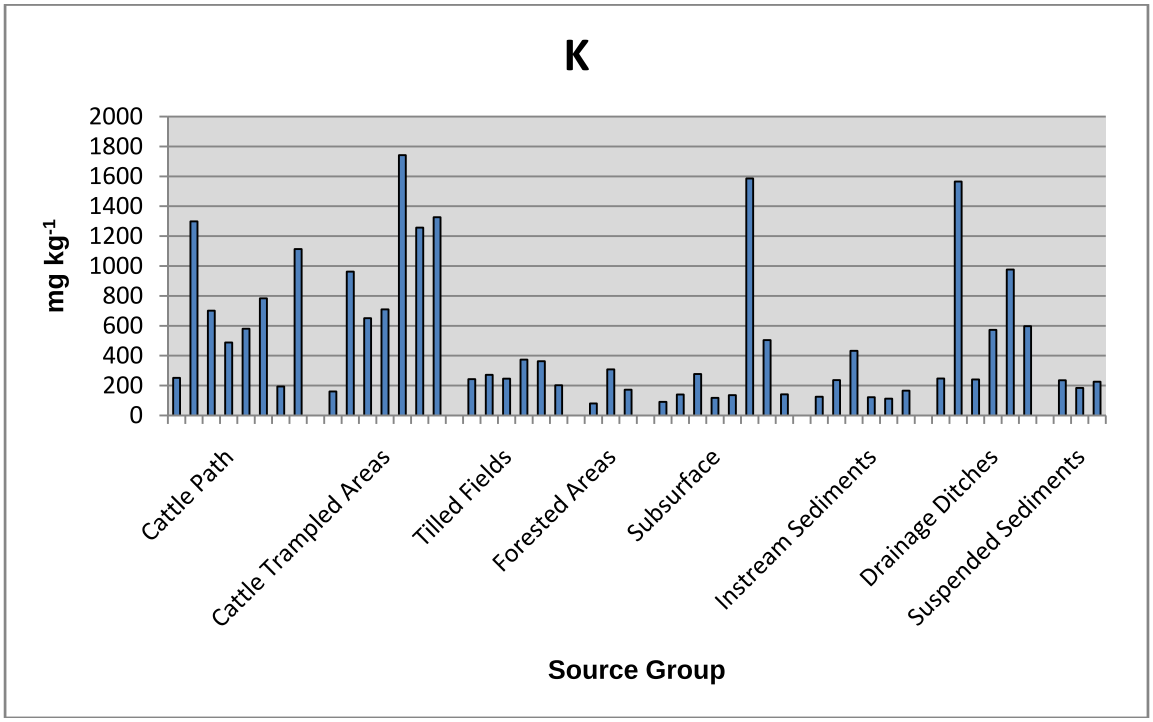


Figure 46. A histogram illustrating the distribution of Mehlich 3-extractable K. Potassium concentrations differed significantly among the source groups (Tables 30 and 32), and provided discriminatory power (Table 31).

The fact that there were eight initial groups and eight elements (Ca, Ce, Co, Fe, K, Ni, Zn, Zr) that were significantly different among the groups and had discriminatory power suggests that it may be possible to quantify the sources of suspended sediment using the initial source group definitions. However, the concentrations of four elements that meet both of these criteria (Ce, Co, Ni, Zr) are very close to the detection limit of the analytical technique used, which causes the accuracy of these measurements to come into question. As the concentration decreases toward the detection limit the error cone becomes larger. This error is then magnified when converting from mg L^{-1} to mg kg^{-1}. Thus, the reliability of the elemental concentration data for some of the potentially useful elements, particularly Ce and Ni, is questionable. Furthermore, Ce, Co, and Ni do not exhibit any significant differences according to the SNK test. If any of these four elements is not included, there are fewer elements that have both significant differences among the groups and the ability to discriminate the groups than there are groups. Therefore, it would not be possible to quantify the sources of suspended sediment using the initial group definitions, or to employ the criteria used to select the elements for discrimination analysis.

Nevertheless, the cluster and canonical discriminant analyses were conducted using these eight elements to create eight clusters (groups) (Table 33; Fig. 47). The analyses suggest that these elements cannot be used to characterize the eight source groups for a number of reasons. First, the results of the cluster analysis indicate that eight is not a realistic number of clusters for the data set (Table 33), because increasing from seven to eight clusters decreases the CCC and PSF. Second, the statistical groups (clusters) created by CDA do not correspond with the groups initially defined (Fig. 47). This indicates that these elements cannot be used in a model to quantify the sources.

Table 33. Results of the cluster analysis when eight clusters were created using only the eight Mehlich 3-extractable elements (Ca, Ce, Co, Fe, K, Ni, Zn, Zr) that had statistically significant differences among groups and provided power for discriminating among the groups.

8 Defined Clusters

Cluster	CCC	PSF	PST2
10	_	43.8	11.2
9	2.83	41.4	8.9
8	2.5	40	8
7	2.53	40.4	8.3
6	2.62	41.3	7.1
5	2.88	43.3	5.8
4	1.93	40.5	18.9
3	0.51	36.8	17.6
2	-0.82	32.4	35
1	0	_	32.4

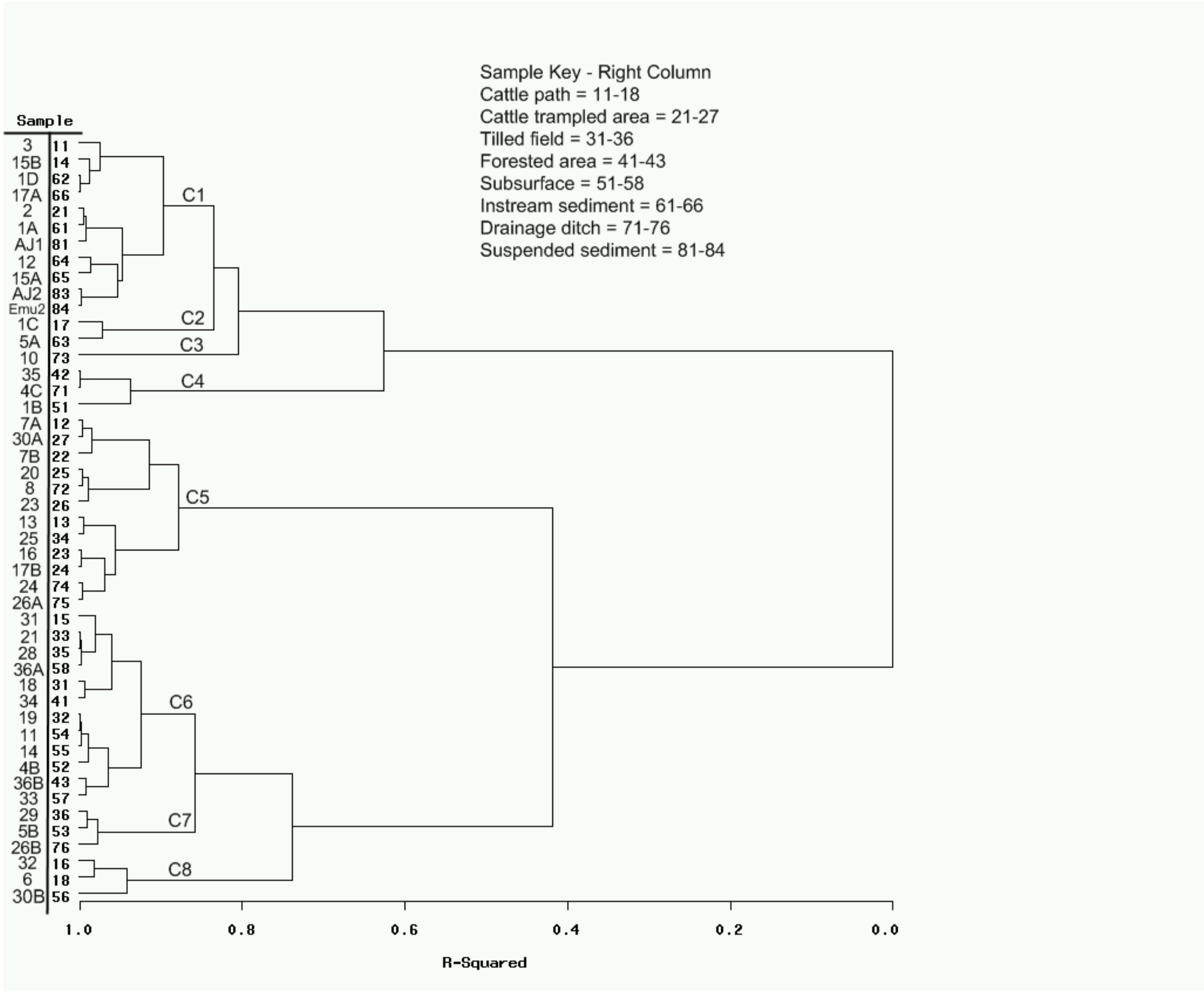


Figure 47. Dendrogram created by divisive hierarchical cluster analysis using the eight Mehlich 3-extractable elements (Ca, Ce, Co, Fe, K, Ni, Zn, Zr) that had statistically significant differences among groups and provided power for discriminating among the groups. Sample numbers in the right column correspond with sample type (group) and are indicated in the key. Sample numbers in the left column correspond with sample location (Table 3).

The next iteration of the stream sediment source identification scheme involved reducing the number of groups to four (surface, subsurface, sediments, and suspended sediments), as was performed for the analysis of total and HNO_3-extractable data. Soil samples from cattle paths, cattle tramped areas, tilled fields, and forested samples were combined to form the surface group; in-stream sediment and drainage ditch samples were combined to form the sediments group. The subsurface and suspended sediment groups remained unchanged. Using these groups, the above statistical analyses were repeated. The results of the analyses showed that 13 elements (Ca, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, Rb, Sr, Zn, Zr) exhibited significant differences between some of the groups according to the KW test (Table 34), and seven elements (Ca, Co, Ce, Zr, Fe, S, P) provided power for discriminating the groups (Table 35). Five elements (Ca, Co, Zr, Fe, P) had both characteristics. Again, the Co and Zr concentrations come into question. Excluding these two elements, the number of useful elements is less than the number of groups. Also, according to the results of the SNK test (Table 36), the mean concentrations of P for each group exhibit no significant differences, and for Zr the means of three of the four groups exhibit no differences. The means of some of the groups did exhibit significant differences for several elements (Ba, Ca, Cd, Co, Hf, Fe, Mg, Mn, Rb, Sr, Zn, Zr) according to the SNK test.

To evaluate the ability of Ca, Co, Fe, P, and Zr to separate the samples into statistically similar groups, cluster analysis and canonical discriminant analysis (CDA) were used to generate four groups using the variability of these elements. The cluster analysis provides a mechanism for evaluating whether or not the selected number of groups (clusters) to be created is realistic for the data set, while the CDA produces canonical variables that have the highest possible multiple correlations within groupings of samples. The metrics generated by the cluster analysis (Table 37) suggest that four is a reasonable number of clusters for the data set. Increasing from

Table 34. Results of the Kruskal-Wallis rank test using four groups (surface, subsurface, sediment, suspended sediment) and Mehlich 3-extractable elemental data.

Kruskal-Wallis Test			
Element	X^2	DF	Pr>X^2
Ba	4.9209	3	0.1777
Ca*	13.9881	3	0.0029
Cd*	13.8036	3	0.0032
Ce	7.6947	3	0.0528
Co*	12.7287	3	0.0053
Cr*	8.3361	3	0.0396
Cu*	13.2749	3	0.0041
Fe*	11.4082	3	0.0097
Hf	6.4821	3	0.0904
K	5.9643	3	0.1134
Mg	7.3756	3	0.0608
Mn*	8.6541	3	0.0343
Nd	5.5542	3	0.1354
Ni*	9.5332	3	0.023
P*	16.4003	3	0.0009
Rb*	9.9872	3	0.0187
S	4.9515	3	0.1754
Sr*	8.4456	3	0.0376
V	7.5587	3	0.0561
Zn*	12.5989	3	0.0056
Zr*	8.9634	3	0.0298

*Indicates elements that exhibited significant differences among the groups at $P<0.05$.

Table 35. Results of the discriminant function analysis using four source groups (surface, subsurface, sediment, suspended sediment) and Mehlich 3-extractable elemental data.

Discriminant Function Analysis			
Element	R^2	F	Pr>F
Ba	0.0255	0.32	0.8085
Ca*	0.4009	8.48	0.0002
Cd	0.1108	1.54	0.2213
Ce*	0.1983	3.13	0.0366
Co*	0.2188	3.55	0.0233
Cr	0.0322	0.41	0.7463
Cu	0.0517	0.67	0.5742
Fe*	0.1666	2.53	0.0714
Hf	0.0161	0.2	0.8945
K	0.0024	0.03	0.9928
Mg	0.0802	1.07	0.3716
Mn	0.0404	0.52	0.6713
Nd	0.0435	0.56	0.6445
Ni	0.0161	0.2	0.8942
P*	0.1974	3.12	0.0374
Rb	0.068	0.9	0.4507
S*	0.2197	3.57	0.0229
Sr	0.028	0.35	0.786
V	0.0038	0.05	0.9861
Zn	0.0502	0.65	0.5871
Zr*	0.2553	4.34	0.01

*Indicates elements that provided power for discriminating the groups Pr>F values must be below 0.15 for an element to be considered to provide discrimination power.

Table 36. Results of the Student-Newman-Keuls multiple-range test using four groups (surface, subsurface, sediment, suspended sediment) and Mehlich 3-extractable elemental data. For each element, groups identified by the same letter are not significantly different at P<0.05.

Student-Newman-Keuls multiple-range test

Barium				Calcium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	146.31	4	Suspended sediment	A	4744.1	4	Suspended sediment
B	98.28	12	Sediment	B	3364.2	12	Sediment
B	83.68	24	Surface	BC	2757.6	24	Surface
B	68.53	8	Subsurface	C	1673.1	8	Subsurface
Cadmium				**Cerium**			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	1.0798	4	Suspended sediment	A	1.4121	8	Subsurface
B	0.1367	12	Sediment	A	1.1383	12	Sediment
B	0.1204	24	Surface	A	0.739	4	Suspended sediment
B	0.0684	8	Subsurface	A	0.7068	24	Surface
Cobalt				**Chromium**			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	5.659	12	Sediment	A	0.6687	12	Sediment
A	4.827	24	Surface	A	0.4372	24	Surface
AB	3.264	8	Subsurface	A	0.3676	4	Suspended sediment
B	1.915	4	Suspended sediment	A	0.3102	8	Subsurface
Copper				**Hafnium**			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	62.99	8	Subsurface	A	0.6288	4	Suspended sediment
A	51.33	24	Surface	AB	0.5789	12	Sediment
A	34.37	12	Sediment	AB	0.5291	24	Surface
A	5.57	4	Suspended sediment	B	0.416	8	Subsurface

Table 36 continued.

Iron				Magnesium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	413.47	12	Sediment	A	943.8	4	Suspended sediment
AB	347.01	4	Suspended sediment	B	533.2	24	Surface
AB	271.81	24	Surface	B	476.8	12	Sediment
B	194.09	8	Subsurface	B	352.3	8	Subsurface

Manganese				Neodymium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	1280.9	12	Sediment	A	5.146	8	Subsurface
AB	935.8	24	Surface	A	3.235	24	Surface
AB	722.5	4	Suspended sediment	A	1.218	12	Sediment
B	515.4	8	Subsurface	A	0.979	4	Suspended sediment

Nickel				Phosphorus			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	1.5622	4	Suspended sediment	A	164.78	24	Surface
A	1.2013	12	Sediment	A	142.24	12	Sediment
A	0.9208	24	Surface	A	34.84	8	Subsurface
A	0.7742	8	Subsurface	A	16.56	4	Suspended sediment

Potassium				Rubidium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	603.4	24	Surface	A	0.9852	12	Sediment
A	449.6	12	Sediment	A	0.9235	4	Suspended sediment
A	374.2	8	Subsurface	AB	0.6452	24	Surface
A	263.8	4	Suspended sediment	B	0.4658	8	Subsurface

Sulfur				Strontium			
SNK Group	Mean	N	Groups	SNK Group	Mean	N	Groups
A	104.81	4	Suspended sediment	A	6.963	4	Suspended sediment
A	99.83	12	Sediment	AB	5.314	12	Sediment
A	73.01	8	Subsurface	AB	5.033	24	Surface
A	65.54	24	Surface	B	3.459	8	Subsurface

Table 36 continued.

Vanadium			
SNK			
Group	Mean	N	Groups
A	1.6429	12	Sediment
A	1.559	8	Subsurface
A	1.5019	24	Surface
A	0.6002	4	Suspended sediment

Zinc			
SNK			
Group	Mean	N	Groups
A	50.27	4	Suspended sediment
AB	30.65	12	Sediment
B	24.13	24	Surface
B	8.77	8	Subsurface

Zirconium			
SNK			
Group	Mean	N	Groups
A	4.3412	8	Subsurface
B	3.0377	24	Surface
B	2.5319	12	Sediment
B	2.4305	4	Suspended sediment

Table 37. Results of the cluster analysis when four clusters were created using only the five Mehlich 3-extractable elements (Ca, Co, Fe, P, Zr) that had statistically significant differences between groups and provided power for discriminating among the groups.

4 Defined Clusters			
Cluster	CCC	PSF	PST2
10	_	32.3	8.9
9	1.01	34	2.7
8	1.25	35.1	5.8
7	1.8	37.9	6.4
6	2.33	40.4	7.1
5	2.88	43.7	5.8
4	2.62	43.9	11.8
3	0.57	38	17.6
2	-1.9	24.7	32.7
1	0	_	24.7

three to four clusters, the CCC and PSF both increase, and the PST2 decreases. The clusters created can be shown in the form of a dendrogram (Fig. 48). As in all of the previously discussed grouping scenarios, the clusters (groups) created by CDA (Fig. 49) were not similar to the initially defined groups (surface, subsurface, sediments, and suspended sediments). These results indicate that the groups initially defined based on current and past management, location on the landscape, and depth in the soil profile did not correspond with the Mehlich 3-extractable elemental concentration differences of these five elements. Three of the four clusters overlapped in the first three dimensions of canonical space, which suggests that they are similar.

The statistical approach was again modified to allow the elemental data to identify a statistically-viable set of potential sediment source groups. This was accomplished using cluster analysis and CDA and all elemental information. Cluster analysis suggested that five was an appropriate number of clusters for this elemental data set; however, it also indicated that four clusters may also be acceptable (Table 38). Increasing from three to four clusters and from four

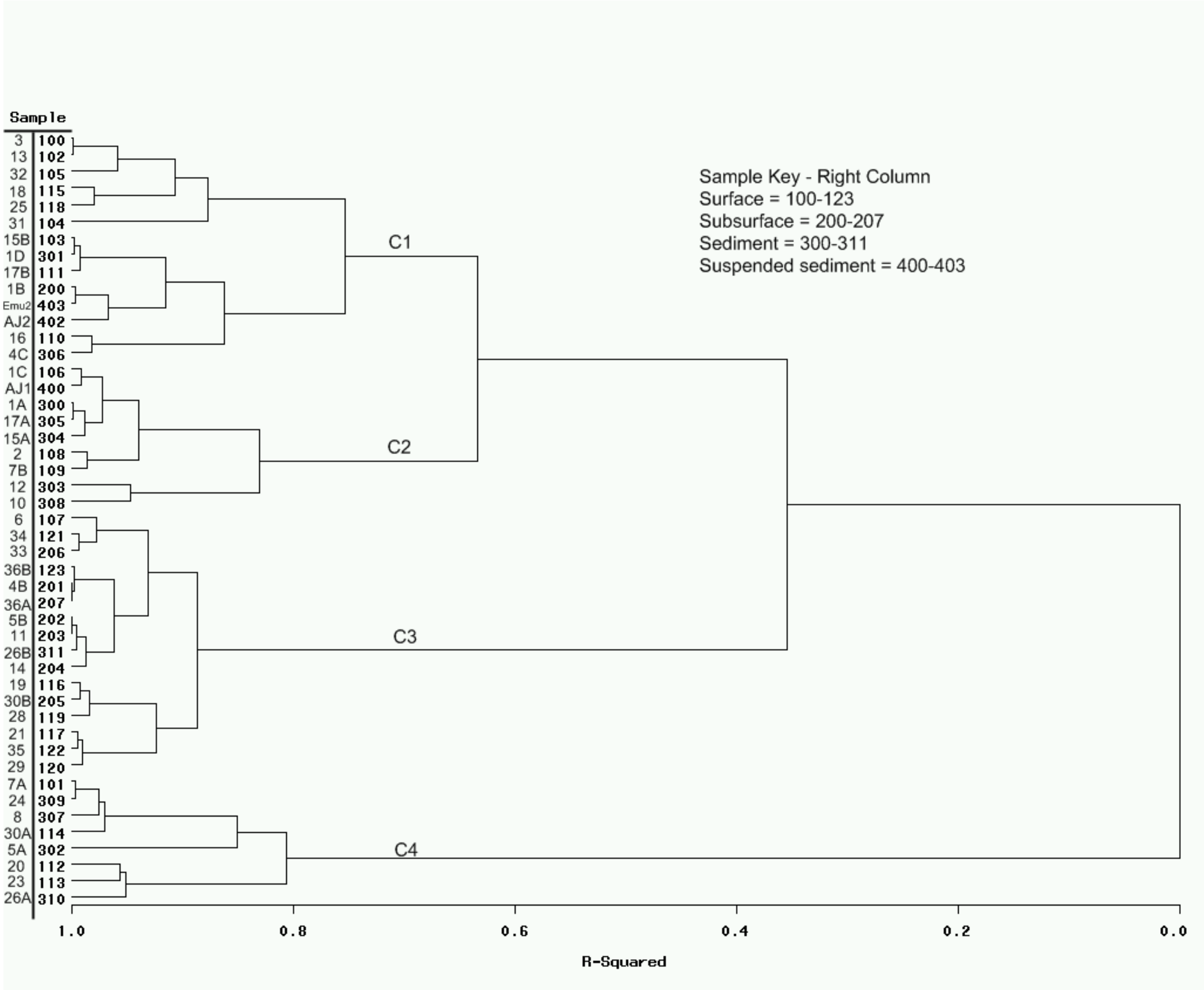


Figure 48. Dendrogram created by divisive hierarchical cluster analysis using the five Mehlich 3-extractable elements (Ca, Co, Fe, P, Zr) that had statistically significant differences between groups and provided power for discriminating among the groups. Sample numbers in the right column correspond with sample type (group) and are indicated in the key. Sample numbers in the left column correspond with sample location (Table 3).

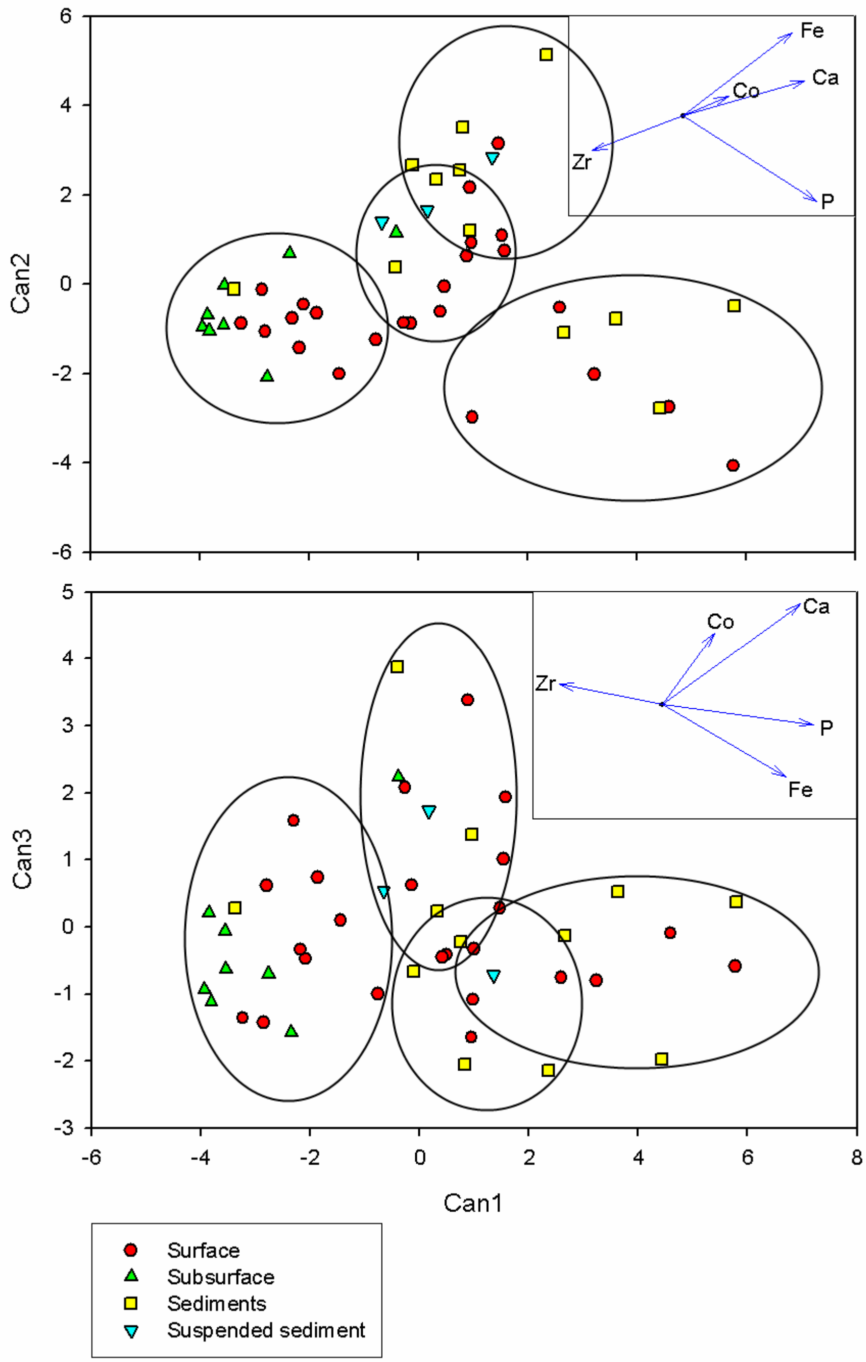


Figure 49. Canonical discriminant analysis of the Pond Creek watershed samples using the Mehlich 3 extraction data to produce four clusters using the concentrations of (Ca, Co, Fe, P, Zr). The data points represent the individual soil or sediment samples and the arrows in the inset illustrate the impact that each element has on the separation of the samples. The ellipses enclose statistically unique groups, while sample type is represented by both color and shape.

Table 38. Results of the cluster analysis using five clusters and all of the Mehlich 3 elemental data.

5 Defined Clusters			
Cluster	CCC	PSF	PST2
10	_	99.2	7.1
9	12	99.1	8.8
8	12.8	105	3.6
7	13.3	108	5.8
6	13.7	111	8.2
5	14.9	120	8.6
4	13.5	103	26.1
3	3.99	46.7	63.4
2	-0.5	23.8	45.8
1	0	_	23.8

to five clusters, the CCC and PSF both increase and the PST2 decreases. The clustering of the samples into five groups can be viewed in the form of a dendrogram derived using divisive hierarchical cluster analysis (Fig. 50). Using the canonical variables for each sample CDA generated five statistically similar groups using all of the elemental data (Fig. 51). The effect that each element has on the separation of the samples (vector magnitude and direction) is shown in the inset in Fig. 51. Many of the elements have similar vectors in the variable 1 and 2 dimension. In particular, Fe, K, Mg, P, Rb, S, and V all have almost identical vectors and separate the samples mostly along the y-axis (canonical variable 2) in this dimension. Barium, Ce, Cu, Nd, and Zr all have vectors that are unique from all the other elements in the variable 1 and 2 dimension. In the variable 1 and 3 dimension, the vectors of many of the elements also overlap. Potassium and P have almost identical vectors in both dimensions, as do Mg and V, which suggests that only one element in each pair is necessary for separating these groups. Cerium and Zr both have vectors that are unique from all the other elements in the variable 1 and 3 dimension.

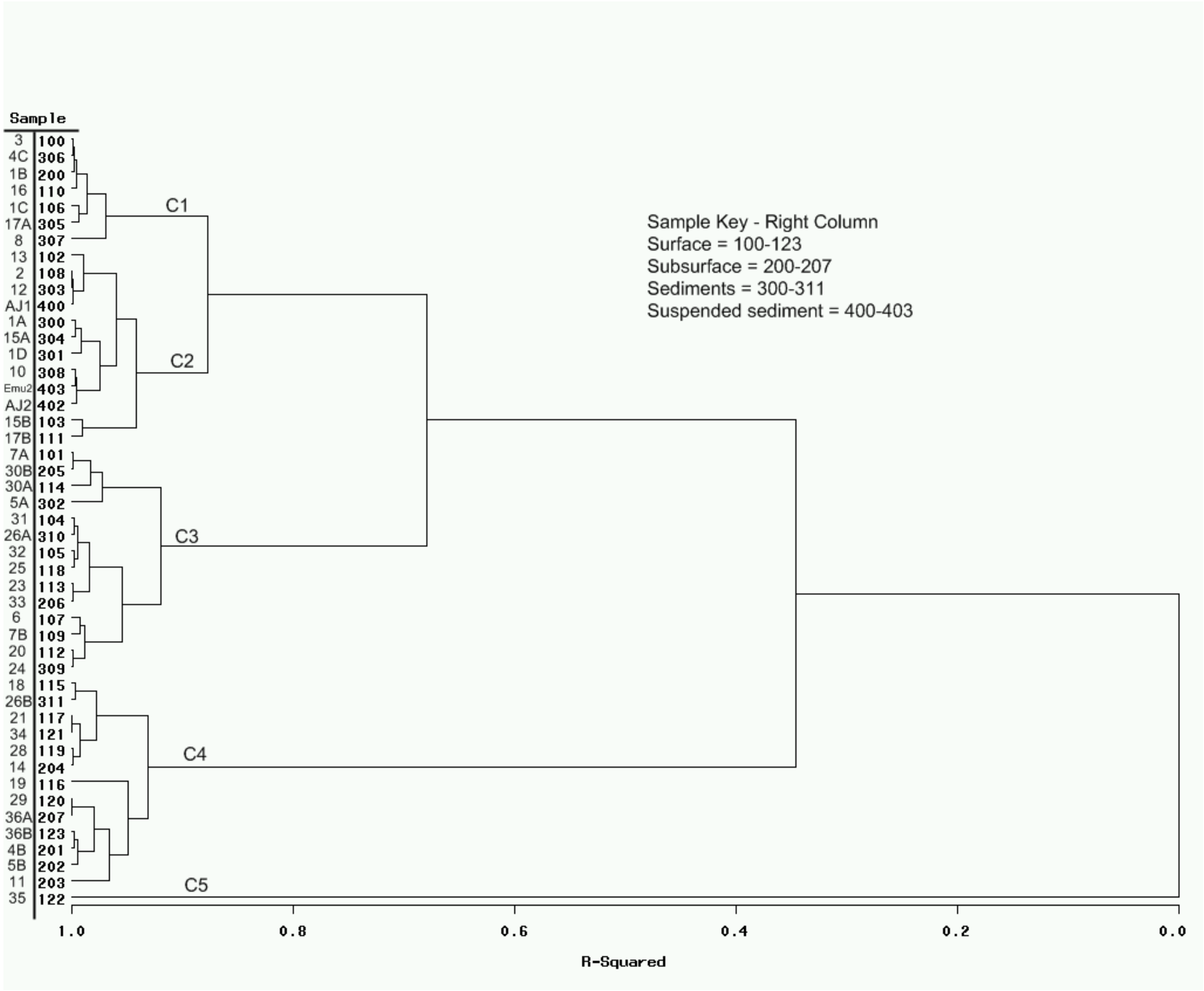


Figure 50. Dendrogram created by divisive hierarchical cluster analysis using all the Mehlich 3-extractable elements. Sample numbers in the right column correspond with sample type (group) and are indicated in the key. Sample numbers in the left column correspond with sample location (Table 3).

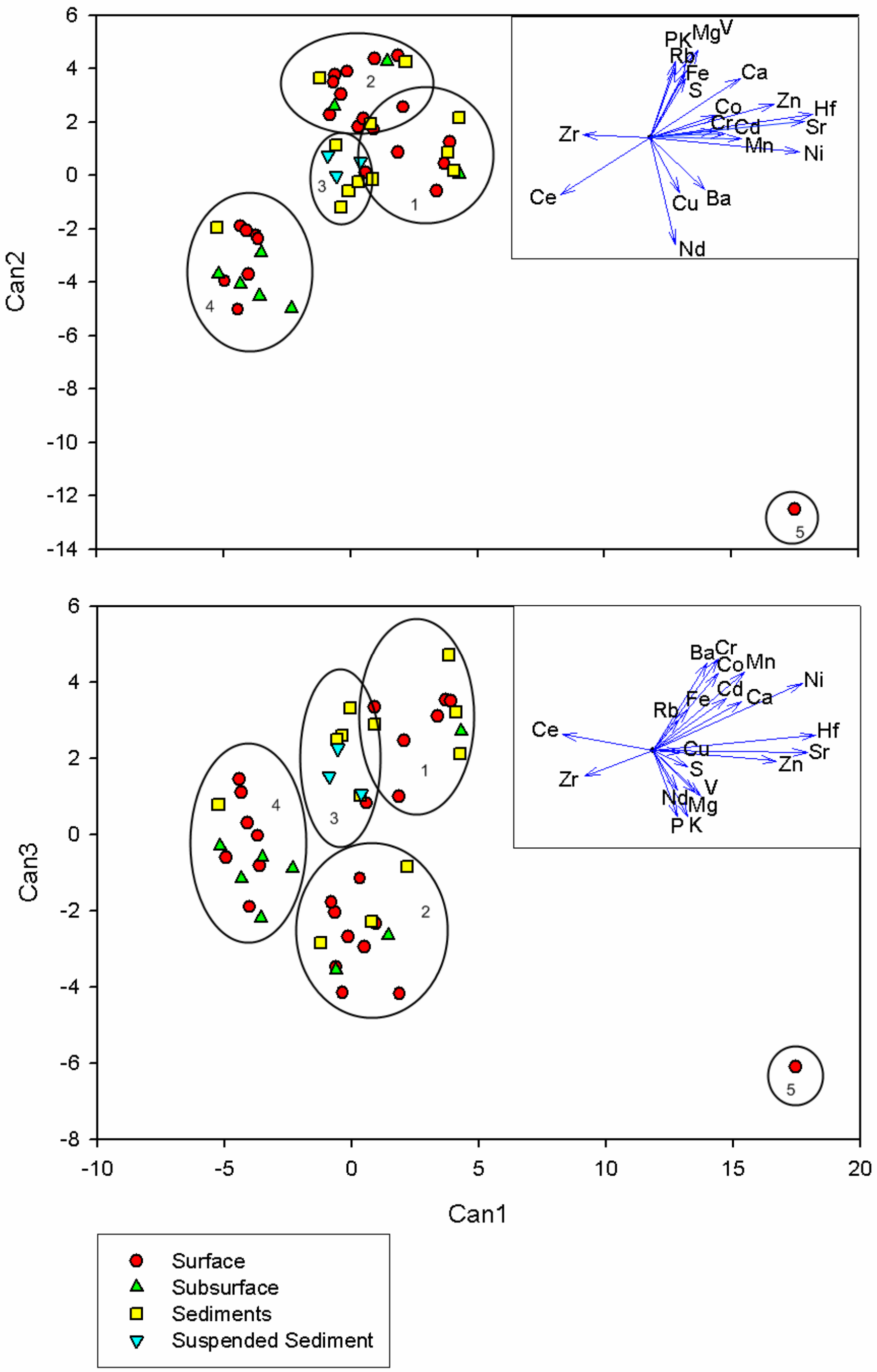


Figure 51. Canonical discriminant analysis of the Pond Creek watershed samples using the Mehlich 3 extraction data to produce five clusters using all detectable elements. The data points represent the individual soil or sediment samples and the arrows in the inset illustrate the impact that each element has on the separation of the samples. The ellipses enclose statistically unique groups, while sample type is represented by both color and shape.

In Fig. 51, the suspended sediment samples fall within cluster C3. The other five samples in cluster C3 are a sample from a cattle trampled area, three in-stream sediment samples from within Pond Creek, and a drainage ditch sample. All of these except for the cattle trampled sample fall into the category of sediments (deposited or suspended). The location of this cluster in canonical space relative to all of the other clusters is also particularly interesting. Cluster C3 falls very close to the origin in the first two dimensions, with all of the other clusters surrounding it. This suggests that the chemical properties of the sediment samples in cluster C3 represent a combination of the chemical properties of the samples contained in the clusters that surround it. However, some clusters are closer in canonical space to cluster three than are others. The shorter the distance between two clusters in canonical space, the more similar the chemistries of the samples in the two clusters. Cluster one and three are close to each other in both the first and second dimension, which indicates that they are the most similar of all the clusters.

Cluster C1 contains four cattle path samples, two trampled area samples, a stream bank sample, two in-stream sediment bar samples, and two drainage ditch samples. Two of the cattle path samples, the stream bank sample, and one of the sediment bar samples in cluster C1 were collected very close to where the cattle trampled sample and one of the sediment bar samples in cluster three were collected, which directly links the two clusters. Excluding the stream bank sample in cluster C1, all samples in clusters C1 and C3 were either sediments (deposited or suspended) or samples collected in areas that had been heavily influenced by cattle (paths and trampled areas). This indicates that the main contributors to sediments, in general, are areas that had been influenced by the presence of cattle. This seems likely based upon a visual assessment of the watershed, because most of the areas influenced by cattle are barren and very susceptible to landscape erosion processes.

Cluster C2 is also similar to clusters C1 and C3. Clusters C1, C2, and C3 all plot close together in canonical space, and all three contain similar types of samples. Cluster C2 contains five cattle path samples, three samples from cattle trampled areas, one tilled field sample, two subsurface samples, an in-stream bar sample, and two drainage ditch samples. Interestingly, the two samples initially defined as subsurface were collected just outside a cattle milking barn near where the cattle entered and exited and manure was scraped out of the barn. Thus, it seems logical that these samples may not represent subsurface material, but instead are more similar to areas impacted by cattle. Also, the tilled sample that falls into cluster C2 was collected from a field known to have had biosolids applied, which may have influenced that chemistry of this samples and caused it to fall into this cluster. All of the samples in cluster C2 have either been affected by cattle (manure) or biosolids or are some type of sediment, which further strengthens the case that areas affected by cattle are the primary contributors of sediments in the watershed.

Cluster C4 is unique from all of the other clusters in terms of the types of samples that it contains. It includes five tilled field samples, two forest samples, five subsurface samples collected from road cuts and stream banks, and one drainage ditch sample that was collected from the subsurface layers of deposited sediment in the ditch. Although a number of different types of samples fall within this cluster, it is distinct from C1, C2, and C3, because no sample in this cluster was affected in any way by the presence of cattle or the application of biosolids. Furthermore, this cluster contains all but one of the tilled field samples, all but one forest sample, and all but one of the samples collected from road cut banks or stream banks. In general, the samples in cluster C4 have high levels of Mehlich 3-extractable Ca, Fe, K, Mg, Mn, P, Zn and Zr, and low levels of Nd and Zr relative to the other samples. Cluster C5 contains only one forest sample, which is distinct from all of the other clusters in canonical space because it has high concentrations of Mehlich 3-extractable Ni, Nd, Sr, and Zn, and low concentrations of Fe and Rb relative to the other samples.

The overall implication of this grouping scheme is that the sediments tend to be associated with samples collected from areas that were influenced by cattle in some way, while the subsurface, forest, and tilled field samples all have similar chemistries. This is strong evidence that the majority of the sediment materials (suspended and deposited) entering the Pond Creek watershed are derived from sources associated with areas that are heavily traveled by cattle. This corresponds with initial expectations, which were that much of the sediment loss in the watershed was associated with dairy operations containing large numbers of cattle in relatively small areas. Large number of animals in small areas usually creates regions of little or no vegetation that are susceptible to erosion, which was a common occurrence in the Pond Creek watershed when the samples were collected.

The clustering of the samples seems logical and the cluster analysis performed suggested that five was a reasonable number of clusters for this particular data set. However, the cluster analysis also gave an indication that four may be a realistic number of clusters to use for the data set. Thus, cluster analysis and CDA were repeated using four as the number of groups. The results of this cluster analysis suggest that four is a valid number of clusters to use (Table 39). Again, the CCC and PSF increase and the PST2 decreases as the number of clusters is increased from three to four. The clustering of the samples into four groups can be viewed in the form of a dendrogram derived using divisive hierarchical cluster analysis (Fig. 52). These groupings are also shown in canonical space in the plots created by CDA (Fig. 53). The effect that each element has on the separation of the samples is shown in the inset of Fig. 53. In the first dimension (variable 1 and 2) very few elements overlap in their effects, and most of the elements

Table 39. Results of the cluster analysis using four clusters and all of the Mehlich 3-extractable elemental data.

4 Defined Clusters			
Cluster	CCC	PSF	PST2
10	_	77.2	5.9
9	8.63	79.4	3.8
8	8.54	78.2	10.5
7	9.44	85.5	4.3
6	9.93	89.6	6.5
5	10.3	93	9
4	12.6	115	11.7
3	5.3	67.6	45.3
2	0.74	35.7	138
1	0	_	35.7

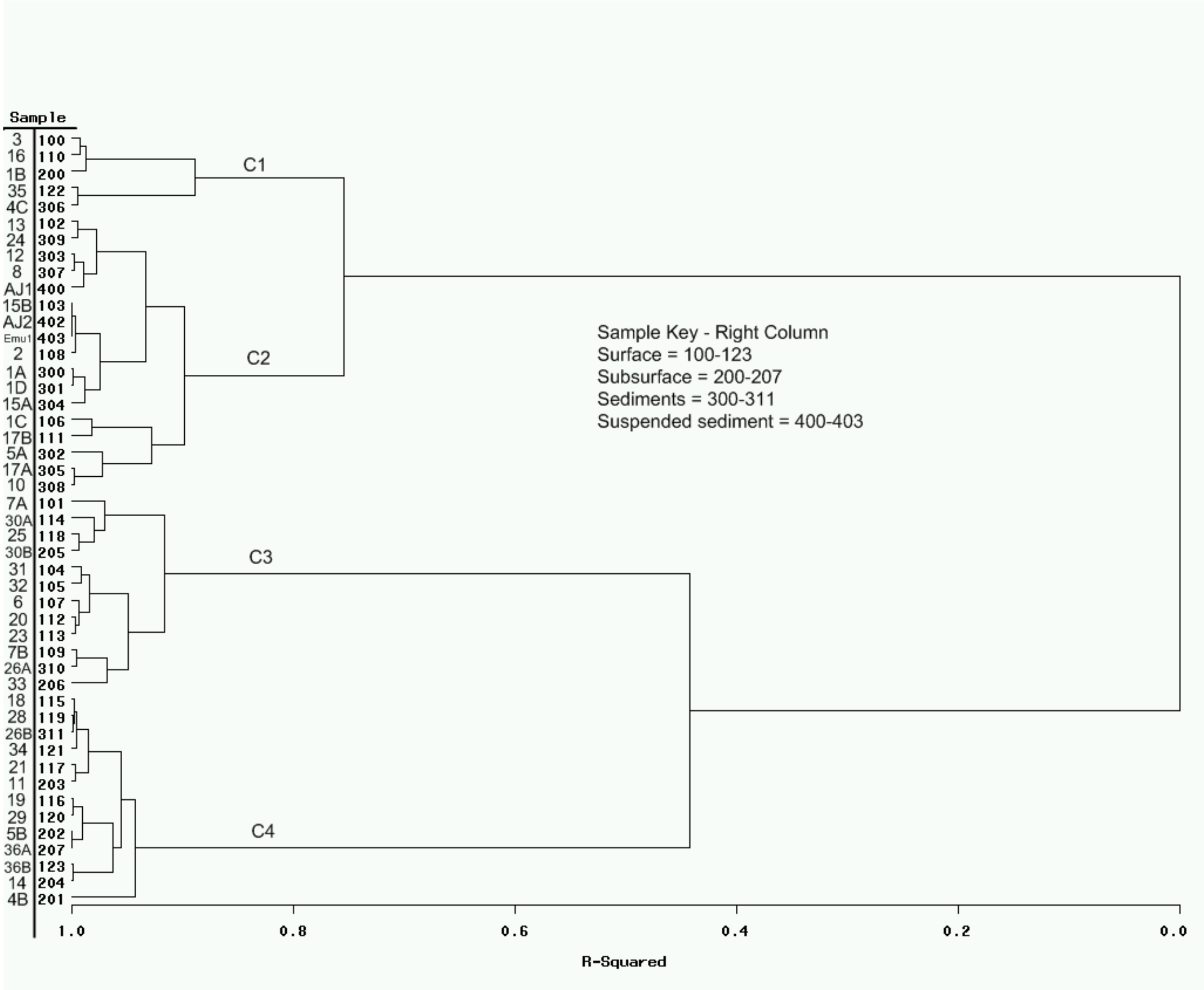


Figure 52. Dendrogram created by divisive hierarchical cluster analysis using all the Mehlich 3-extractable elements. Sample numbers in the right column correspond with sample type (group) and are indicated in the key. Sample numbers in the left column correspond with sample location (Table 3).

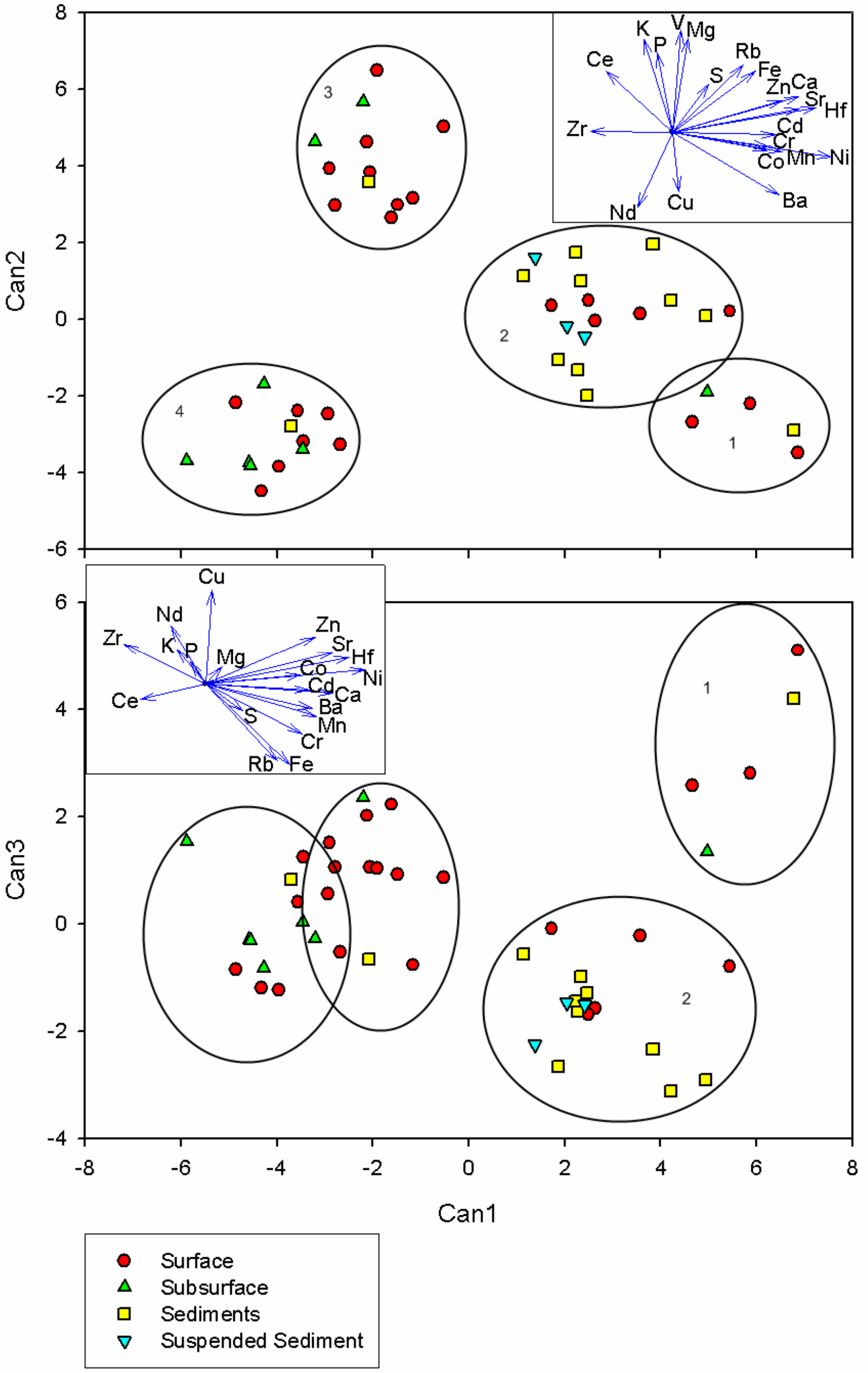


Figure 53. Canonical discriminant analysis of the Pond Creek watershed samples using the Mehlich 3 extraction data to produce four clusters using all detectable elements. The data points represent the individual soil or sediment samples and the arrows in the inset illustrate the impact that each element has on the separation of the samples. The ellipses enclose statistically unique groups, while sample type is represented by both color and shape.

provide some utility for separating the samples. In variable 1 and 2 space the vectors for the elements vary widely in their direction, but all are comparable in size. Similarly, in the second dimension (variable 1 and 3) very few of the vectors overlap. However, the vectors of Co and Ni have similar directions in both dimensions suggesting that only the more powerful element (Ni) is necessary for the separation. The effects of Mehlich 3-extractable K, Mg, P, and S in variable 1 and 3 space are small relative to the power of the other elements for separating the samples.

The clusters shown in Fig. 53 are similar to the clusters in Fig. 51, although slight differences do exist. Similarly to Fig. 52, in Fig. 53, all of the suspended sediment samples, and many of the other sediment samples are found in cluster C2 near the origin and surrounded by the other clusters. This indicates that the properties of the samples in cluster C2 are a combination of the properties of the samples creating the three clusters by which it is surrounded. Cluster C2, the largest cluster in Fig. 53, consists of three cattle path samples, two cattle trampled samples, six in-stream sediment bar samples, three drainage ditch samples, and the three suspended sediment samples. A set of four samples in cluster C2 were collected proximate to each other. One was a cattle path, another a cattle trampled sample, and the other two were in-stream sediment bar samples. Another set of proximate samples in C2 were a cattle trampled area sample and an in-stream sediment bar sample. All but three samples initially defined as sediment (drainage ditch or bar) are part of C2. One drainage ditch sample that was not in cluster C2, was found in cluster C3, which contained almost all of the samples heavily impacted by cattle. This particular sediment sample was collected from the surface layers of deposited sediment in a drainage ditch containing a significant amount of manure. One of the other sediment samples not in cluster C2, was in cluster C4, which contains most of the samples representing subsurface material (tilled fields and stream and road cut banks). This is logical because this particular sample was collected from the subsurface layers of deposited sediment in the drainage ditch just previously mentioned. The only other sediment sample that does not fall into cluster C2 was also collected from a drainage ditch, and was found in cluster C1. The drainage ditch from which it was collected was located adjacent to a gravel road, which may have influenced the chemical characteristics of this sample.

Cluster C1 is the smallest of all the clusters in Fig. 53. It contains a cattle path sample, a cattle trampled area sample, a forest sample, a stream bank sample, and a drainage ditch sample. Relative to the other samples, the samples in cluster C1 have high levels of Mehlich 3-extractable Ba, Co, Cu, Mn, Ni, Zn. Cluster C3 contains five cattle path samples, three cattle trampled area samples, a tilled field sample on which biosolids were applied, two subsurface samples, and a drainage ditch sample. This cluster is very similar to cluster C2 in Fig 51, except one bar sample and one drainage ditch sample are absent. All samples in cluster C3 (Fig. 53) appeared to be influenced by cattle or biosolids. The one tilled field sample was collected from a location known to have received biosolids applications. The two sample thought to be subsurface were collected just outside a milking barn near were the cattle enter and exit, and the drainage ditch sample was collected from the surface layers of a ditch in which manure was deposited. All of these samples had been influenced by manure or biosolids.

The fourth cluster in Fig 53 includes the same samples as cluster C4 in Fig. 51, which was discussed in detail above. The commonality among the samples in C4 is that none of them have been affected in any way by cattle or manure. Another common theme among the samples in this cluster is that, excluding the forest samples, all of the other samples seem to be representative of subsurface materials. The only tilled sample not included in this cluster is the one that was known to have had biosolids applied to it, and the only stream or road bank sample not in cluster C4 is in cluster C1, and was collected near the headwaters of Pond Creek. Again, the results of the clustering and canonical analyses suggest that sampling was successful at obtaining sources of suspended sediment because the deposited and suspended sediment samples tended to be found in clusters with large number of source samples. However, the majority of the samples were too similar to differentiate into meaningful groups using the Mehlich 3-extractable elemental data.

Summary

Three different extraction procedures were employed to develop elemental concentration data for the soil and sediment samples from the Pond Creek watershed: total dissolution, HNO_3-extraction, and Mehlich 3-extraction. Interestingly, each procedure provided different statistical interpretations. The ability of the elemental variation in each data set to differentiate the source groups (initially defined based on current and past management, location in the landscape, or depth in the soil profile) was evaluated using the Kruskal-Wallis rank test and a discriminant function analysis. Using eight groups (Table 4, excluding gravel roads), for the Mehlich 3-extractable data there were eight elements that were significantly different among the groups and provided discrimination power. Only seven of the HNO_3-extractable and four of the total-dissolution elements had these characteristics. Zirconium met both criteria for all three sets of data, while K met them for the HNO_3-extractable and Mehlich 3-extractable data. The rest of the elements meeting these criteria differed for all three sets of data.

In the next step, the groups were redefined as: surface, subsurface, sediment, and suspended sediment. For the total-dissolution dataset only Ca and Zr exhibited significant differences between groups and had the ability to discriminate among groups. In the HNO_3-

extractable data, Ca, Cu, and Li had both properties, and in the Mehlich 3-extractable data Ca, Co, Fe, P, and Zr had both properties. Thus, only the Mehlich 3-extractable data had the number of elements equal to the number of source and suspended sediment groups, which is a necessary condition for source identification using this approach. These five elements were used to cluster the samples into statistically similar groups of samples. However, the statistically defined groups differed from the predefined groups.

The approach was then modified to use the variation in detectable element concentrations to create statistically defined groups for each dataset. Two clustering (grouping) scenarios were used for each dataset, such that four and five clusters of samples were produced. For each dataset, samples contained within the clusters differed only slightly when four or five clusters were developed. However, clustering was strongly influenced by the datasets used. Although there were a few watershed samples that always tended to cluster together, none of the clusters are similar from one dataset to another. This indicates that the elemental variation provided by each dataset differed. Two of the forest soil samples clustered together in both scenarios (four groups and five groups) for all data sets, as did two cattle path samples collected in close proximity to one another, two tilled field samples, and two stream bank samples. Furthermore, using four or five groups for the totals and HNO_3-extractable datasets, five cattle path samples clustered together. Because the composition of the clusters differed as a function of dataset and number of clusters, it is difficult to draw conclusions. Specifically, it is difficult to identify sources of suspended sediment in the watershed. Indeed, even the suspended sediment samples clustered with different samples from one dataset to another.

No dataset proved to be successful at differentiating (grouping) the samples and determining the source(s) of suspended sediment. Further, none of the datasets provided enough power to discriminate the samples to a level that would allow the sediment sources to be identified and quantified. The most likely reason for this result is related to the methodology used to collect the sediment source samples. The procedure was biased towards sampling "sources" that visually appeared to be potential contributors to the suspended sediment load in Pond Creek. Many of the samples had very similar elemental chemistries, which created problems for grouping and statistically differentiating the samples. The results of the multivariate analyses of the datasets support these conclusions. The groups created by the canonical discriminant analysis indicated that the soil samples were quite similar, and in many cases too similar to differentiate using the elemental concentration data. This suggests that the sampled sources were potentially contributing to the sediment load in Pond Creek, making it difficult, if not impossible to identify the suspended sediment sources. It is postulated that a more random sampling procedure would lead to greater elemental variability, potentially allowing for adequate differentiation of the samples and for source identification.

The initial expectation was that the Mehlich 3 extraction procedure would be particularly useful in the study. The Mehlich extraction results are generally more responsive to land management practices than either the total dissolution analysis or the nitric acid extraction. The total dissolution procedure and the nitric acid extraction are more reflective of geological differences (e.g., parent material, depth in soil profile). The results of the multivariate analyses of the Mehlich 3 dataset suggested that this extraction procedure was the best method for obtaining data for grouping the samples. The Mehlich 3 extraction procedure provided a better mechanism for characterizing and differentiating the watershed materials, particularly the surficial materials, than did the nitric acid extraction and total dissolution procedures. The clusters created using the

Mehlich 3 extraction data were the most realistic overall, even though the data didn't provide enough discrimination power to quantify the sources of suspended sediment.

Correlations

It has been suggested that the HNO_3-extraction procedure may be used as a substitute for the total dissolution procedure for determining the elemental content of soils (Chang et al., 1984). The HNO_3-extraction procedure is both safer (does not require the use of HF) and less time consuming than the total dissolution procedure. Secondly, the dilution factor in the HNO_3-extraction procedure (3.5g/35ml) is less than that for the total dissolution procedure (0.2g/100ml). Thus, elemental detection limits (mg/kg basis) and errors associated with laboratory manipulations are lower for the extraction procedure. Correlations of the total dissolution data to the nitric acid extraction data for each element are shown in Fig. 54. For all of the elements, except Cr, the correlation between the total and HNO_3-extraction is positive. The strength of the correlation for each element is illustrated in Table 40, along with the corresponding level of significance. Higher r values (Pearson correlation coefficient) indicate stronger relationships, and lower $P>F$-values indicate greater statistical significance. Linear regression models were constructed for each element using the HNO_3-extractable concentrations as the explanatory variables and the total elemental concentrations as the dependent variables (Table 40). For all elements, except Cr, Ni, Ti, and Zr, the HNO_3 concentrations are statistically significant indicators of total soil metal levels at $P<0.05$.

A strong significant correlation suggests that data obtained using a nitric acid extraction may be used to predict total dissolution data. Correlations for Cr, Ni, Ti, and Zr are poor, as these elements tend to occur as minor inclusions in aluminosilicates (Cr and Ni), or as resistant

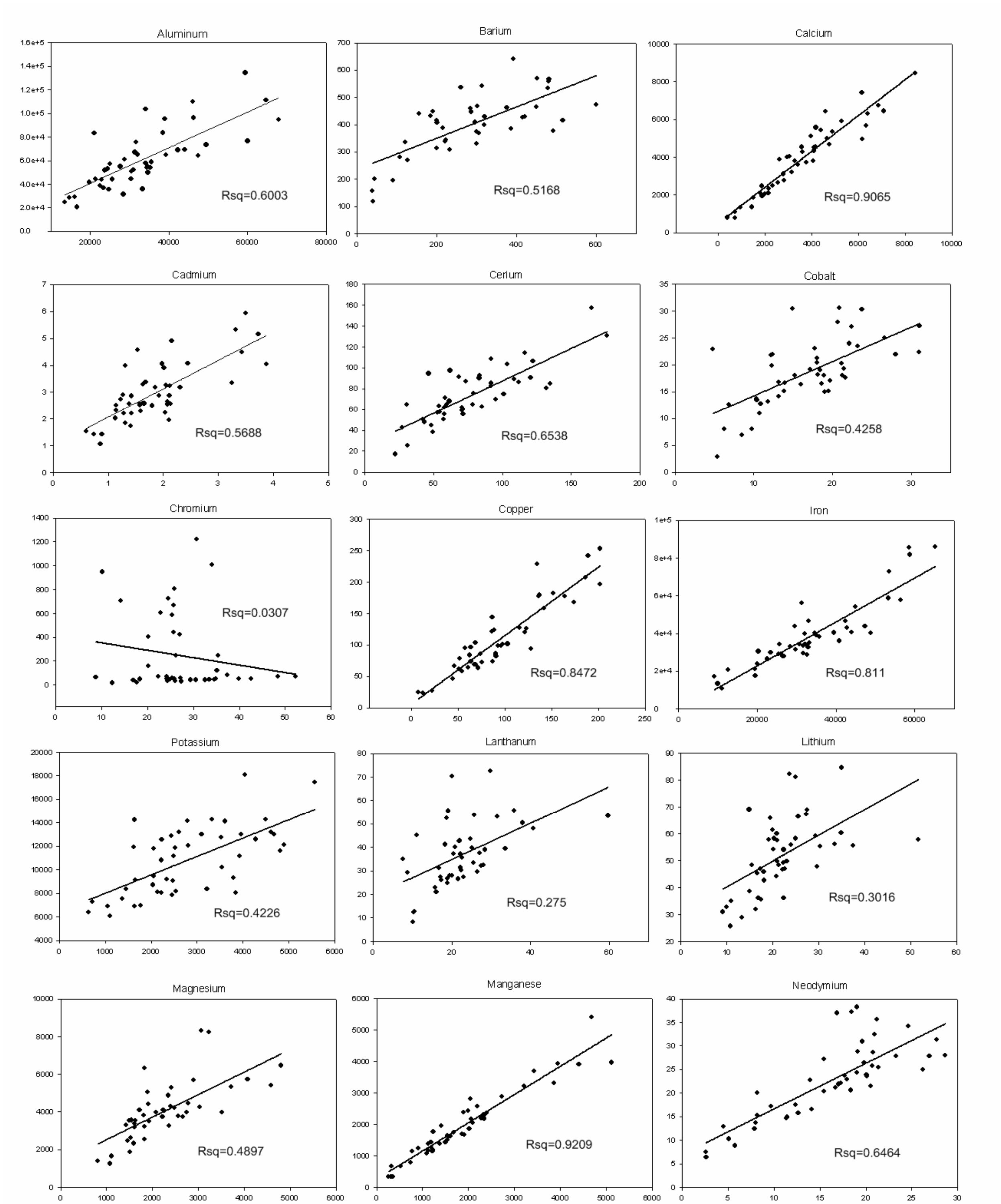


Figure 54. Correlation plots of the total dissolution data versus the nitric acid extraction data for all of the elements that were detectable in both sets of data. All values are expressed as mg kg^{-1}.

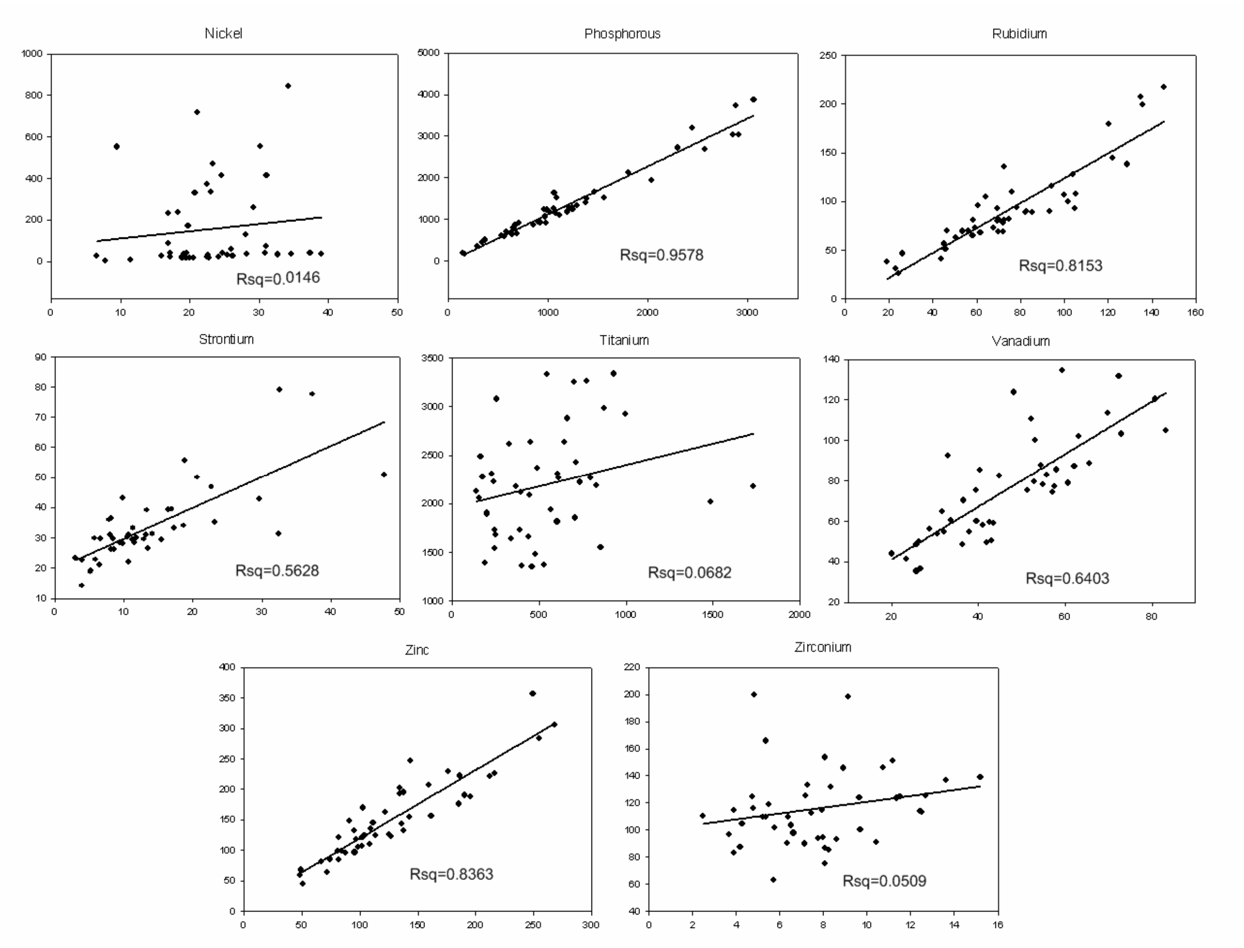


Figure 54 continued.

Table 40. Correlation table showing Pearson correlation coefficients, linear regression models, associated levels of significance, and the mean % relative error of prediction for total dissolution data (y) vs. HNO_3-extractable data (x) for each element.

Element	Model equation	F	P>F	r	R-square	%REP
Al	y = 1.513x+10438	66.1	<.0001	0.775	0.6003	20.66
Ba	y = 0.5728x+235.67	41.71	<.0001	0.719	0.5168	19.15
Ca	y = 0.9505x+507.134	407.07	<.0001	0.952	0.9065	12.37
Cd	y = 1.059x+1.0158	58.04	<.0001	0.754	0.5688	19.7
Ce	y = 0.6202x+25.516	83.11	<.0001	0.809	0.6538	18.98
Co	y = 0.6385x+7.848	32.63	<.0001	0.653	0.4258	25.7
Cr	y = -6.228x+413.8	1.33	0.2555	-0.175	0.0307	308.74
Cu	y = 1.088x+6.2027	244.02	<.0001	0.920	0.8472	16.79
Fe	y = 1.165x-454.604	188.78	<.0001	0.901	0.811	14.63
K	y = 1.5636x+6437.213	32.2	<.0001	0.650	0.4226	17.54
La	y = 0.772x+19.4087	16.31	0.0002	0.524	0.275	31
Li	y = 0.9574x+30.7898	19	<.0001	0.549	0.3016	18.27
Mg	y = 1.195x+1336.969	40.3	<.0001	0.700	0.4897	21.36
Mn	y = 0.8981x+258.938	512.24	<.0001	0.960	0.9209	14.11
Nd	y = 0.968x+6.969	78.59	<.0001	0.804	0.6464	16.31
Ni	y = 3.479x+74.556	0.64	0.4288	0.121	0.0146	398.95
P	y = 1.1554x-34.473	998.9	<.0001	0.979	0.9578	11.07
Rb	y = 1.276x-3.7298	194.29	<.0001	0.903	0.8153	15.56
Sr	y = 1.0265x+19.476	54.07	<.0001	0.750	0.5628	17.55
Ti	y = 0.4391x+1958.472	3.22	0.0795	0.261	0.0682	21.04
V	y = 1.303x+15.121	76.53	<.0001	0.800	0.6403	15.39
Zn	y = 1.12x+7.7129	224.77	<.0001	0.914	0.8363	13.94
Zr	y = 2.167x+98.949	2.36	0.1317	0.226	0.0509	17.38

minerals (e.g., rutile and zircon), suggesting that the HNO_3-extraction procedure is not as effective as the total dissolution procedure in accessing these pools. For elements with a significant relationship, the mean % relative error of prediction (%REP) may be used as a criterion for evaluating the power of the HNO_3-extraction procedure for predicting total elemental content (Table 40). For Ca, Fe, Mn, P, and Zn, the %REP values are <15% suggesting that, for these elements, the HNO_3-extraction procedure may be used to predict total content. However, for the remaining elements, the relationship, while statistically significant, may not be good enough to predict total elemental content. This is evidenced by their %REP values, which are all >15%. The %REP values for Ba, Cd, Ce, Cu, K, Li, Nd, Rb, Sr, and V lie between 15 and 20%, which is acceptable in analytical chemistry; however, the degree of scatter in the correlation plots indicates that the predictive power of the HNO_3-extraction procedure for these elements is limited. The %REP values for Al, Co, La, and Mg are >20%, indicating that the HNO_3-extraction procedure may not be a good predictor of total content for these elements.

Summary

Suspended sediments are found in most waterways as a result of naturally occurring erosion processes. However, the presence of excess sediment in waterways is often the result of human activities and can have adverse impacts on the biological, chemical, and physical properties of the water body. Sediment is often listed as one of the main contributors to the impairment of surface waters throughout the United States. The U.S. Environmental Protection Agency (U.S. EPA) estimated in 2002 that sediment and turbidity (siltation) were responsible for almost one-third of all impaired stream miles in the U.S. Approximately 8,850 km (5,500 mi) of the assessed waterways in Tennessee are impaired by sediment. The importance of sediment as a pollutant is further enhanced by its ability to act as a vector for the transport of a variety of nutrients, pathogens, and other environmental contaminants. Minimizing the negative impacts of sediment on waterways often relies on the implementation of best management practices (BMP's), which are directly aimed at reducing the amount of a defined pollutant entering a waterway.

An important component of the Tennessee Department of Environment and Conservation's (TDEC) strategy for improving water quality in Tennessee is the creation and implementation of total maximum daily loads (TMDLs) for point and non-point source pollutants identified on the Tennessee 303(d) list of impaired streams. It is often very difficult to accurately identify the sources of some of the most common non-point source pollutants, including sediments and nutrients, due to their wide spatial distribution on the landscape. However, the creation of TMDLs requires that the pollutant and its sources be identified in order to quantify the pollutant load entering a waterway. Once the sources have been identified, land

management practices can be employed to reduce pollutant loads in areas of highest priority. The success of TMDLs and thus, BMPs relies on accurate identification of the sources of a pollutant. In particular, the erosion of sediments cannot be efficiently abated if the contributing sources are not known.

Sediment source identification is a difficult task in watersheds with complex combinations of land uses and non-point sources because of the complexities involved in correlating water quality data, which are relatively easy to collect, to the source of a degrading component. Conventionally, the assessment of sediment sources and their relative importance has relied on direct monitoring techniques such as erosion pins and troughs, and sediment load measurements. The high costs and time-consuming nature of employing these methods, as well as operational difficulties and sampling constraints associated with field work have recently led to the development of less labor-intensive and more cost-effective means for determining sediment sources. These new techniques recognize that the chemical and mineralogical properties of soils are spatially variable depending on landscape position and current and past management (soil forming factors). Thus, the properties of a particular soil on the landscape may be viewed as a “fingerprint”. The underlying principle for this approach is that sediment sources can be characterized based on their chemical and mineralogical properties, which can then be compared with the properties of suspended sediments to predict the relative importance of sediment contributions from different sources. The properties used in the fingerprinting technique will depend on the nature of the source in a watershed. A variety of sediment-tracing characteristics have shown promise for determining the sources of in-stream sediments. These properties include mineralogic, mineral-magnetic, colorimetric, organic, chemical, physical, and radiometric properties. The use of multiple properties has been shown to be the most effective at determining stream sediment sources.

Preliminary results from the Pond Creek watershed indicated thattotal elemental contents of sediments could be used to develop fingerprints, rather than properties that are difficult to measure and require special instrumentation, such as magnetism, isotopics, and radionuclides. It was then hypothesized that extractable elemental data may also be effective for fingerprinting. The objectives of this investigation were to (1) sample suspended stream sediment and the potential sources of stream sediment in an impaired watershed, the Pond Creek watershed in east Tennessee; (2) determine the total elemental content of the watershed samples; (3) determine the extractable elemental content of the watershed samples; (4) investigate the variability of elemental concentrations in stream sediment source materials throughout the watershed; (5) group stream sediment source materials as a function of landscape position and land management practices; and (6) employ multivariate statistical techniques to identify and quantify the contributing sediment sources in the impaired watershed.

The Pond Creek watershed was selected for this study because its land use is very typical of the Appalachian region. Therefore, it may be considered a model system for evaluating the effectiveness of the fingerprint procedure in the Valley and Ridge physiographic region. Further, Pond Creek has been listed on the 303(d) list of impaired streams prepared by TDEC since 1998. Sediment source samples were collected throughout the watershed from potential source locations. Only material susceptible to erosion (top 1-2 cm) was collected. Material was also collected from stream banks and in-stream sediment deposits. Suspended sediment samples were collected following rainfall events. All samples were dried, disaggregated, and sieved to 53 μm to isolate the clay and silt-sized material. Subsamples of the <53 μm material and suspended sediment (3-fold replication) were then subjected to microwave total dissolution in *aqua regia* and HF. Subsamples were also subjected to chemical extractions using nitric acid and the Mehlich 3 solution. All extracts were analyzed using ICP-OES.

Descriptive statistics were determined for all elements for all three data sets (totals, HNO_3-extracts, Mehlich 3-extracts). Elemental fingerprinting for each set of data involved a series of nested multivariate statistical procedures. The nonparametric Kruskall-Wallis rank test (nonparametric one-way ANOVA) and the Student-Newman-Keuls multiple-range test (parametric ANOVA) were used to test for significant differences in elemental concentrations between the eight initially defined source and sediment groups: cattle paths, cattle trampled areas, tilled fields, forested areas, subsurface material, in-stream sediment, drainage ditches, and suspended sediment. Next, a multivariate discriminant function analysis was used to establish a group of elements that was capable of optimum discrimination of the groups. This process was also conducted with the source groups being defined as surface material, subsurface material, in-stream sediments, and suspended sediments. Finally, multivariate techniques, including divisive hierarchical cluster analysis and canonical discriminant analysis, were employed to examine relationships among the elemental composition variables and to identify statistically similar clusters (groups) of samples. The clusters created by these multivariate techniques were evaluated for similarities to the defined sediment source groups. If distinguishable groups were established using the multivariate techniques that match the defined sediment source groups, then the significant elements identified using the Kruskall-Wallis rank test and the multivariate discriminant function analysis may be evaluated using a multivariate mixing model in order to quantify the suspended sediment sources. One requirement of the above procedures is that the number of numerical variables (elemental concentration) used to characterize the sources must be greater than or equal to the number of sources (groups). Also, it is important to use multivariate statistical analyses, such as cluster and canonical discrimnant analyses to evaluate whether or not a quantitative model can be applied to a dataset.

Each element in each dataset (total, HNO_3-ex, Mehlich 3-ex) contained considerable variability based on the coefficient of variation values. Furthermore, many of the elements were not normally distributed in the watershed samples, indicating the potential for several sediment source groups to exist. Relative to the objectives of this study, the heterogeneity observed suggested that sediment source groups may be distinguishable in the watershed.

The results of the Kruskall-Wallis rank test and the multivariate discriminant function analysis of the total elemental content of the samples using the eight initial source and sediment groups showed that four elements (Al, P, Ti, Zr) were both significantly different among groups and provided discrimination power. Similarly, the results of these tests using HNO_3-extractable elemental data found seven elements (Ba, Cd, Cu, K, Li, V, Zr) with both of these characteristics. For the Mehlich 3-extractable elemental data, eight elements (Ca, Ce, Co, Fe, K, Ni, Zn, Zr) had both characteristics. Only in the case of the Mehlich 3 data is the number of elements with both properties equal to the number of groups, which is a requirement to continue with this approach. The eight Mehlich 3-extractable elements providing utility were used in a cluster analysis and canonical discriminant analysis to statistically group the samples. The eight groups created using these analyses did not match the initially defined groups, suggesting that these elements could not be used to characterize the sources.

The next iteration of the stream sediment source identification scheme involved reducing the number of groups to four: surface, subsurface, sediments, and suspended sediments. The Kruskall-Wallis rank test and the multivariate discriminant function analysis were repeated using four groups for each of the three datasets. In this case, two elements (Ca and Zr) differed significantly among groups and provided discrimination power in the total elemental data. For the HNO_3-extractable elemental data three elements (Cu, Ca, Li), and for the Mehlich 3-extractable elemental data five elements (Ca, Co, Zr, Fe, P) had both characteristics. Again, only for the Mehlich 3 data did the number of elements that provided utility exceed the number of defined groups. The five Mehlich 3-extractable elements providing utility were used in a cluster analysis and canonical discriminant analysis to statistically group the samples. The clusters created did not align with the initially defined groups, suggesting that these elements could not be used to differentiate the sources.

The statistical approach was again modified to allow the elemental data to identify a statistically-viable set of potential sediment source groups. This was accomplished using the cluster analysis and canonical discriminant analysis for each dataset, and including all of the elemental information. Cluster analysis indicated that either four or five groups of samples could be generated for each dataset. Within each dataset, samples contained within the clusters differed only slightly when four or five clusters were used. However, cluster contents differed among datasets in all cases. A few samples tended to always cluster together. However, none of the clusters were similar from one dataset to another. Even the suspended sediment samples cluster with different samples from one data set to another. Because the composition of clusters is widely variable from one dataset to another, it was difficult to draw conclusions concerning the cluster contents, or to identify sources of suspended sediment in the watershed. Furthermore, none of the data sets provided enough power to discriminate the samples to a level that would allow sediment sources to be either identified or quantified.

The lack of elemental content variability for differentiating the source and sediment samples and characterizing suspended sediment sources is likely an artifact of the watershed sampling procedure that was employed. Potential sediment source materials throughout the watershed were not collected at random. Instead, sampling was directed to obtain materials from locations that would likely contribute to the suspended sediment load in Pond Creek. The results of the clustering and canonical analyses suggest that sampling was successful at obtaining sources of suspended sediment, but the majority of the samples were too similar to clearly differentiate. For all three data sets, the samples form a number of clusters that appear rather similar based on the type of samples they contain and their location in canonical space relative to one another. This fact suggests that the chemistry of most of the samples is quite similar, and reinforces the conclusion that these similarities are likely a result of the directed sampling protocol.

Lithologically, the Pond Creek watershed is relatively homogeneous. However, the barite mine samples from the previous Pond Creek evaluation and the gravel road samples in this evaluation were both easily distinguishable from all of the other samples. This suggests that a similar method may be used to characterize sediments from roads or mined areas and evaluate their relative importance as a potential sediment source. A study of this nature may provide valuable information because roads and mined areas are often thought to be major contributors of sediments to waterways.

Further, a number of modifications to the procedures used in this evaluation may provide for a greater ability to differentiate watershed source samples. Using a more random sampling procedure of the potential upland source materials may capture more sample types and supply greater elemental variation for differentiating the samples. Including a laboratory analysis of total carbon (C) and total (N) may also prove useful for differentiating the samples into meaningful groups, as both of these elements should serve as indicators of the relative intensity of cattle use in an area. In a future study it would also be useful to collect a larger number of suspended stream sediment samples, to characterize the storm conditions under which they were collected, and also to document the conditions of the landscape within the watershed. This may provide further insight to the contributing sources during different storm conditions and during different times of the year. In an agricultural watershed such as Pond Creek the conditions on the landscape vary greatly throughout the year, which indicates that the contributing sources of sediment may also vary temporally. Documenting landscape changes may provide a relative indication as to sources likely to be contributing on a particular suspended sediment sampling date. Evaluating storm characteristics may also provide insight into why suspended sediment characteristics vary from one storm to another. In this initial elemental analysis of suspended sediments and their potential sources in Pond Creek watershed significant variability was evident. A similar study coupled with C and N analyses, storm characterization, and documentation of landscape conditions may improve the ability to differentiate the source samples into meaningful groups and allow for quantification of the sources contributing to the suspended sediment load in the watershed.

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Appendices

A

Total elemental concentrations averaged from replicates for each sample and shown in mg kg $^{-1}$. Corresponding percent relative standard error values for the replicates of each sample are also shown.

	Aluminum		**Barium**		**Calcium**		**Cadmium**		**Cerium**	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	43812.84	5.46	397.52	5.84	4518.99	7.28	2.90	14.06	61.67	9.25
1B	83334.15	1.74	565.42	1.40	6414.91	1.73	3.98	2.03	91.21	0.91
1C	51875.00	0.82	425.25	1.59	4982.50	0.75	2.58	0.97	58.90	4.58
1D	44494.27	5.77	383.75	1.61	5350.82	3.36	2.51	3.02	59.40	2.50
2	41447.64	1.21	414.70	1.01	3179.68	1.58	2.19	4.79	56.76	2.27
3	51593.10	3.36	572.89	3.29	3298.42	3.25	2.80	9.18	81.06	3.03
4A	44078.44	1.42	329.65	4.06	6727.31	0.96	2.58	1.86	74.44	1.22
4B	60836.14	1.75	280.51	0.46	790.56	2.23	2.73	3.84	156.95	0.50
4C	58766.81	8.77	373.86	6.41	8447.39	6.51	3.30	12.51	89.21	7.70
5A	36653.19	1.32	377.00	1.86	6279.82	0.47	2.20	1.21	50.63	2.84
5B	83617.91	1.21	448.75	11.81	1844.92	1.64	3.90	0.37	61.63	0.92
6	54046.19	1.90	338.28	1.79	2640.62	1.50	2.50	1.92	47.90	3.54
7A	103677.64	1.33	439.04	1.91	5110.42	1.23	4.90	2.32	94.48	2.58
7B	109875.29	4.03	431.93	4.56	3990.18	3.57	5.33	5.43	97.33	3.87
8	64722.13	2.80	344.14	2.19	3729.06	2.81	3.26	4.42	71.22	6.43
10	52955.80	2.00	464.72	2.20	4332.17	2.37	2.57	5.45	60.11	5.06
11	52101.80	2.23	446.57	1.90	2045.43	2.44	2.31	2.95	50.56	3.70
12	57231.06	2.12	536.56	16.27	4023.94	17.70	4.57	39.47	86.70	23.66
13	56964.88	14.09	534.30	6.09	4221.62	6.02	3.15	22.27	73.27	11.91
14	51803.06	1.44	461.32	0.59	2040.22	1.98	2.30	1.87	57.64	3.51
15A	50774.10	2.33	467.52	7.82	3610.10	1.28	2.60	2.30	62.70	5.06
15B	44397.12	2.15	458.39	5.24	5437.57	1.24	2.65	3.36	69.82	1.32
16	63948.20	5.49	670.03	14.07	5672.93	4.95	3.18	6.64	64.62	2.41
17A	54913.13	8.04	533.84	7.49	4263.60	7.50	2.86	10.86	75.28	6.61
17B	66888.01	2.36	974.66	3.37	7403.51	1.16	3.38	4.27	63.45	2.06
18	78929.52	4.35	312.18	3.64	3359.50	1.79	3.46	2.78	58.88	4.74
19	35838.66	7.15	408.00	4.32	1348.73	5.10	1.74	5.91	84.59	15.36
20	35500.88	3.43	636.50	1.61	6434.44	1.25	1.85	7.82	55.30	4.24
21	76460.72	1.18	428.96	0.49	2743.14	1.70	3.34	1.89	85.16	3.75
22	28439.85	4.96	12653.19	2.31	130475.50	0.44	1.42	12.77	38.56	0.79
23	111333.33	1.43	386.67	2.03	5560.00	1.13	5.17	2.52	92.67	1.29
24	94818.17	2.06	472.24	3.79	4532.31	0.30	4.05	2.71	82.56	1.26
25	96267.00	1.60	334.55	1.73	5910.40	1.32	4.49	2.90	64.93	1.45
26A	65139.69	7.04	429.42	11.42	4530.64	7.28	2.88	5.65	90.11	2.94
26B	55211.05	5.29	307.22	5.71	2097.85	3.91	2.56	3.23	80.60	4.92
27	31328.89	2.19	10961.28	3.68	67265.60	2.32	1.95	2.70	55.57	3.09
28	75467.98	0.97	541.38	1.15	3881.77	0.89	4.06	17.42	108.51	3.87
29	69168.91	9.53	405.83	6.30	2495.18	8.23	2.87	10.08	130.90	7.88
30A	59167.50	0.78	192.51	0.33	4380.85	1.59	2.73	0.55	61.09	3.87
30B	134447.78	3.22	156.36	2.22	2457.36	3.34	5.94	2.71	42.74	3.89
31	49767.83	2.88	268.66	1.02	3097.84	1.92	2.24	2.22	90.61	2.29
32	57613.60	6.66	312.94	6.38	2314.29	6.41	2.56	5.97	86.31	5.81
33	95218.91	0.73	116.91	0.95	1922.47	0.05	4.08	2.24	67.93	4.33
34	24588.23	6.12	200.28	4.55	1088.46	5.33	1.53	14.74	25.61	6.26
35	38531.01	1.10	639.48	0.96	3778.90	0.76	2.03	2.72	106.16	0.42
36A	20457.66	2.44	195.84	3.68	766.38	3.67	1.06	2.58	17.14	3.01
36B	29121.27	1.55	414.53	1.36	1314.10	1.46	1.41	0.77	44.46	0.81
AJ1	53766.24	2.16	369.37	2.53	3792.51	2.88	2.51	2.69	64.93	4.61
Emu1	59578.88	7.07	417.04	6.29	6855.00	6.96	8.76	3.70	72.37	6.19
AJ2	68866.36	0.28	569.07	0.55	4655.53	6.05	3.18	2.72	103.35	12.10
Emu2	73207.98	1.50	559.04	1.44	4938.20	3.54	3.23	0.89	113.99	17.70

	Cobalt		**Chromium**		**Copper**		**Iron**		**Potassium**	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	17.99	9.40	248.10	48.62	72.30	5.83	29069.17	4.05	11836.13	1.20
1B	30.54	3.90	70.75	2.00	77.78	2.74	56104.84	0.95	14231.71	0.53
1C	19.28	0.65	44.58	0.06	120.03	3.65	34875.00	1.65	13197.50	0.09
1D	18.00	0.43	43.11	3.47	101.30	3.59	33489.71	1.57	12021.89	6.61
2	14.16	11.73	156.54	36.22	64.29	1.88	26458.33	0.79	10807.01	5.67
3	22.70	1.74	46.90	3.95	694.80	3.60	38301.72	3.53	10843.95	1.25
4A	27.16	1.58	46.84	2.57	68.80	3.23	38087.89	1.21	9152.09	7.38
4B	27.06	0.48	40.51	1.76	253.02	2.10	30442.14	1.48	7507.11	0.41
4C	25.04	5.39	441.52	54.51	207.07	5.48	40413.83	7.01	10183.26	1.77
5A	17.60	3.71	33.99	0.74	196.31	1.74	29403.62	0.20	9054.72	1.20
5B	19.00	0.31	52.52	2.17	176.77	1.01	54067.74	1.16	14150.96	0.52
6	13.66	6.13	607.26	5.04	85.56	1.19	39021.23	2.25	11178.78	15.58
7A	21.97	2.94	588.56	2.74	95.63	1.31	81707.30	2.48	18056.16	0.81
7B	21.73	5.18	1009.17	21.18	95.33	5.69	86001.91	4.74	17419.04	0.76
8	23.40	2.88	49.30	2.71	101.47	3.06	43129.42	2.91	12997.25	1.66
10	13.15	5.34	46.19	1.95	98.20	2.93	23774.09	1.94	12543.89	1.45
11	12.76	6.43	404.12	40.36	61.31	7.20	29908.74	3.19	11896.35	3.11
12	18.17	10.37	59.79	21.24	176.88	13.52	33153.58	2.16	12892.41	0.14
13	17.41	8.37	39.30	12.09	68.96	15.04	32436.57	10.64	10047.52	7.07
14	10.95	1.53	73.38	26.65	58.12	2.77	28895.11	0.90	11794.51	1.89
15A	16.49	3.29	42.97	2.00	68.55	0.89	31441.99	0.90	12991.49	0.59
15B	17.03	2.80	42.14	3.59	84.03	2.95	34359.50	0.89	12580.22	1.17
16	20.25	4.27	44.16	5.47	82.17	5.22	40434.98	5.86	11597.36	4.81
17A	30.33	20.47	1220.11	54.67	178.97	11.95	39613.17	13.05	11168.66	6.48
17B	27.91	3.18	724.39	5.88	124.10	3.34	46545.23	3.50	12748.56	6.33
18	11.93	2.06	189.40	30.11	135.11	3.04	45794.94	3.06	10882.99	2.08
19	15.16	10.17	23.39	9.51	63.26	7.02	17706.63	7.41	8708.00	5.89
20	8.02	3.95	48.10	20.20	87.07	2.02	20940.18	3.49	8055.46	5.15
21	19.18	1.95	121.22	19.92	68.97	2.36	43794.09	2.38	8365.43	2.59
22	16.32	3.55	29.61	3.19	93.52	1.64	27738.37	1.48	6905.99	1.51
23	30.43	9.32	1413.50	23.77	143.37	3.24	72766.67	2.01	12076.67	1.04
24	21.21	3.08	71.38	2.08	125.93	1.63	57601.74	2.35	14246.34	1.12
25	16.73	3.55	73.32	0.72	73.24	1.51	58707.63	1.81	13199.02	1.66
26A	13.43	11.09	55.85	9.91	182.09	6.63	34349.97	7.47	8180.18	6.34
26B	23.94	7.91	806.97	13.52	66.42	4.67	34380.20	6.53	9440.38	1.08
27	20.45	2.15	247.96	47.04	46.21	5.31	32557.94	2.36	7821.36	11.13
28	19.84	1.94	54.06	1.46	103.17	9.18	43891.63	0.62	9133.00	1.28
29	23.04	15.85	665.42	23.77	83.68	12.56	40332.67	11.97	8362.21	0.84
30A	10.18	3.10	127.21	10.10	63.25	1.33	32695.52	0.62	7375.97	1.78
30B	22.95	15.14	3247.21	25.28	228.65	5.55	85385.47	4.63	9320.66	1.39
31	15.09	2.22	33.67	0.91	167.66	3.19	27694.86	2.35	8107.79	0.73
32	16.62	15.95	420.29	56.23	98.69	11.44	34288.85	9.23	8014.11	1.46
33	7.99	4.11	81.51	7.89	127.21	0.66	46623.43	0.31	6958.38	0.06
34	6.90	11.08	66.10	45.80	158.35	5.42	13299.03	6.43	6358.35	4.86
35	18.02	3.10	703.52	9.45	242.07	0.33	20560.71	1.93	6879.83	0.63
36A	2.87	23.39	17.56	3.34	73.82	4.13	10862.11	2.71	6050.72	0.58
36B	12.64	19.59	947.18	22.64	120.59	4.07	16945.79	6.13	7293.19	1.42
AJ1	14.95	2.89	53.79	3.72	27.23	6.00	28619.35	3.58	12982.02	1.09
Emu1	18.68	7.12	54.15	8.55	45.47	4.52	34276.03	8.00	11519.06	1.77
AJ2	21.97	3.11	53.57	0.89	23.07	3.20	35981.04	0.46	14267.04	0.62
Emu2	22.41	2.61	53.11	1.18	24.65	10.11	40077.80	1.18	14098.89	2.34

	Lanthanum		Lithium		Magnesium		Manganese		Sodium	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	35.55	13.71	49.63	6.21	4059.13	6.16	1589.75	6.62	1105.91	5.21
1B	52.50	1.85	69.06	1.21	6310.30	1.07	2808.88	1.71	1157.53	1.59
1C	30.03	4.25	49.20	1.42	4460.00	0.78	2159.25	0.61	965.75	0.60
1D	27.94	14.13	45.90	1.56	4110.73	2.95	2365.04	1.92	961.73	0.98
2	27.31	0.52	38.68	2.89	3177.11	0.72	1074.33	0.53	864.83	0.39
3	40.72	4.73	50.31	2.30	3631.60	4.46	3402.83	3.21	1001.45	2.69
4A	24.65	5.92	48.32	1.11	5710.72	1.60	2222.56	1.37	547.94	0.89
4B	53.12	0.98	54.04	1.21	3360.14	1.20	2379.29	1.69	641.64	1.32
4C	39.79	18.92	56.06	5.87	6456.63	6.80	2201.80	5.94	554.64	5.24
5A	26.62	5.31	36.01	1.03	3258.05	0.86	2178.79	0.46	755.08	1.77
5B	42.84	2.89	66.39	0.94	5039.62	1.51	2885.34	1.13	1309.91	2.01
6	31.07	5.41	47.07	0.38	3738.90	2.09	781.40	1.99	853.06	0.74
7A	70.33	2.32	82.39	0.84	8316.34	1.47	1232.25	1.76	1645.35	0.66
7B	72.54	5.98	84.66	3.13	8236.38	3.55	1137.98	4.15	1504.54	3.60
8	37.27	1.69	46.76	5.67	4222.04	3.05	3216.02	2.98	1201.49	2.74
10	37.43	4.77	54.21	2.89	3809.72	1.84	1164.96	1.32	984.91	1.89
11	33.45	1.58	48.38	3.19	3542.49	2.00	1389.41	2.30	925.68	2.79
12	43.52	23.68	58.21	3.75	4869.61	11.87	1389.22	14.78	1120.49	9.05
13	39.24	8.53	48.11	7.22	3843.26	9.46	2435.85	6.29	1221.16	4.69
14	31.29	2.66	45.30	1.94	3554.22	0.82	1197.83	1.22	878.98	1.09
15A	32.03	4.02	49.75	2.00	3747.63	1.44	2298.32	0.73	916.05	1.51
15B	32.40	1.41	44.21	3.03	3789.77	1.96	2566.03	2.17	950.56	2.46
16	37.02	3.42	55.37	7.05	3975.91	5.34	1855.30	5.28	1187.77	3.31
17A	38.91	10.80	55.78	6.04	3979.79	7.69	3689.58	8.49	1036.65	6.10
17B	41.17	5.17	59.98	1.59	4413.72	3.38	2428.61	2.33	1473.62	1.84
18	25.58	5.88	70.41	6.43	5503.19	4.11	685.09	2.83	468.63	4.86
19	53.51	7.64	35.62	4.02	1881.96	5.82	3313.00	6.68	810.48	1.99
20	27.37	3.79	31.88	2.03	3971.58	3.01	1140.24	3.05	631.93	2.49
21	26.01	4.56	60.40	1.72	4067.28	0.66	1501.10	1.09	576.44	1.27
22	12.54	2.88	28.84	4.72	11958.69	1.64	1681.79	2.33	844.39	2.68
23	55.50	1.14	68.85	0.65	5275.00	1.15	1758.67	1.70	1069.17	1.46
24	42.71	2.35	59.28	1.41	4290.48	1.19	1649.19	1.98	867.67	0.84
25	45.18	1.09	57.53	1.04	5687.65	0.33	1270.29	0.82	1149.02	1.21
26A	39.97	9.99	58.24	6.94	3506.20	7.68	661.67	6.84	690.21	6.08
26B	39.38	8.72	67.23	3.14	2618.10	4.82	1429.07	4.57	671.50	1.39
27	20.90	4.43	36.01	3.35	15314.08	2.17	2058.74	1.97	647.93	1.45
28	53.73	2.63	66.01	5.86	3556.65	4.04	1954.35	1.12	878.98	3.75
29	55.63	12.36	57.84	2.34	3214.15	7.75	3936.82	9.46	960.78	1.01
30A	20.90	3.99	42.83	0.49	3434.21	1.01	870.04	0.41	699.66	0.13
30B	34.96	5.52	81.10	2.14	4082.20	2.60	664.59	8.55	938.89	2.25
31	26.52	2.16	42.65	2.60	2535.49	1.71	1742.12	2.12	720.23	1.73
32	22.92	12.56	46.97	5.40	2476.18	6.74	1616.40	7.82	781.61	3.88
33	29.32	2.90	61.50	0.29	3282.80	0.58	334.09	0.79	391.23	2.31
34	12.26	11.48	30.96	5.18	1396.88	5.29	327.35	4.96	587.69	3.85
35	120.86	1.14	35.02	2.33	2325.73	1.49	5403.13	0.83	926.96	1.24
36A	8.08	18.12	25.69	8.94	1249.14	3.04	326.58	2.49	452.36	1.32
36B	27.99	6.67	32.88	1.40	1647.16	1.64	1436.82	2.50	840.99	0.74
AJ1	29.63	6.06	47.86	7.31	4249.44	3.01	1667.29	2.98	767.90	1.90
Emu1	74.24	7.68	63.73	5.79	4993.80	7.09	2658.12	6.54	1186.89	3.51
AJ2	50.37	1.25	55.64	4.51	5319.43	2.22	3902.84	2.92	769.60	4.08
Emu2	47.98	3.97	57.77	2.22	5388.99	0.95	3967.15	2.10	799.22	2.94

	Neodymium		Nickel		Phosphorous		Rubidium		Silica	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	24.28	7.36	169.67	40.75	927.56	5.27	72.54	7.65	205647.65	6.96
1B	37.18	2.81	38.55	2.66	1626.72	1.22	135.75	1.70	189098.69	5.78
1C	22.88	2.73	21.58	1.04	1279.00	0.82	81.68	1.38	241000.00	0.48
1D	21.85	2.00	18.52	3.56	1172.70	2.37	77.43	1.95	236839.91	3.55
2	20.33	3.56	88.37	38.78	1288.31	0.95	63.09	0.54	197702.49	19.57
3	30.42	2.65	22.37	3.64	1860.04	2.39	90.93	2.88	221594.17	4.27
4A	14.58	2.73	23.86	2.33	573.56	1.09	88.37	0.89	260737.98	2.00
4B	28.75	1.33	39.86	0.79	501.12	0.66	69.52	1.11	234067.20	6.48
4C	15.76	6.89	259.84	54.60	789.24	5.06	88.86	5.47	220864.72	3.81
5A	21.16	0.67	16.54	1.91	3037.87	0.96	68.69	0.64	199540.23	21.21
5B	34.15	1.01	36.46	2.55	917.08	0.94	127.97	1.26	239339.14	1.79
6	17.14	2.50	327.99	3.55	1397.53	0.73	89.59	2.31	174771.06	7.42
7A	36.97	2.35	333.76	2.29	3731.40	0.99	199.45	1.98	132274.64	5.88
7B	38.24	4.58	554.05	22.01	3194.53	3.12	217.13	5.18	178072.64	4.76
8	28.64	1.72	30.20	3.64	2677.00	1.92	106.42	2.95	229086.63	11.11
10	25.74	2.30	20.82	2.77	1063.02	2.00	56.48	2.53	206331.97	4.90
11	25.41	2.77	230.02	41.40	449.33	1.88	69.46	3.09	223485.86	3.16
12	32.39	19.18	30.49	24.02	1249.99	12.08	95.99	17.86	254245.11	0.38
13	31.14	8.88	26.14	22.11	1916.76	11.13	77.82	13.02	196872.85	20.31
14	22.02	1.56	38.09	29.87	611.45	0.87	70.20	1.80	224441.71	1.25
15A	23.83	2.68	20.66	1.12	868.12	1.61	72.83	0.83	246790.51	0.89
15B	23.47	2.34	17.60	3.51	1500.31	1.38	80.52	1.62	243339.59	3.75
16	31.34	5.07	36.13	5.26	1516.64	3.55	99.60	4.65	218337.89	4.65
17A	26.40	10.08	716.00	57.57	1220.91	6.33	92.71	13.38	218039.29	6.35
17B	30.93	2.76	414.90	6.01	2127.02	1.93	109.36	2.94	209624.39	1.25
18	11.82	6.56	107.78	31.57	1347.73	3.14	112.97	3.39	169605.89	11.88
19	24.94	8.12	14.82	9.14	919.59	4.11	40.69	10.05	229715.65	5.41
20	14.84	8.72	25.42	21.10	1939.94	1.86	51.25	4.67	174084.36	15.47
21	12.45	4.14	74.40	17.88	922.34	1.19	108.01	1.31	207620.36	1.90
22	8.81	2.76	7.17	3.27	622.97	2.81	68.02	2.69	172967.08	3.69
23	27.23	0.31	842.00	25.22	3875.00	1.04	179.12	1.90	182133.33	3.16
24	23.70	2.73	41.81	2.11	3028.38	1.21	138.09	2.31	172170.53	10.18
25	20.02	0.88	39.77	3.93	1659.36	1.89	144.42	1.50	183352.65	8.08
26A	22.67	7.56	32.49	8.63	2716.26	5.38	81.02	6.40	211656.68	6.98
26B	21.40	4.10	468.76	12.96	670.75	3.62	79.63	6.07	224986.27	1.60
27	16.57	1.69	130.27	49.37	649.12	1.39	77.58	1.92	176023.60	4.60
28	35.65	0.89	33.37	4.25	1518.88	1.27	104.73	0.58	214614.12	4.50
29	27.77	10.39	369.82	22.75	766.43	6.13	94.07	12.40	186936.65	11.03
30A	9.34	2.38	70.98	12.95	1458.21	0.70	79.41	1.65	193926.29	2.67
30B	12.90	2.36	1847.62	25.21	1230.37	1.96	207.36	4.37	167192.45	0.66
31	17.48	1.74	18.92	3.33	1332.17	1.19	64.99	1.93	231276.95	4.32
32	13.68	5.67	235.20	56.40	1097.45	4.81	81.00	9.17	216667.82	9.62
33	10.23	3.21	58.15	6.78	702.17	0.50	115.81	0.37	197385.79	8.49
34	7.48	8.67	24.62	51.85	184.94	4.45	30.92	5.51	238419.41	4.18
35	97.03	0.82	411.75	10.17	851.86	0.74	46.43	3.33	204516.21	10.52
36A	6.33	7.83	3.26	2.13	168.57	2.32	25.94	2.64	217206.00	13.72
36B	15.23	3.34	551.13	24.44	352.60	0.53	37.80	6.48	201404.95	3.29
AJ1	20.57	3.53	27.29	2.91	1234.37	2.06	68.71	0.62	199432.73	2.85
Emu1	23.83	9.05	36.54	6.68	1387.07	5.03	83.24	6.87	219214.88	5.97
AJ2	27.85	0.93	33.12	4.86	1141.07	3.54	89.80	4.04	225109.52	4.16
Emu2	27.94	0.98	33.85	3.64	1178.40	2.24	92.96	2.78	227261.97	0.92

	Strontium		Titanium		Vanadium		Zinc		Zirconium	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	30.24	8.92	1385.84	15.35	53.51	6.68	84.64	7.04	124.33	9.13
1B	55.53	1.03	2125.52	2.93	92.57	1.37	148.51	2.04	165.72	1.92
1C	33.10	5.14	1363.50	15.36	58.05	0.34	107.05	1.07	103.33	5.83
1D	31.25	3.77	1542.53	12.45	54.64	4.04	95.38	2.57	109.45	6.41
2	29.23	1.46	1887.24	4.39	48.45	0.09	175.84	0.26	119.05	0.71
3	39.59	3.09	2182.97	1.02	67.51	3.85	204.87	3.63	150.39	1.83
4A	21.98	1.00	1655.95	0.81	78.84	1.24	125.48	0.91	86.49	1.45
4B	23.31	0.86	2172.90	1.18	82.24	1.29	162.35	1.16	116.07	0.74
4C	26.54	6.73	2016.31	4.46	87.07	5.48	225.32	6.62	91.15	6.87
5A	35.20	0.86	1852.99	0.84	54.51	2.61	190.28	1.86	123.63	1.56
5B	50.07	1.53	1677.53	4.21	99.95	1.15	132.77	1.35	114.75	0.81
6	39.35	2.59	2631.60	5.35	78.04	1.93	109.89	1.03	133.32	1.95
7A	78.97	1.22	2483.54	5.28	123.74	1.11	192.54	0.88	198.40	0.93
7B	77.58	3.86	2303.20	4.50	134.40	5.68	194.87	4.09	199.88	4.90
8	46.82	1.41	2637.97	3.52	79.69	2.57	143.40	2.43	145.55	0.50
10	30.89	1.31	2060.73	1.59	56.16	2.47	98.55	1.52	101.80	0.85
11	30.97	1.89	2274.26	2.54	64.57	2.79	67.47	3.04	104.65	1.52
12	36.29	19.13	1725.16	12.67	70.21	4.59	145.08	16.25	109.21	16.35
13	39.75	5.83	2191.59	4.52	71.40	8.12	134.86	14.62	118.15	9.45
14	29.80	0.75	1901.66	2.24	60.44	0.89	81.14	2.41	109.71	0.44
15A	28.28	7.02	1641.10	17.59	59.97	0.34	96.00	1.88	89.82	5.98
15B	29.95	0.83	1373.38	7.00	58.80	1.03	104.54	0.41	85.29	1.63
16	42.72	3.27	2616.09	4.58	77.19	5.76	131.58	4.09	125.26	1.60
17A	33.34	6.88	2221.55	1.82	75.14	9.10	134.74	8.49	114.62	5.38
17B	50.74	1.69	2225.62	1.29	85.11	2.92	221.92	2.54	150.86	1.93
18	21.28	3.72	2389.75	3.83	107.63	3.99	198.42	3.10	112.43	3.72
19	22.80	5.86	2188.72	1.28	49.57	5.93	63.78	6.50	99.95	5.26
20	31.19	3.21	1812.70	1.56	48.34	3.52	187.26	2.87	92.93	4.11
21	28.03	1.77	3255.10	10.87	105.05	0.60	120.82	1.16	136.76	1.38
22	497.59	3.10	1347.04	4.04	36.28	4.06	124.11	0.16	63.05	3.58
23	39.15	1.28	2918.33	1.32	131.50	1.13	356.17	1.01	138.95	2.06
24	34.00	3.15	3335.25	3.72	103.17	2.34	283.44	1.71	124.46	2.39
25	43.19	0.23	3076.14	2.64	113.67	0.88	206.23	1.86	153.50	0.43
26A	31.05	9.28	2265.53	13.35	87.55	6.76	229.07	7.20	113.52	7.25
26B	21.00	3.60	2362.67	1.75	75.34	5.03	99.33	4.77	97.63	4.79
27	217.14	3.40	1549.75	3.73	50.23	1.93	221.15	1.59	75.11	2.25
28	35.91	2.22	3328.41	4.02	110.51	5.32	169.52	3.20	145.81	2.00
29	29.78	11.53	3259.46	6.19	102.00	8.28	120.84	9.71	123.44	8.82
30A	23.54	1.39	2359.95	4.75	83.69	0.57	146.25	1.13	111.64	1.80
30B	18.65	3.63	2427.14	5.32	183.59	2.51	246.89	2.54	131.82	3.74
31	26.10	2.26	2985.07	3.59	74.36	2.45	124.18	2.26	113.18	2.74
32	26.15	6.97	2877.64	1.67	88.69	7.57	118.13	6.74	125.19	4.19
33	14.18	1.54	2088.60	4.39	120.40	0.81	201.31	0.36	112.24	1.96
34	22.67	5.47	1724.98	7.57	41.32	6.54	58.42	5.22	87.32	7.26
35	39.47	0.66	1482.28	2.05	49.83	1.15	305.90	0.73	82.76	1.34
36A	19.19	3.50	1934.92	3.95	35.29	6.70	44.61	4.39	96.50	2.64
36B	29.89	1.53	2117.93	1.30	43.92	4.41	85.08	1.99	110.37	1.84
AJ1	28.38	1.91	2306.36	0.32	59.45	3.35	121.93	0.46	89.70	0.59
Emu1	32.55	6.01	1959.22	1.66	67.68	7.37	294.32	6.28	84.05	4.76
AJ2	29.52	0.92	2265.63	0.60	82.66	1.78	154.87	2.31	94.06	0.14
Emu2	29.46	0.78	2179.65	3.65	85.47	0.89	156.10	1.62	93.52	1.65

B

HNO_3-extractable elemental concentrations averaged from replicates for each sample and shown in mg kg^{-1}. Corresponding percent relative standard error values for the replicates of each sample are also shown.

	Aluminum		**Barium**		**Calcium**		**Cadmium**		**Cerium**	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	22875.21	7.21	319.31	0.22	4096.07	1.52	1.27	4.28	70.70	1.14
1B	21028.98	3.75	482.25	0.77	4597.39	1.07	1.31	4.17	68.21	3.78
1C	30982.67	9.45	415.97	4.31	4668.71	3.18	2.13	8.68	70.69	6.44
1D	21286.79	1.94	387.38	1.26	4888.58	1.34	1.14	3.01	71.31	2.55
2	19792.61	2.10	516.67	0.09	3152.81	1.12	1.42	6.34	52.78	3.39
3	23938.32	9.47	411.04	2.78	2213.44	2.15	1.44	13.41	74.02	1.47
4A	25566.75	1.39	299.42	0.27	6865.46	0.17	1.65	1.06	100.96	0.66
4B	28691.53	3.33	107.39	2.27	388.24	1.71	1.23	1.43	165.01	3.07
4C	35531.22	3.97	299.71	1.40	8425.63	2.84	1.63	7.43	108.36	6.99
5A	23380.53	1.28	491.89	1.61	6405.77	2.06	1.28	2.18	41.93	0.17
5B	38441.34	5.60	190.38	1.81	1511.95	0.92	2.01	2.32	57.57	8.30
6	35242.86	1.61	221.59	0.78	2546.99	0.63	1.80	0.64	43.10	1.28
7A	34045.46	7.95	156.19	5.98	3973.03	2.13	2.15	2.45	46.39	12.77
7B	46113.08	4.53	184.83	2.57	2962.97	0.91	3.32	3.30	62.03	6.67
8	39261.12	3.51	222.36	1.20	3762.88	0.23	2.05	0.85	58.51	3.50
10	24394.88	2.45	449.41	1.78	4095.28	1.52	1.38	9.14	70.97	1.58
11	23976.36	7.89	287.14	3.34	2006.12	3.02	1.14	5.22	57.38	8.42
12	25081.15	3.45	260.61	5.78	3046.45	5.58	1.54	4.19	73.21	7.33
13	34789.55	14.24	511.99	13.22	3321.75	3.09	1.47	10.94	78.53	8.78
14	23620.02	2.84	376.19	1.28	1823.63	1.46	1.59	2.24	54.37	4.15
15A	30446.59	1.03	301.80	1.63	3398.01	1.90	1.63	1.76	85.33	1.04
15B	30417.32	8.75	284.95	1.41	4379.95	4.69	2.07	4.21	95.33	7.15
16	47442.62	4.40	932.59	2.22	6329.13	2.15	2.31	3.56	59.56	4.76
17A	27662.63	8.49	478.31	3.33	3617.75	3.43	1.42	8.51	79.00	3.11
17B	31356.68	5.90	1423.86	8.14	6152.03	4.27	1.68	4.95	54.06	6.01
18	49334.88	13.17	234.75	4.05	3414.31	0.94	2.68	17.69	59.76	3.11
19	33340.78	1.75	295.43	0.33	1423.18	0.34	1.41	0.93	134.65	4.27
20	24764.55	1.09	1483.88	1.35	7074.53	1.40	1.30	2.83	57.58	1.60
21	60003.96	4.90	320.29	0.39	2820.54	0.57	3.25	1.61	91.82	3.00
22	14645.98	6.28	202.38	4.70	157044.15	6.69	0.89	3.02	49.20	5.84
23	64681.93	3.53	216.16	1.96	4180.00	1.22	3.72	2.58	83.29	1.25
24	67913.13	5.38	601.22	1.85	4174.52	2.59	3.87	4.22	91.65	3.46
25	46300.59	0.73	120.86	0.62	5291.34	1.30	3.43	0.72	30.36	6.30
26A	32046.91	5.22	421.77	4.01	3572.95	1.80	1.92	2.96	83.18	4.34
26B	34556.79	3.58	233.47	4.18	2143.39	4.75	1.58	3.87	131.83	4.15
27	28467.18	3.71	590.53	0.45	69733.37	1.63	2.10	2.97	71.46	6.33
28	31608.32	4.21	313.50	1.21	2622.17	1.47	1.98	4.71	91.84	2.92
29	44027.76	11.60	200.75	9.01	2312.61	8.88	2.11	8.34	175.77	7.85
30A	40745.57	11.05	94.78	5.38	4366.83	0.44	2.02	16.05	59.33	3.44
30B	59404.99	11.15	38.58	5.34	1856.17	0.95	3.49	7.11	26.89	1.73
31	34702.56	5.25	125.91	2.36	2773.87	1.43	2.03	5.11	120.52	1.77
32	34087.05	1.64	199.18	1.19	2169.52	1.17	2.07	1.76	111.74	0.82
33	38922.61	8.75	40.15	3.25	1880.20	1.23	2.44	6.33	61.41	4.12
34	13527.14	3.93	44.19	2.34	709.99	1.62	0.60	1.95	30.85	2.73
35	22435.95	4.08	391.59	2.40	3273.15	4.90	1.13	5.77	122.20	5.89
36A	16630.80	0.85	90.29	0.74	698.80	1.05	0.86	1.35	22.18	9.10
36B	16090.34	4.18	200.19	1.14	945.89	2.24	0.74	1.58	48.49	7.32
AJ1	34361.06	2.00	305.34	0.49	4076.55	1.50	1.58	3.72	78.37	2.95
AJ2	42297.07	0.67	451.36	0.48	4744.38	0.47	1.86	4.29	103.63	5.61
EMU2	49498.67	0.27	480.51	1.70	6164.93	1.49	2.12	5.66	116.53	8.70

	Cobalt		**Chromium**		**Copper**		**Iron**		**Hafnium**	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	18.92	2.02	26.25	5.99	75.36	3.35	25994.07	2.63	2.69	12.22
1B	20.84	1.89	24.18	5.01	51.54	2.19	31273.32	1.52	3.88	9.12
1C	21.47	4.08	32.52	6.93	121.47	4.41	33241.32	4.70	3.61	6.71
1D	21.29	0.68	29.36	2.06	97.15	1.32	31720.42	1.97	2.86	20.01
2	13.19	0.50	20.19	2.64	60.23	1.07	22424.92	1.57	2.53	10.57
3	19.05	2.41	23.94	6.50	549.81	1.38	27342.69	2.53	2.71	7.99
4A	31.04	1.16	34.56	2.08	67.56	0.35	35856.03	1.57	3.04	4.63
4B	22.43	1.71	16.92	2.84	201.91	1.45	20258.02	2.07	1.79	5.62
4C	26.63	1.90	25.75	41.39	186.08	2.92	39539.34	2.56	4.64	16.41
5A	21.67	0.77	26.06	0.30	202.07	0.53	31713.13	1.24	4.29	1.24
5B	18.46	1.30	25.79	5.59	163.99	1.27	44971.72	2.85	4.26	6.84
6	10.33	0.53	22.85	3.22	73.64	0.41	35069.39	2.55	3.52	3.19
7A	12.35	2.57	25.37	4.88	63.44	1.18	58797.77	2.73	6.07	4.17
7B	12.23	1.92	34.05	4.22	57.56	1.78	65162.39	1.94	7.11	2.20
8	23.20	0.62	25.65	2.70	102.82	0.95	42859.50	1.46	4.74	6.36
10	11.84	1.72	24.77	3.58	95.93	1.56	19993.83	1.96	2.16	2.38
11	10.88	4.15	20.24	7.32	50.53	2.37	23410.13	5.70	2.26	8.21
12	18.13	5.97	27.18	4.69	136.10	5.91	28412.34	3.88	2.88	11.40
13	17.72	11.55	25.42	15.87	55.37	17.87	28712.84	15.61	3.49	12.86
14	10.74	1.57	22.39	3.11	54.11	0.82	25412.30	2.24	2.25	9.26
15A	18.65	1.29	30.53	1.51	68.91	0.86	29786.66	0.22	3.02	4.32
15B	19.73	3.19	32.51	4.44	89.90	11.83	32897.50	1.62	2.97	11.21
16	21.12	0.69	33.44	4.14	90.49	1.28	44017.69	2.88	5.57	2.59
17A	23.74	4.21	30.73	1.09	137.15	1.65	32048.26	5.17	1.92	43.93
17B	20.66	4.33	24.46	7.20	88.49	4.25	33069.92	4.28	5.31	12.90
18	9.68	2.64	48.48	6.08	137.26	3.21	46785.71	4.33	4.55	3.66
19	19.53	0.39	17.72	3.20	71.33	1.15	19488.75	2.24	2.26	1.85
20	9.77	0.38	18.31	2.53	90.35	0.59	19445.50	1.74	3.89	6.08
21	17.14	0.90	35.10	1.57	68.78	0.78	47373.16	1.04	4.20	7.56
22	15.98	6.05	27.29	6.42	128.09	6.65	26349.39	6.07	23.08	4.70
23	14.95	1.95	47.98	3.22	86.39	1.37	53461.11	1.74	4.51	1.91
24	18.09	2.02	52.19	4.13	123.18	3.11	56389.12	2.34	5.35	0.24
25	13.19	1.32	48.35	0.67	63.41	0.60	53266.31	2.01	4.67	8.93
26A	10.40	3.12	25.37	6.31	151.97	1.34	25673.40	4.10	2.90	10.39
26B	22.11	4.00	25.79	4.84	45.87	2.66	30731.22	4.07	2.57	12.49
27	18.01	1.09	35.34	6.69	44.42	0.49	32945.51	3.53	9.26	8.49
28	12.26	1.92	24.24	2.65	68.37	2.35	29504.32	2.59	2.68	3.80
29	17.75	6.66	25.64	9.65	62.42	8.51	34562.21	8.67	3.38	7.52
30A	9.13	1.40	35.58	4.56	52.96	4.65	32996.36	2.03	3.39	7.40
30B	4.83	3.48	70.21	1.63	134.17	0.74	58604.64	2.25	5.04	3.59
31	13.86	1.65	24.37	4.01	173.98	1.12	26693.14	2.46	3.05	5.45
32	13.93	0.67	27.04	2.40	92.22	0.78	32176.26	0.96	3.20	2.02
33	6.27	3.48	37.36	5.88	115.62	2.14	42452.74	5.10	3.61	3.26
34	8.47	0.85	8.73	7.76	141.87	1.88	9947.33	1.62	1.08	13.93
35	15.25	5.05	14.18	7.73	189.07	3.78	12653.07	5.02	2.46	3.58
36A	5.42	0.13	12.39	5.18	87.10	1.26	11102.72	2.16	1.32	6.31
36B	6.88	3.31	10.12	3.52	85.73	0.77	9084.09	4.53	1.23	5.23
AJ1	19.05	0.16	34.88	4.00	22.05	0.76	32727.70	1.05	3.21	17.03
AJ2	28.04	2.84	42.49	7.32	11.99	4.91	40749.48	0.58	4.09	2.47
EMU2	30.98	3.29	39.87	8.70	7.32	45.36	48811.33	2.37	2.23	25.37

	Potassium		**Lanthanum**		**Lithium**		**Magnesium**		**Manganese**	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	2526.70	11.02	22.61	3.07	21.00	5.68	2257.56	4.66	1553.26	2.25
1B	1636.62	5.45	18.61	2.26	14.85	4.32	1822.45	2.28	2044.93	1.64
1C	4618.11	12.97	22.32	5.52	22.25	8.60	2776.45	8.34	2060.84	3.77
1D	2809.18	1.62	20.05	1.14	18.04	0.87	2237.22	1.09	2397.69	0.43
2	2228.50	1.74	17.13	1.34	14.99	2.18	1606.06	1.57	1094.26	2.26
3	2909.90	13.12	20.79	2.29	15.57	5.96	1696.72	7.33	2656.66	2.65
4A	2342.91	2.23	18.92	0.85	21.31	0.21	4076.40	0.64	2306.91	0.43
4B	1374.94	4.87	31.61	1.80	22.36	2.28	1614.78	3.19	1890.58	1.85
4C	3541.09	8.53	25.04	5.05	33.54	8.59	4807.32	3.35	2285.34	1.60
5A	2478.99	3.05	18.81	0.01	16.85	1.38	2366.91	0.16	2337.76	2.21
5B	2792.00	5.25	21.95	3.50	25.55	3.44	1897.76	3.76	2730.71	0.99
6	3930.76	1.36	16.76	0.95	22.59	1.13	2661.60	1.33	740.44	0.50
7A	4035.21	6.31	20.07	10.72	23.64	7.80	3058.29	4.59	912.81	1.39
7B	5562.10	3.70	29.78	3.89	34.90	3.80	3235.45	3.10	780.88	1.64
8	4677.76	2.71	20.33	2.30	22.18	3.04	2476.15	2.59	3213.14	1.14
10	2232.41	2.50	26.97	1.74	20.12	1.93	1814.96	2.23	1127.19	2.07
11	1620.86	9.70	25.46	4.14	15.44	7.30	1496.32	5.90	1371.80	3.35
12	2445.48	7.34	24.74	4.96	24.94	8.24	2346.24	7.46	1123.38	6.07
13	3192.10	11.22	27.25	11.31	21.01	16.73	2573.18	9.46	2162.12	3.68
14	2055.51	3.07	22.22	1.29	16.64	1.73	1627.08	2.48	1230.63	2.33
15A	3099.32	3.02	27.35	1.80	23.05	1.40	2219.34	1.05	2336.01	1.32
15B	4281.60	6.24	28.01	3.96	20.84	9.37	2563.54	3.84	2194.02	6.39
16	4816.21	4.17	22.21	2.54	30.33	3.66	2750.21	3.24	2015.99	0.77
17A	2486.96	1.57	28.38	10.47	24.00	12.85	2077.49	9.84	3423.00	4.12
17B	3523.62	7.02	18.26	4.29	20.85	6.12	1906.47	5.51	1990.46	3.81
18	3622.08	16.30	15.33	5.41	31.29	13.24	2160.39	12.70	698.29	1.11
19	2036.84	1.87	59.72	0.55	17.39	0.86	1502.48	1.46	3858.45	0.47
20	3847.16	1.07	22.97	1.37	16.23	0.30	3519.63	0.42	1214.93	0.61
21	3218.66	5.61	17.26	1.84	34.87	4.48	2265.49	4.31	1536.82	0.59
22	1641.02	5.94	10.47	5.74	13.27	5.66	12894.99	5.18	1855.38	6.15
23	4900.26	4.20	19.06	3.31	27.46	3.97	2413.49	3.66	1232.74	1.16
24	4496.42	7.07	21.88	3.66	29.29	6.30	2394.85	5.00	1539.70	1.05
25	2605.67	0.72	11.03	0.64	21.02	0.63	2894.04	0.62	1192.65	1.39
26A	2537.38	4.78	20.78	2.64	20.32	5.33	1929.35	4.02	516.46	2.04
26B	2056.75	3.37	33.59	3.24	27.29	2.95	1530.90	3.63	1500.90	3.74
27	2454.11	4.70	16.02	1.91	22.37	2.03	15744.39	2.69	2100.85	0.56
28	1652.33	4.82	25.66	1.63	19.40	4.56	1539.14	3.09	1404.65	2.00
29	1458.03	11.97	35.87	8.77	19.18	12.05	1835.02	10.08	3952.42	7.65
30A	3345.89	7.58	11.07	5.61	20.92	9.68	2674.08	4.10	841.86	1.17
30B	3799.37	4.12	7.60	6.57	24.93	8.42	1719.00	3.33	329.77	0.77
31	2137.26	6.02	21.56	2.18	18.14	6.94	1835.00	4.82	1669.26	0.40
32	2226.79	0.39	15.68	0.37	17.29	0.70	1463.66	0.31	1614.17	1.10
33	1768.96	6.47	8.74	4.04	19.94	7.60	1419.97	4.35	314.70	1.35
34	640.91	5.44	10.22	3.15	9.08	2.12	812.36	2.75	257.74	1.88
35	1054.80	7.37	92.06	3.30	10.93	9.04	1595.60	8.32	4684.35	3.12
36A	1107.62	2.56	10.14	1.49	10.71	1.22	1070.32	1.76	349.27	0.58
36B	716.47	4.45	19.47	2.00	9.99	6.01	1109.55	4.82	1184.11	1.53
AJ1	3967.07	3.02	26.54	0.18	29.65	1.78	3024.48	1.64	1909.00	1.25
AJ2	3327.74	6.78	37.92	0.18	37.51	3.97	3711.31	2.90	4405.59	0.29
EMU2	3603.93	1.31	40.71	2.34	51.67	1.92	4590.27	0.94	5115.87	2.69

	Molybdenum		Neodymium		Nickel		Phosphorous		Rubidium	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	0.37	13.93	19.04	1.74	19.76	4.42	906.76	2.63	59.17	3.49
1B	0.59	6.24	18.43	1.68	19.51	3.23	1061.09	2.21	72.50	3.09
1C	0.49	17.16	17.97	4.26	24.19	6.27	1209.32	4.62	74.88	5.48
1D	0.66	18.24	17.02	1.03	19.48	0.46	1018.07	1.01	72.15	0.55
2	0.33	14.30	15.45	0.93	16.90	1.01	1237.53	0.31	50.56	1.68
3	0.52	7.21	16.96	1.42	18.71	3.09	1447.67	1.34	60.79	0.94
4A	1.18	6.84	11.35	0.66	26.09	0.78	564.94	0.98	82.19	0.60
4B	0.87	5.48	19.09	1.64	30.92	2.55	366.92	2.30	46.58	2.56
4C	1.60	52.10	12.64	4.11	29.15	2.27	653.19	5.17	85.37	1.97
5A	1.18	2.48	16.70	1.46	19.92	0.26	2849.00	1.72	70.02	0.03
5B	0.79	2.20	24.63	1.44	28.23	2.89	707.80	2.50	103.88	1.85
6	0.73	5.14	9.64	1.13	20.73	1.19	1379.10	1.22	82.61	0.70
7A	0.89	4.85	16.89	4.67	23.09	5.98	2877.76	2.42	135.68	2.56
7B	0.92	12.75	19.00	2.56	30.18	3.48	2445.25	2.89	145.58	2.25
8	0.82	6.14	20.76	0.14	25.39	1.84	2566.78	1.43	99.88	0.29
10	0.21	22.54	20.72	1.44	17.15	2.76	973.38	1.58	44.97	1.88
11	0.47	11.70	21.38	2.86	16.94	4.61	338.74	5.77	53.43	5.43
12	0.45	30.40	20.96	5.60	22.59	6.23	1059.55	5.58	60.76	5.62
13	0.52	36.24	23.48	13.18	24.45	15.66	1647.76	11.35	64.00	15.48
14	0.37	18.91	17.29	1.19	17.14	1.81	533.43	1.28	56.19	1.27
15A	0.55	4.41	20.07	1.35	22.53	1.58	855.40	1.44	67.73	0.91
15B	0.67	6.95	20.08	4.88	22.82	5.86	1387.03	3.49	72.59	2.30
16	0.69	6.32	27.75	1.58	34.63	3.20	1560.30	1.51	101.81	1.92
17A	0.86	15.09	19.81	4.60	21.08	1.95	992.89	1.38	69.36	0.98
17B	0.59	6.90	19.58	4.12	24.63	5.31	1802.48	4.32	76.08	4.91
18	0.90	7.30	7.47	3.42	28.67	10.97	1263.08	4.99	107.29	3.70
19	0.73	22.96	26.20	1.03	20.54	0.59	979.17	1.52	43.63	0.50
20	0.72	24.29	11.43	0.34	15.94	1.68	2040.42	0.39	45.79	1.76
21	0.92	8.19	7.88	1.03	30.97	3.68	917.88	1.54	105.39	0.79
22	0.60	10.02	5.73	5.48	11.40	5.39	637.17	4.87	61.70	5.09
23	0.84	3.61	15.44	1.43	34.22	3.17	3058.53	2.43	120.41	1.67
24	0.89	12.09	17.66	1.63	37.37	4.27	2906.77	1.77	128.51	2.70
25	0.65	6.72	8.16	1.04	24.74	0.53	1469.00	1.23	121.86	1.03
26A	1.04	2.95	13.97	1.70	19.23	5.18	2300.27	2.02	58.46	3.38
26B	0.63	12.41	20.53	3.66	23.38	3.41	634.55	3.76	69.45	3.61
27	0.84	9.99	14.13	0.18	28.11	28.63	688.69	0.76	71.93	2.03
28	0.67	14.21	21.17	1.25	19.07	3.58	1086.26	2.99	64.14	2.45
29	0.68	13.53	23.27	6.86	22.51	10.14	657.27	7.24	78.32	9.61
30A	1.01	8.02	5.25	1.91	20.62	8.05	1351.18	2.07	73.77	1.28
30B	1.31	4.02	4.48	2.95	28.71	8.79	957.22	0.76	134.63	1.86
31	0.63	5.22	12.32	0.37	18.91	5.07	1287.07	0.73	58.18	2.84
32	0.84	10.33	7.98	0.80	18.24	0.46	1114.74	0.97	70.38	0.22
33	1.31	16.90	5.07	2.58	25.93	6.72	586.50	4.17	94.33	3.64
34	0.53	12.34	2.58	3.14	6.56	2.67	148.33	0.86	23.14	1.51
35	0.75	15.02	83.05	3.13	31.09	6.38	671.68	7.09	26.07	5.47
36A	0.30	23.40	2.62	1.60	7.76	2.16	162.71	0.81	24.30	1.02
36B	0.45	13.30	8.15	1.51	9.52	4.43	289.64	4.06	18.90	1.02
AJ1	0.70	26.33	18.33	0.96	26.26	0.82	1245.76	1.26	72.07	1.04
AJ2	1.49	14.75	26.93	0.50	32.71	4.86	1073.23	1.21	93.44	1.29
EMU2	0.64	56.25	28.64	1.26	39.01	1.67	1191.99	3.38	104.63	0.99

	Sulfur		**Strontium**		**Titanium**		**Vanadium**		**Zinc**	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	374.49	1.45	10.53	2.68	186.44	10.08	30.61	4.60	81.83	3.24
1B	318.59	1.61	18.79	2.50	139.68	5.95	33.00	2.71	91.09	3.26
1C	463.47	4.24	17.25	6.01	399.84	15.62	41.02	7.03	101.74	5.37
1D	453.77	1.28	14.12	0.99	244.76	1.92	32.07	1.10	87.62	0.85
2	461.23	0.48	11.24	0.62	200.06	2.19	25.74	1.39	185.40	2.21
3	303.53	1.76	10.19	4.91	440.77	18.05	35.19	5.82	154.96	1.81
4A	362.55	1.34	10.67	0.67	438.48	3.62	60.67	0.46	125.47	1.87
4B	148.42	2.02	2.97	3.67	364.78	7.13	44.76	2.95	121.84	1.99
4C	368.20	16.48	13.43	1.56	1489.92	29.18	62.12	3.55	216.13	2.06
5A	1843.86	1.06	23.12	0.73	705.68	4.38	37.86	1.52	190.43	0.16
5B	260.34	1.94	20.61	3.48	247.68	6.06	53.12	3.18	95.04	2.21
6	243.70	0.59	16.46	0.79	644.31	0.79	54.84	0.81	108.33	1.51
7A	554.49	0.93	32.50	12.34	163.44	5.03	48.14	3.32	134.14	3.62
7B	400.70	0.93	37.36	3.38	229.47	3.19	59.23	2.50	137.72	2.78
8	450.05	1.17	22.68	2.93	449.58	6.98	52.82	1.47	136.00	2.09
10	532.96	1.17	10.65	1.85	155.40	3.26	28.80	3.16	84.36	1.54
11	129.93	3.72	7.95	5.08	174.40	10.94	31.70	5.46	49.40	6.36
12	454.34	6.25	8.20	4.96	242.14	5.96	36.49	4.18	111.38	5.80
13	609.25	7.24	16.81	2.62	1099.13	15.68	47.94	13.25	108.14	12.97
14	216.94	1.93	8.39	1.97	197.62	4.74	33.62	2.16	66.56	1.08
15A	424.20	1.04	9.45	0.82	341.06	4.60	39.55	1.04	95.62	1.79
15B	709.65	1.66	11.85	1.92	527.17	11.22	43.52	4.47	98.32	6.09
16	722.06	1.99	29.67	6.81	326.93	6.19	57.56	2.30	138.18	2.14
17A	455.78	8.70	11.29	4.06	737.00	57.75	39.40	1.83	109.18	1.78
17B	900.38	3.33	47.66	4.90	239.51	6.60	40.42	5.45	186.51	4.36
18	217.36	3.98	7.55	7.31	685.13	14.44	75.82	6.97	158.84	10.18
19	205.55	1.61	5.92	0.97	826.93	0.47	41.84	1.05	71.93	0.82
20	1280.84	0.69	32.42	2.86	602.93	3.40	36.36	1.25	195.32	1.93
21	278.58	1.54	9.81	2.09	701.10	4.01	83.19	1.80	102.22	3.11
22	3781.97	6.58	309.43	7.83	458.55	4.88	26.62	6.51	103.95	5.02
23	706.19	2.28	13.34	2.09	995.70	6.90	72.38	1.57	249.55	2.91
24	676.27	1.29	18.70	2.65	930.48	7.14	73.00	3.92	255.08	3.75
25	321.37	1.02	9.85	0.32	252.64	1.10	69.81	0.08	159.42	0.85
26A	994.10	2.77	13.17	3.31	610.44	6.74	54.44	3.87	176.15	2.92
26B	178.75	3.94	6.46	3.26	486.66	3.77	51.31	3.00	80.72	3.51
27	1716.87	1.60	139.74	2.87	855.32	8.48	42.99	1.73	212.48	1.10
28	325.41	2.53	7.90	2.02	547.37	5.77	52.17	2.77	102.50	2.20
29	207.81	6.12	6.59	9.58	773.25	12.46	63.17	7.07	82.10	11.90
30A	531.16	1.76	9.86	4.80	942.59	16.20	66.89	5.87	130.09	5.28
30B	244.45	0.32	5.13	3.46	710.14	6.15	110.87	2.64	143.81	5.56
31	455.57	0.41	8.56	3.16	875.05	11.00	57.17	3.66	113.79	4.16
32	344.28	0.93	8.18	0.65	663.70	1.15	65.63	0.19	96.86	0.94
33	209.00	1.69	4.00	3.32	445.24	8.48	80.72	3.65	134.47	4.81
34	124.41	2.37	3.99	3.97	387.57	8.86	23.29	2.21	48.40	2.29
35	607.08	6.39	16.92	2.90	479.87	8.94	26.25	5.02	267.91	6.21
36A	123.68	0.43	5.27	1.67	567.39	2.89	25.74	1.71	50.62	0.18
36B	221.50	2.51	5.74	2.01	392.74	7.32	19.97	3.32	74.39	3.57
AJ1	720.91	0.86	11.49	1.46	606.46	3.59	42.51	0.91	126.55	1.73
AJ2	406.86	0.17	12.88	2.61	794.03	7.68	55.78	2.71	142.96	0.15
EMU2	347.35	1.82	15.39	1.78	1732.13	4.30	57.91	4.44	161.60	2.10

	Zirconium	
Sample	mg kg^{-1}	%RSE
1A	4.74	1.70
1B	5.34	2.57
1C	6.52	4.74
1D	5.36	0.67
2	5.50	1.49
3	7.15	4.36
4A	8.05	1.03
4B	4.77	3.16
4C	10.43	6.17
5A	9.64	1.18
5B	3.90	2.10
6	7.25	1.32
7A	9.13	4.73
7B	4.84	1.81
8	8.90	4.28
10	5.77	2.08
11	4.27	6.39
12	6.39	7.10
13	10.92	13.18
14	5.20	1.44
15A	6.35	3.31
15B	8.23	3.79
16	7.16	3.96
17A	7.94	4.03
17B	11.18	4.55
18	10.82	4.53
19	9.69	2.19
20	8.59	2.89
21	13.61	0.93
22	5.71	8.27
23	15.20	1.85
24	11.50	4.77
25	8.06	1.13
26A	12.44	4.71
26B	6.62	3.32
27	8.07	2.22
28	10.75	3.21
29	11.34	10.20
30A	12.90	1.82
30B	8.32	8.62
31	12.50	2.47
32	12.67	1.42
33	7.45	1.19
34	4.18	1.68
35	3.89	5.02
36A	3.66	0.66
36B	2.48	7.19
AJ1	7.12	2.42
AJ2	7.98	2.88
EMU2	7.75	1.12

C

Mehlich 3-extractable elemental concentrations averaged from replicates for each sample and shown in mg kg $^{-1}$. Corresponding percent relative standard error values for the replicates of each sample are also shown.

	Barium		Calcium		Cadmium		Cerium		Cobalt	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	115.26	2.45	3172.89	1.90	0.12	1.52	1.18	1.65	5.99	1.94
1B	121.99	1.65	3834.30	1.74	0.13	0.97	0.74	1.93	10.11	1.63
1C	115.16	0.66	3487.13	2.11	0.12	0.86	0.83	1.31	8.54	0.55
1D	100.85	0.95	3964.53	0.67	0.10	0.92	0.72	1.53	6.10	0.95
2	116.65	1.18	2591.83	1.14	0.20	0.73	0.66	3.31	4.14	1.47
3	151.56	1.32	1942.91	1.31	0.16	0.78	1.03	2.18	7.76	1.61
4A	111.61	1.26	3349.18	1.35	0.14	1.31	1.31	1.34	10.36	0.21
4B	42.31	0.19	324.78	3.78	0.06	0.52	1.61	11.78	4.60	1.49
4C	115.95	0.27	5131.54	1.36	0.17	0.51	0.90	2.14	5.65	0.56
5A	41.15	0.98	4579.47	1.98	0.12	0.04	0.18	18.12	6.01	0.54
5B	28.67	0.64	1502.24	2.11	0.07	1.02	2.60	1.13	2.22	0.11
6	49.02	0.40	2265.57	2.41	0.08	0.07	0.32	6.29	2.97	1.85
7A	22.75	1.01	3227.26	1.44	0.08	0.70	0.04	16.51	3.44	1.15
7B	29.29	0.20	2787.97	0.31	0.07	0.71	0.12	12.10	2.70	0.95
8	50.97	1.07	3441.63	0.22	0.13	0.95	0.37	3.34	9.87	0.23
10	146.91	2.63	3794.71	1.09	0.17	0.79	0.77	3.67	2.55	0.80
11	150.19	1.49	1916.97	2.37	0.06	0.90	1.54	1.76	2.23	0.40
12	132.24	2.13	2565.75	4.09	0.20	2.41	1.69	1.76	3.78	3.14
13	96.06	4.16	2305.45	5.29	0.11	3.93	0.63	5.31	6.54	1.42
14	138.52	2.53	1758.99	0.73	0.09	1.35	1.56	1.21	2.28	1.69
15A	118.88	0.88	2855.10	1.54	0.18	0.20	1.86	2.08	4.96	1.74
15B	97.07	1.02	3964.04	0.90	0.13	0.29	0.59	4.43	5.78	1.02
16	146.25	0.74	4928.41	0.55	0.16	1.86	0.38	9.65	8.77	0.93
17A	162.18	2.52	2960.69	0.48	0.19	0.20	1.08	2.58	8.19	0.96
17B	119.08	0.73	4501.92	0.86	0.12	0.95	0.13	4.25	7.59	0.11
18	128.97	0.17	3342.95	0.54	0.11	1.02	0.91	2.68	2.47	1.36
19	137.83	0.71	1202.91	0.52	0.13	3.90	1.82	0.79	5.81	0.53
20	43.26	0.73	4260.02	1.24	0.11	1.16	0.22	2.96	2.14	0.23
21	109.84	36.51	2800.33	3.37	0.09	3.52	1.33	1.95	5.21	2.77
22	107.61	3.43	14463.86	2.56	0.06	2.63	2.17	43.27	4.11	4.57
23	35.62	1.10	3752.80	0.75	0.09	0.40	0.24	5.91	4.65	0.52
24	88.28	1.05	3482.43	0.57	0.09	6.35	0.44	5.16	4.90	0.64
25	50.13	0.94	3815.16	0.51	0.31	1.24	0.40	6.58	6.12	0.05
26A	39.42	0.28	2713.39	1.19	0.09	0.76	0.50	1.83	2.78	0.83
26B	67.28	0.92	1708.22	0.31	0.07	0.73	3.97	2.10	7.12	1.16
27	150.30	1.38	10566.91	3.10	0.11	1.67	2.33	1.66	7.79	0.68
28	104.09	0.41	2238.76	0.93	0.13	3.53	1.17	1.25	3.54	0.46
29	70.82	0.70	1930.05	1.15	0.12	1.16	1.96	1.39	3.55	0.96
30A	25.70	0.89	3349.90	1.03	0.07	0.91	0.36	1.73	2.76	0.15
30B	12.06	0.20	1832.24	1.51	0.04	1.55	0.68	4.17	0.67	0.36
31	49.38	0.76	2217.15	1.52	0.10	0.04	1.15	2.10	6.51	0.89
32	54.88	0.94	1640.01	1.28	0.10	13.82	0.99	1.00	6.17	0.81
33	19.10	1.13	1628.70	1.43	0.04	1.93	1.75	5.03	1.66	0.91
34	14.01	0.37	607.67	0.46	0.06	1.12	0.62	2.01	4.14	0.23
35	164.54	2.81	2329.94	0.26	0.16	0.95	0.51	5.87	3.00	3.21
36A	35.43	0.20	586.91	0.82	0.05	10.23	0.83	4.37	2.35	0.55
36B	76.31	0.89	692.30	1.01	0.10	0.36	0.55	1.06	1.56	0.96
AJ1	95.81	12.23	3255.50	0.51	0.12	12.44	0.90	9.91	3.90	12.20
EMU1	108.51	0.81	7054.06	3.70	3.96	4.89	0.54	2.71	2.10	4.84
AJ2	218.03	0.75	3745.67	0.41	0.12	0.54	0.79	0.93	0.89	3.89
EMU2	162.91	2.73	4921.20	1.96	0.11	1.89	0.72	2.74	0.77	3.15

	Chromium		**Copper**		**Iron**		**Hafnium**		**Potassium**	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	0.71	2.51	11.43	0.56	460.62	0.94	0.50	1.18	124.92	1.55
1B	0.62	3.98	30.95	1.67	283.02	1.05	0.76	1.88	90.50	1.57
1C	0.76	1.54	13.85	0.31	490.45	0.64	0.63	0.78	194.16	0.20
1D	0.73	1.88	61.90	1.94	305.22	0.34	0.64	2.42	236.99	0.46
2	0.42	1.25	7.85	1.93	542.47	1.07	0.44	0.79	160.28	0.22
3	1.12	4.09	211.16	1.51	284.79	3.30	0.54	3.93	251.80	0.36
4A	0.31	0.05	44.15	0.71	116.19	0.72	0.50	0.36	127.92	0.68
4B	0.22	17.26	142.95	0.49	106.32	6.06	0.17	5.02	139.86	0.73
4C	0.26	1.80	157.71	0.59	97.64	1.17	0.65	1.75	247.39	0.20
5A	0.42	2.84	4.54	0.38	425.48	1.32	0.69	1.47	432.61	0.64
5B	0.34	0.22	99.15	1.41	95.25	2.42	0.45	2.53	277.38	0.52
6	0.18	1.83	39.96	0.26	297.10	1.34	0.56	1.52	1113.30	0.31
7A	0.18	1.72	6.89	7.03	395.42	0.34	0.57	1.80	1298.55	0.19
7B	0.26	5.39	5.96	1.10	420.39	0.50	0.44	1.37	962.51	0.36
8	1.37	1.88	28.47	0.87	355.68	0.16	0.72	4.44	1565.05	2.54
10	0.45	2.05	12.23	0.82	811.18	1.59	0.59	0.97	241.26	0.31
11	0.28	0.73	32.98	0.48	139.93	0.47	0.49	1.00	118.30	0.94
12	0.51	0.87	27.11	1.01	621.54	3.94	0.43	5.14	122.23	3.24
13	0.65	4.95	13.34	20.92	322.09	9.92	0.55	1.45	701.47	2.61
14	0.35	1.83	37.39	0.89	260.65	0.21	0.38	2.24	136.19	0.56
15A	1.01	6.25	10.94	3.90	479.41	0.65	0.53	0.75	112.51	0.68
15B	0.84	1.18	31.23	2.76	341.45	0.53	0.58	1.18	488.12	0.51
16	0.36	2.68	65.45	1.47	200.47	3.39	0.80	1.88	650.48	0.30
17A	1.49	1.47	29.64	2.02	411.56	0.51	0.60	0.33	165.48	0.51
17B	0.52	0.92	39.34	3.22	325.20	2.51	0.75	1.87	710.01	0.74
18	0.44	1.08	80.47	0.78	224.77	0.46	0.48	0.91	242.62	0.53
19	0.74	1.19	48.20	1.40	139.79	1.83	0.27	0.82	271.56	1.18
20	0.25	1.07	29.64	1.52	345.36	0.09	0.68	1.85	1741.96	1.55
21	0.33	8.75	36.74	2.27	96.96	4.09	0.58	1.55	245.83	2.34
22	0.30	2.34	148.54	0.31	37.11	2.28	3.77	2.98	201.79	0.75
23	0.34	5.48	16.48	3.73	353.49	0.89	0.61	2.67	1256.48	0.69
24	0.43	1.34	24.77	2.77	363.92	0.62	0.73	2.56	573.16	6.80
25	0.32	1.70	37.06	3.54	162.74	0.85	0.44	2.68	374.00	0.51
26A	0.22	2.20	22.89	1.43	409.96	0.11	0.44	2.36	976.21	0.79
26B	0.42	2.81	20.85	0.70	219.45	1.67	0.42	1.55	597.65	0.87
27	0.40	1.08	39.80	1.14	68.19	1.14	1.21	0.99	222.48	1.28
28	0.28	3.30	42.89	0.49	164.38	0.38	0.39	1.32	363.20	0.34
29	0.39	1.55	32.35	1.14	67.29	2.10	0.31	2.11	202.33	0.59
30A	0.42	0.24	8.33	1.67	368.15	1.29	0.60	2.92	1326.23	0.86
30B	0.14	8.72	63.05	0.62	188.78	1.62	0.45	2.05	1585.89	0.34
31	0.42	0.75	80.19	1.00	231.41	0.80	0.51	0.45	580.69	0.08
32	0.40	0.15	42.94	1.23	311.54	0.40	0.49	1.97	783.69	0.90
33	0.33	0.38	23.72	2.37	358.23	0.26	0.40	1.13	504.81	5.11
34	0.29	2.81	134.74	1.61	211.89	1.37	0.21	1.76	80.04	0.77
35	0.39	3.88	137.11	1.22	81.74	1.28	0.96	3.93	308.87	0.29
36A	0.20	21.79	73.76	1.91	120.54	0.59	0.23	1.65	140.84	0.59
36B	0.20	1.31	69.80	0.54	144.11	1.45	0.29	0.81	172.86	0.50
AJ1	0.53	13.61	0.47	16.77	492.00	13.58	0.48	12.46	235.89	12.26
EMU1	0.37	4.61	17.52	5.97	276.35	0.12	0.83	5.99	409.32	4.77
AJ2	0.30	0.98	1.76	4.53	317.40	0.83	0.56	0.68	184.07	0.13
EMU2	0.27	2.97	2.52	8.26	302.30	0.97	0.65	4.80	225.76	0.09

	Magnesium		**Manganese**		**Neodymium**		**Nickel**		**Phosphorous**	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	304.87	1.48	1113.00	0.82	0.61	1.60	1.42	0.98	38.49	2.77
1B	305.74	3.32	1430.21	1.21	3.45	3.68	2.49	1.31	68.87	1.75
1C	344.96	0.40	1533.16	1.14	0.41	0.16	1.95	0.34	41.46	2.12
1D	416.01	0.20	1278.62	1.22	0.66	10.36	1.51	0.69	80.30	1.25
2	260.98	0.22	866.95	0.78	0.44	0.32	1.33	1.25	90.49	1.09
3	247.01	0.83	2040.75	0.92	0.39	0.75	1.38	4.33	145.87	0.70
4A	680.14	1.00	809.06	1.11	3.58	0.11	1.95	1.04	13.03	1.22
4B	68.90	1.13	549.39	0.21	11.08	3.32	0.39	12.96	9.01	1.55
4C	734.93	0.35	716.28	1.08	2.94	0.35	1.78	1.57	28.54	0.26
5A	727.75	0.44	1289.90	0.19	0.13	2.95	1.67	0.58	361.43	2.31
5B	227.04	0.84	540.67	1.13	7.67	0.44	0.57	6.81	4.81	0.68
6	575.44	0.56	428.29	0.51	1.49	7.99	0.59	1.94	100.29	0.69
7A	1169.87	1.09	504.72	1.12	0.10	0.35	0.75	4.03	257.58	1.47
7B	933.89	0.96	373.09	0.64	0.12	1.64	0.82	20.08	121.25	1.11
8	738.58	0.20	2703.35	5.31	0.29	1.88	1.20	1.92	320.37	1.43
10	286.72	0.75	967.70	0.52	0.68	0.52	0.76	1.59	20.54	2.76
11	265.86	1.25	512.39	0.41	9.19	0.78	0.60	0.29	3.81	1.37
12	366.40	2.09	702.63	3.19	0.89	1.05	1.09	2.21	21.69	4.38
13	568.43	3.50	1451.09	1.51	4.09	24.21	1.45	3.57	197.15	1.95
14	299.90	1.03	547.27	0.08	7.54	0.84	0.58	1.86	14.22	0.42
15A	293.90	0.48	1667.01	0.80	0.94	0.28	1.21	2.26	10.63	5.29
15B	731.20	0.06	1473.39	0.47	0.47	3.56	1.39	1.26	115.30	1.50
16	522.92	2.06	1088.80	1.86	7.15	2.50	1.17	2.31	99.59	0.97
17A	325.56	0.75	2669.46	1.17	0.46	0.19	1.54	0.69	34.84	4.16
17B	417.86	0.72	1343.49	1.18	0.43	9.58	1.07	0.62	148.29	0.41
18	278.55	1.18	352.57	0.79	1.67	4.67	0.52	4.13	146.16	1.56
19	113.34	0.32	1683.45	1.72	9.93	0.13	0.46	0.49	108.88	0.89
20	1047.06	1.52	603.48	0.48	0.27	4.31	0.69	1.39	440.05	1.01
21	201.64	2.70	717.41	1.82	2.70	1.79	0.49	8.95	49.43	1.46
22	383.62	1.30	832.67	3.60	1.40	1.52	0.41	4.11	8.44	7.27
23	809.39	0.82	724.23	1.06	0.17	2.51	0.83	20.75	575.53	1.19
24	517.18	1.32	1031.03	0.84	0.20	1.16	0.72	1.61	297.29	1.22
25	899.82	1.43	651.75	2.02	2.25	1.19	0.81	1.08	141.73	1.53
26A	620.43	0.94	270.12	0.75	0.18	2.23	0.63	1.15	458.23	0.91
26B	389.04	0.99	962.28	1.32	6.63	0.83	0.87	2.06	34.50	1.38
27	349.42	1.35	1312.61	1.29	6.48	1.09	0.80	0.73	52.61	0.41
28	447.09	0.71	629.25	1.45	8.23	0.48	0.60	1.55	172.17	0.44
29	571.29	0.92	1186.88	1.03	8.59	0.88	0.37	0.87	30.05	0.93
30A	1161.12	0.08	556.26	0.88	0.08	2.34	0.48	1.38	365.24	0.84
30B	924.10	0.24	147.54	2.00	0.92	1.20	0.35	1.95	140.21	0.78
31	577.69	1.16	1199.02	1.27	4.06	3.44	0.62	0.40	340.79	0.66
32	419.80	0.63	1055.91	1.50	1.44	4.21	0.62	3.37	204.99	0.62
33	579.04	0.39	156.13	1.16	0.17	4.46	0.26	5.77	25.52	1.72
34	105.98	0.63	162.43	0.56	1.05	1.34	0.97	50.68	16.34	0.61
35	275.66	0.51	1356.49	0.54	19.13	0.55	2.34	1.01	26.64	1.13
36A	147.53	2.18	239.75	1.14	1.15	0.76	0.96	57.18	12.25	1.06
36B	116.82	0.89	476.97	1.13	2.97	1.32	0.39	1.23	19.36	0.28
AJ1	446.99	11.92	1327.78	0.72	0.37	12.02	1.24	12.46	31.29	14.18
EMU1	1377.23	4.54	766.09	7.02	1.84	3.04	3.50	5.83	24.30	2.94
AJ2	877.33	0.14	412.47	2.11	0.70	3.75	0.79	1.21	4.71	2.07
EMU2	1073.46	0.38	383.60	1.77	1.00	2.82	0.73	4.50	5.94	0.44

	Rubidium		**Sulfur**		**Strontium**		**Vanadium**		**Zinc**	
Sample	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE	mg kg^{-1}	%RSE
1A	1.13	0.61	71.71	1.46	4.26	1.06	1.52	5.50	16.67	1.56
1B	0.64	1.20	56.88	1.73	7.29	1.52	0.64	3.23	19.57	0.65
1C	1.19	0.45	85.42	0.24	5.90	0.73	2.09	1.19	20.63	1.03
1D	0.70	0.92	127.33	0.90	6.74	0.77	0.52	2.61	22.39	0.57
2	1.35	1.70	53.32	0.94	3.53	0.20	1.23	2.86	48.16	0.34
3	0.56	2.95	60.64	1.69	4.41	1.33	1.69	2.09	45.45	1.05
4A	0.22	1.29	58.34	5.11	4.46	0.77	0.33	1.07	18.94	0.61
4B	0.21	6.61	75.48	1.27	1.50	1.32	0.23	1.73	5.14	1.75
4C	0.21	0.81	74.96	1.40	7.24	0.74	0.32	0.98	71.36	0.92
5A	1.03	1.41	240.38	3.34	8.05	0.02	1.67	0.01	48.15	0.13
5B	0.19	2.13	167.89	1.15	3.91	1.61	0.14	3.32	5.66	1.15
6	0.78	0.88	48.44	1.24	4.69	0.20	1.69	6.98	12.58	1.76
7A	1.07	0.26	84.76	0.42	6.04	0.21	1.97	15.84	18.96	1.58
7B	1.10	0.37	61.20	2.01	4.91	0.65	1.84	13.44	14.96	1.82
8	0.69	0.81	77.12	8.10	6.74	5.68	2.82	0.52	25.84	0.21
10	2.01	1.52	73.61	0.63	5.19	0.38	2.07	6.07	15.64	1.19
11	0.34	0.84	29.81	2.28	4.27	1.19	0.27	1.14	2.49	0.96
12	1.55	2.29	70.51	3.37	3.49	2.28	1.73	1.84	21.09	3.18
13	0.73	11.40	75.68	11.62	4.32	4.44	2.22	2.45	15.40	3.06
14	0.63	0.75	29.47	9.60	3.35	0.48	0.32	5.76	6.56	1.38
15A	1.13	1.29	69.38	1.77	3.63	1.28	1.71	4.31	15.35	1.45
15B	0.80	0.42	120.99	1.04	5.61	0.67	1.41	8.17	16.78	0.13
16	0.43	2.93	66.91	5.23	7.88	1.17	0.65	2.07	25.04	2.06
17A	0.88	1.03	82.87	0.60	4.33	1.31	2.38	0.68	25.75	1.71
17B	0.76	2.09	80.62	0.96	7.51	0.81	1.54	6.11	42.59	1.28
18	0.57	1.81	65.61	1.07	4.45	0.40	0.47	1.32	14.74	1.78
19	0.20	4.28	21.69	7.37	1.91	5.21	0.61	0.31	8.22	1.38
20	0.88	0.39	115.00	2.43	8.21	0.49	1.51	3.12	34.13	1.98
21	0.18	4.51	58.13	2.63	5.41	1.86	0.46	2.07	5.37	2.65
22	0.05	6.72	106.90	43.47	44.93	2.93	0.58	0.18	9.46	3.77
23	0.90	0.50	81.84	1.34	7.01	1.08	2.46	2.84	43.96	1.13
24	0.88	0.24	77.58	13.62	7.07	1.46	2.12	3.50	40.36	0.56
25	0.37	1.79	64.58	2.90	4.07	1.74	1.22	5.42	29.77	0.07
26A	1.08	0.66	191.15	0.59	4.27	1.10	2.31	6.81	58.92	1.32
26B	0.52	0.90	41.37	1.74	2.77	1.19	0.54	2.28	6.25	1.42
27	0.07	6.31	94.74	1.27	8.47	6.51	0.57	0.58	17.67	1.11
28	0.37	0.47	47.42	6.72	3.16	2.99	0.41	0.11	20.51	1.29
29	0.08	12.47	30.50	13.48	2.78	0.73	0.46	1.32	10.54	0.13
30A	0.98	0.32	93.61	1.05	6.03	1.02	3.72	1.87	25.76	1.21
30B	0.48	1.12	101.23	0.89	3.11	2.57	5.53	1.41	16.75	0.06
31	0.51	1.12	80.62	6.92	4.46	1.10	3.32	0.71	29.80	0.40
32	0.71	0.38	52.85	5.16	3.55	2.11	3.65	2.45	17.68	1.06
33	0.95	1.08	95.43	2.08	2.62	1.81	4.84	0.30	8.19	0.32
34	0.52	0.82	37.57	1.22	1.27	1.37	0.40	1.02	11.68	0.78
35	0.10	3.54	48.56	0.83	11.12	1.42	0.61	3.14	53.75	0.70
36A	0.28	3.23	27.88	17.85	1.64	7.08	0.49	2.16	5.76	3.85
36B	0.34	1.33	37.07	0.69	2.56	1.20	0.40	1.24	12.65	0.43
AJ1	1.26	13.35	86.64	1.03	5.39	0.84	1.68	11.20	22.65	12.74
EMU1	0.78	4.36	196.50	6.56	9.46	5.20	0.36	5.18	142.28	5.70
AJ2	0.84	0.60	55.37	1.42	5.83	0.65	0.19	0.18	21.52	0.64
EMU2	0.82	0.45	80.72	0.51	7.17	0.42	0.18	2.90	14.65	1.20

Sample	Zirconium mg kg^{-1}	%RSE
1A	2.07	5.98
1B	4.89	1.41
1C	1.83	1.02
1D	2.05	7.80
2	2.58	2.06
3	1.37	18.32
4A	4.75	0.33
4B	2.79	2.65
4C	3.22	1.11
5A	0.22	37.07
5B	3.23	1.62
6	5.87	0.41
7A	1.97	7.31
7B	1.88	10.65
8	2.01	1.21
10	2.72	4.75
11	5.04	0.76
12	2.12	3.26
13	3.52	14.63
14	5.77	1.15
15A	2.88	7.55
15B	1.95	3.95
16	3.36	5.85
17A	2.35	2.13
17B	3.55	3.15
18	3.44	0.36
19	3.16	0.47
20	2.58	0.66
21	4.04	3.37
22	0.32	8.14
23	2.75	3.14
24	2.97	3.52
25	4.22	0.53
26A	1.74	8.20
26B	6.03	1.17
27	3.58	0.07
28	4.58	0.30
29	2.69	2.56
30A	2.77	0.75
30B	5.95	1.95
31	4.29	0.51
32	5.02	0.94
33	4.24	0.63
34	2.18	0.24
35	1.29	3.03
36A	2.81	14.09
36B	2.03	0.42
AJ1	0.77	15.16
EMU1	3.36	9.55
AJ2	2.85	2.77
EMU2	2.74	3.36

D

SAS Programs Used

Cluster analysis and Canonical Discriminant Analysis

```
options nodate;
data test;
   set a;
run;
proc standard data=test out=stand mean=0 std=1;
var ca -- zr;
proc fastclus data=stand out=clust
maxclusters=8 maxiter=10 least=2;
var ca -- zr;
run;
proc freq data=clust; tables sample*cluster;
run;
proc candisc data=Clust distance anova out=Can;
      class Cluster;
      var ca -- zr;
   legend1 frame cframe=ligr label=none cborder=black
           position=center value=(justify=center);
   axis1 label=(angle=90 rotate=0) minor=none;
   axis2 minor=none;
proc cluster data=can outtree=Tree method=eml
                ccc pseudo print=15;
      var can1 -- can3;
      id sample;
   run;
goptions vsize=8in htext=1.75pct htitle=2.5pct;
   axis1 order=(0 to 1 by 0.2);
   proc tree data=Tree out=New nclusters=8
            graphics haxis=axis1 horizontal;
      height _rsq_;
      copy can1 -- can3;
      id sample;
   run;
proc freq data=new; tables sample*cluster;
run;
legend1 frame cframe=ligr cborder=black
           position=center value=(justify=center);

   axis1 label=(angle=90 rotate=0) minor=none;
   axis2 minor=none;

   proc gplot data=New ;
      plot can2*can1=cluster/frame cframe=ligr
                     legend=legend1 vaxis=axis1 haxis=axis2;
symbol value=dot;
   run;
   proc gplot data=New ;
      plot can3*can1=cluster/frame cframe=ligr
                     legend=legend1 vaxis=axis1 haxis=axis2;
symbol value=dot;
   run;
proc gplot data=Can;
      plot Can2*Can1=cluster/frame cframe=white
```

```
                     legend=legend1 vaxis=axis1 haxis=axis2;
symbol value=dot;
   run;
proc gplot data=Can;
      plot Can3*Can1=cluster/frame cframe=white
                     legend=legend1 vaxis=axis1 haxis=axis2;
symbol value=dot;
   run;
quit;
```

Discriminant Function Analysis

```
proc stepdisc data=v;
      var al--zr; class Group;
   run;
```

Descriptive Statistics and Frequency Plots

```
options nodate;
data test;
   set a;
run;
proc capability data=test;
var li;
histogram /normal midpoints = 8 to 38 by 1.5
kernel(c = 0.3 0.4 0.5 mise
                                l = 1 20 2 34
                                color=yellow)
                         cfill  = blue
                         cframe = ligr;
title "Li Distribution";

run;
```

Vita

Robert Alexander Hull was born in Bristol, Tennessee, on January 10, 1984, the son of Alexander Harold Hull III, and Nancy McKinney Hull. He attended Tennessee High School, where he graduated as a Valedictorian in 2002. Then in 2006 he graduated summa cum laude with a Bachelor of Science degree in Environmental and Soil Science from the University of Tennessee-Knoxville. He received an award for Top Scholar in Environmental and Soil Science all four years of his undergraduate education. He is a member of the Soil Science Society of America and the American Water Resources Association. He is also a member of a number of honor societies including: Gamma Sigma Delta Agricultural Honor Society, Phi Kappa Phi National Honor Society, Phi Eta Sigma-National Honor Society, Mortar Board National Honor Society, and Golden Key International Honor Society. He served as an undergraduate researcher at the University of Colorado-Boulder in the summer of 2004. He then worked as a campground manager for the Tennessee Valley Authority in the summers of 2005 and 2006. Since the fall of 2006 he has served as a Research Assistant in the Biosystems Engineering and Soil Science Department at the University of Tennessee-Knoxville. He will be receiving a Master's of Science degree in Environmental and Soil Science from the University of Tennessee-Knoxville in December of 2008.