

7-22-1992

Depth-related variations of trace metal abundances in south Florida sediments

Donna Wade Booth

Florida International University

DOI: 10.25148/etd.FI14051193

Follow this and additional works at: <https://digitalcommons.fiu.edu/etd>



Part of the [Geology Commons](#)

Recommended Citation

Booth, Donna Wade, "Depth-related variations of trace metal abundances in south Florida sediments" (1992). *FIU Electronic Theses and Dissertations*. 1730.

<https://digitalcommons.fiu.edu/etd/1730>

This work is brought to you for free and open access by the University Graduate School at FIU Digital Commons. It has been accepted for inclusion in FIU Electronic Theses and Dissertations by an authorized administrator of FIU Digital Commons. For more information, please contact dcc@fiu.edu.

FLORIDA INTERNATIONAL UNIVERSITY
Miami, Florida

Depth Related Variations of Trace Metal Abundances
in South Florida Sediments

A thesis submitted in partial satisfaction of the
requirements for the degree of Master of Science
in Geology

by

Donna Wade Booth

1993

ABSTRACT OF THE THESIS

Depth Related Variations of Trace Metal Abundances in South Florida Sediments

by

Donna Wade Booth

Florida International University, 1993

Miami, Florida

Professor Rosemary Hickey-Vargas, Major Professor

Variations in trace element abundances with depth in soils and sediments may be due to natural processes or reflect anthropogenic influences. The depth related variations of five major elements (Fe, Si, Al, Ca and Mg), seventeen trace elements (Mn, Cr, Ti, P, Ni, Ba, Sc, Sr, Sb, Zn, Pb, Cd, Co, V, Be, Cu and Y) and volatile loss patterns were examined for sediment cores from five sites in South Florida (Lake Okeechobee, SFWMD Water Conservation area 3B, F.I.U., the Everglades and Chekika State Recreation Area). Principal component analysis of the chemical data combined with microscopic examination of the soils reveal that depth-related variations can be explained by varying proportions of three natural soil constituents and one anthropogenic component. The results can be used as a geochemical baseline for human influence on South Florida soils.

To Professors Hickey-Vargas, Clement, and Maurrasse:

This thesis, having been approved in respect to form and mechanical execution, is referred to you for judgement upon its substantial merit.

Dean Arthur Herriott
College of Arts and Sciences

The thesis of Donna Wade Booth is approved.

Bradford Clement

Florentin Maurrasse

Rosemary Hickey-Vargas,
Major Professor

Date of Examination: 22 July 1992

Dean Richard Campbell
Division of Graduate Studies

Florida International University, 1993

ACKNOWLEDGEMENTS

Many people were instrumental in the completion of this thesis. I am very appreciative of their support and encouragement. I would like to thank Tom Beasley of the geology department and Mr. Wu of the physics department for their help in sample preparation. Thank you to Dr. Charles Connor for the principal component analysis, and to Dr. Grenville Draper for his assistance with the computers. Many thanks to my thesis committee for their critical review of this work. I would like to thank Dr. Rosemary Hickey-Vargas for her invaluable advice, assistance and encouragement through the course of this work. I would like to close this by thanking my husband Frank and son Brian for their consideration and understanding during this time.

TABLE OF CONTENTS

CHAPTER ONE INTRODUCTION	1
CHAPTER TWO BACKGROUND INFORMATION	
Geographic and geologic setting of the South Florida region	5
Origin and composition of soils	7
Sources of metals in soils	9
Known geochemical behavior of elements	11
CHAPTER THREE SAMPLE DESCRIPTIONS	21
Core descriptions	
LOTI	23
WCA3B-2	26
FIU	29
FCEG	33
CSRA	37
CHAPTER FOUR CHEMICAL ANALYSIS	41
CHAPTER FIVE RESULTS AND INTERPRETATIONS	43
Results	43
Data Analysis	43
Discussion	117
Summary and Conclusions	129
REFERENCES	135
APPENDICES	136

LIST OF FIGURES

1	Map of South Florida with core sites	4
2	Geologic map of South Florida	6
3	Chemical analysis flow chart	42
4	Plot of <550° C volatile loss vs Mn	49
5	Plot of >550° C volatile loss vs Mn	49
6-25	FIU elements vs depth plots	52-61
26-45	CSRA elements vs depth plots	62-71
46-65	LOTI elements vs depth plots	72-81
66-85	FCEG elements vs depth plots	82-91
86-91	CSRA enrichment/depletion of organic and carbonate fractions relative to Al	95-97
92-96	FCEG enrichment/depletion of organic and carbonate fractions relative to Al	98-100
97-104	FIU enrichment/depletion of organic and carbonate fractions relative to Al	101-104
105-108	LOTI enrichment/depletion of organic and carbonate fractions relative to Al	105-106
109-112	WCA3B-2 enrichment/depletion of organic and carbonate fractions relative to Al	107-108
113	Ca vs Sr from FIU core	115
114	Fe vs Cd from LOTI core	115
115	FCEG <550° C volatile loss vs Cd	116
116	FIU >550° C volatile loss vs Ca	116
117	Principal components 1 vs 3	119

118	Principal components 2 vs 3	119
119	Principal components 1 vs 2	120

LIST OF TABLES

1	Known geochemical behavior of the elements	12
2	World and Florida ranges	45
3	Depth comparison between cores	46
4	Peak element concentrations with depth	47
5	Enrichment/depletion of elements in organic and carbonate fractions relative to Al	109
6	Correlation matrix of element vs element	111-113
7	Correlation coefficients of elements vs volatile loss	114
8	Volatile loss study	149

LIST OF PLATES

1	Core from Lake Okeechobee	25
2	Core from Water Conservation District 3B	28
3	Core from Florida International University	32
4	Core from Everglades	36
5	Core from Chekika Recreation Area	40

LIST OF APPENDICES

A	Sites sampled but not analyzed	136
B	Sample collection	140
C	Sample preparation and chemical analysis	142
D	Volatile loss procedure and results	148
E	Raw data and data quality	150
F	Whole soil concentrations corrected for dilution	169
G	Definitions	173

CHAPTER ONE

INTRODUCTION

In recent decades a considerable amount of work has been carried out on trace element concentration and behavior in the earth surface environments. Studies have included analyses of trace element concentrations in plants, animals, soils and sediments in different environments such as the oceans, rivers, lakes, wetlands and forests. Background concentrations accepted as natural and presumably safe in the case of toxic elements have been determined based on concentrations commonly encountered in these studies. For example, since soils develop in situ from inorganic (rock) and organic parent materials, trace and major element concentrations should reflect natural processes such as weathering and the accumulation of organic material in the soil profile. Anthropogenic inputs of trace elements in contrast, should produce distinct geochemical signals.

South Florida presents a unique situation for study of background trace element concentrations in soils because of its unique natural environment. Many South Florida soils contain a large proportion of organic material as reflected by the proliferation in the Holocene of the Everglades, a large freshwater marsh. Since organic matter acts as a sink for certain elements, a high organic content will influence the trace element composition of a soil.

The large amount of organic matter in the area is related to the water saturated conditions for a greater part of the year as South Florida receives runoff of fresh water from Lake Okeechobee, and receives steady as well as significant precipitation (150 cm/yr) in non-drought years. Thus, some

areas are water saturated except during dry periods. In addition, water is always abundant close to the surface because of the presence of the Biscayne aquifer, a surface limestone aquifer. The overall flow pattern of water in South Florida is southward through agricultural areas and along natural depressions or sloughs, where eventually it reaches the man-made canal systems, the Gulf of Mexico, or Florida Bay. Therefore, sediments and trace elements are transported over a wide area in the flow and deposited along the route.

Vertical variations in the geochemistry of soils and sediments can result from a variety of processes. In underwater environments, vertical changes largely reflect time-related variations in inputs of transported materials. In subaerial environments, vertical changes are commonly related to the development of a soil profile by progressive weathering of bedrock and downward migration of soluble elements. In the South Florida environment, alternate periods of wet and dry conditions lead to unique processes affecting vertical geochemical profiles. Fluctuations in the water table causes upward and downward migration of soluble elements within the soil column. In addition the alternate proliferation and drying of plant matter produces significant changes in the organic content of soils and sediments. These processes should be reflected in unique geochemical signatures.

This thesis addresses the causes of depth-related geochemical variations in South Florida soils and sediments.

The purpose of this study is twofold:

- 1) to determine variations in elemental abundances with depth in South Florida soils and explain the observations based on geochemical and sedimentological principles.

- 2) to determine if variations produced by natural and anthropogenic processes can be distinguished, including the variations produced by vertical migration and changes in whole soil composition.

To this end cores of soils and sediments were collected from South Florida sites including Lake Okeechobee, South Florida Water Management District Conservation Area 3B, Florida International University, the Everglades and Chekika State Recreation Area (Fig. 1). The cores were divided into vertical segments and geochemical analyses were conducted on the carbonate and organic fractions (humic and fulvic acids) and the whole soil (bulk) composition of each segment. Major soil elements Fe, Al, Si, Ca and Mg; and trace elements P, Ni, Ba, Mn, Cr, Ti, Sc, Sr, Sb, Zn, Pb, Cd, Co, V, Be, Cu and Y were determined. Interpretations are based on: 1) a knowledge of the sampling sites, including their history of use; 2) microscopic examination of the core segments; 3) statistical interpretation of chemical trends and 4) principles of elemental behavior in natural materials. The results of the present study contribute important information on the geochemical behaviors of major and trace elements in South Florida soils and sediments, including "baseline" concentrations produced by natural processes, against which anthropogenic influence can be measured. Furthermore, the present results add to the accumulating body of knowledge which deals with the abundances and behaviors of trace elements in soils and sediments worldwide.

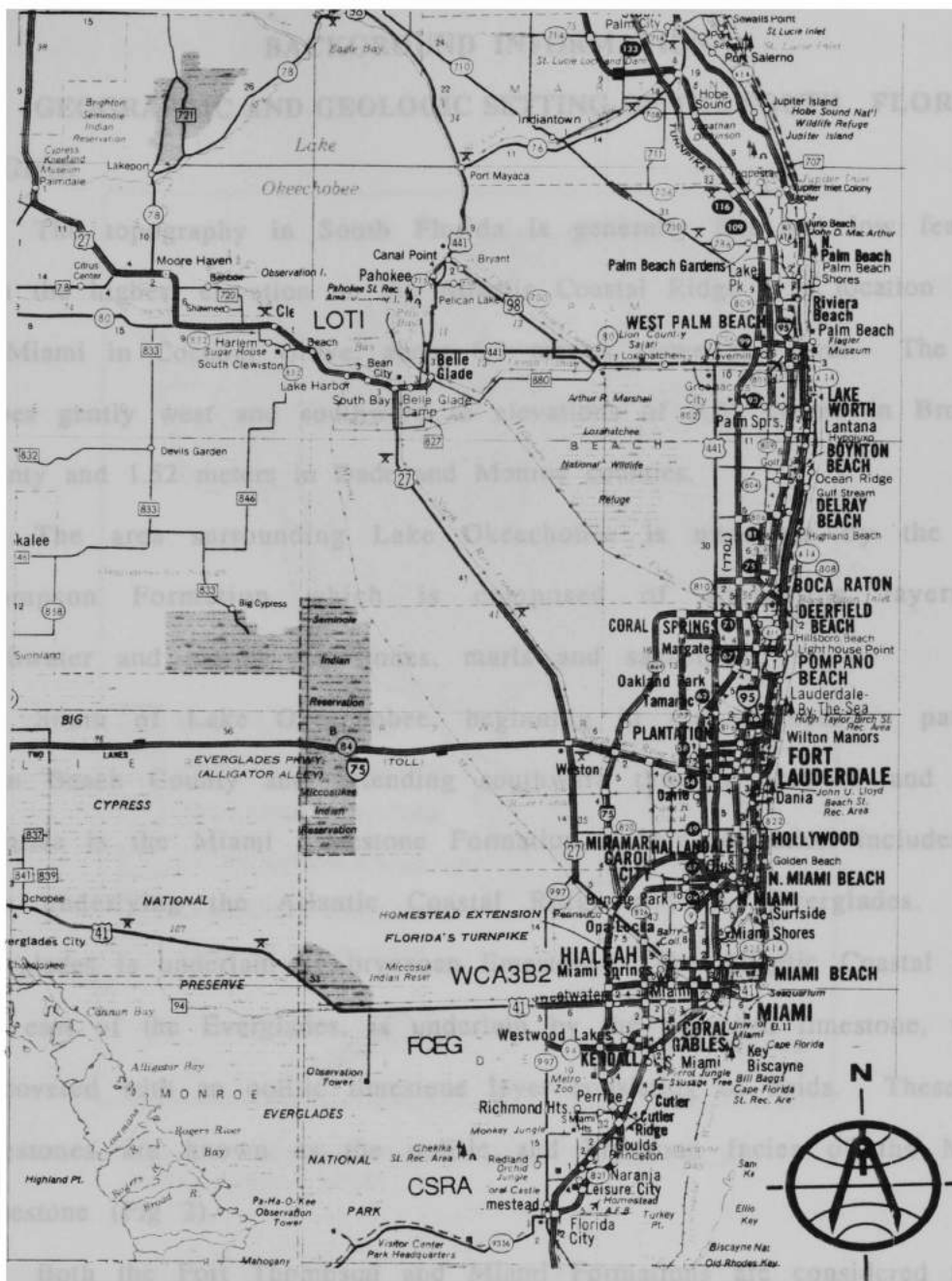


Fig. 1: Map of South Florida with core sites (from Rand McNally, 1991).

CHAPTER TWO

BACKGROUND INFORMATION

1. GEOGRAPHIC AND GEOLOGIC SETTING OF THE SOUTH FLORIDA REGION

The topography in South Florida is generally flat and low featured with the highest elevation on the Atlantic Coastal Ridge at a location south of Miami in Coconut Grove, about 6.1 meters above sea level. The land slopes gently west and southward to elevations of 3.05 meters in Broward County and 1.52 meters in Dade and Monroe counties.

The area surrounding Lake Okeechobee is underlain by the Fort Thompson Formation which is composed of alternating layers of freshwater and marine limestones, marls and sandstones.

South of Lake Okeechobee, beginning in the southeastern part of Palm Beach County and extending southward through Broward and Dade counties is the Miami Limestone Formation. This formation includes the rock underlying the Atlantic Coastal Ridge and the Everglades. The Everglades is underlain by bryozoan limestone. The Atlantic Coastal Ridge lies east of the Everglades, is underlain by the bryozoan limestone, which is covered with an oolitic limestone layer consisting of ooids. These two limestones are known as the oolitic and bryozoan facies of the Miami Limestone (Fig 2).

Both the Fort Thompson and Miami Formations are considered to be approximately 100,000 years old (Hoffmeister, 1974).

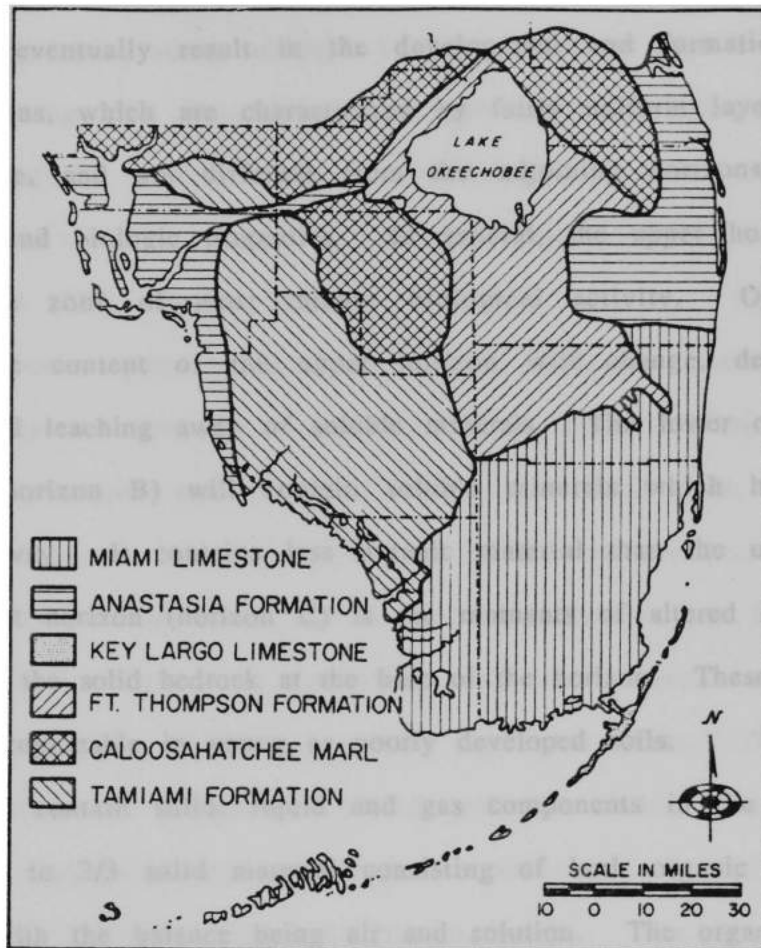


Fig. 2: Geologic map of South Florida (from Hoffmeister, 1974).

2. ORIGIN AND COMPOSITION OF SOILS

Soils develop slowly over time as a result of the local or regional climate which influences physical and chemical weathering of bedrock and the gradual accumulation of organic material. These interacting processes eventually result in the development and formation of mature soil horizons, which are characterized by fairly uniform layers parallel to the surface, and are different from the adjoining horizons in physical, chemical and biologic properties. In general, the upper horizon (horizon A) is the zone of most intense biological activity. Over time the mineralogic content of the upper horizon will change, decreasing with the gradual leaching away of soluble minerals. The lower or intermediate horizon (horizon B) will contain soluble minerals which have not been leached away. It contains less organic material than the upper horizon. The lowest horizon (horizon C) is the remnants of altered bedrock which grade into the solid bedrock at the base of the horizon. These horizons may not be recognizable in young or poorly developed soils.

Soils contain solid, liquid and gas components in the proportion of about 1/2 to 2/3 solid material consisting of both organic and inorganic matters, with the balance being air and solution. The organic fraction of soils in general is typically less than 10% of the total soil, and in most soils does not exceed 2%. However, in certain soils, peat and muck soils, which are found in South Florida, the organic fraction may account for up to 50% of the soil volume. Peat soils are composed of undecomposed or slightly decomposed organic matter accumulated under water in anaerobic conditions. Muck soils consist of the very decomposed organic material in which the original plant components are not recognizable. Muck is

usually darker than peat and contains more minerals (Sposito, 1989; Adriano, 1986).

The coarse fraction of soils contain all the materials which are recognizable as unaltered or partially altered flora or fauna, along with mineral aggregates, rocks, etcetera having a diameter greater than 1 mm. The remaining fine fraction consists of mineral particulates, and the organic material which cannot be positively identified with complete accuracy and which is known as humus (FitzPatrick, 1979; Kabata-Pendias and Pendias, 1984; Sposito, 1989).

The humus plays a significant role as it absorbs quantities of water, adds solidity and structure to soil, exhibits a strong binding capacity, and can be flocculated and dispersed like clays (FitzPatrick, 1979). The structure of humus is complex, and the biochemical processes by which it forms is not yet completely understood (Kabata-Pendias and Pendias, 1984; Sposito, 1989). Humus is categorized as having humic and non-humic substances. Humic substances are dark organic materials. The structure of humic substances is that of coiled polymer chains which contain a relatively high proportion of oxygen containing functional groups such as phenolic hydroxyl, carboxyl and carbonyls. The large number of functional groups in the matrices bind with trace elements known to have affinity for organic matter. Humic substances have the ability to react chemically with metal ions and this is reflected in the present study as one of the main carriers of ions found in the samples.

Humic substances may be further divided into the fractions of humic acid, fulvic acid and humin, which are similar in structure but are fractionated on the basis of their differing solubility reactions. Humic

substances are adsorbed by oxides and clays and have the ability to form organo-metallic complexes with cations.

Because of these characteristics soils are an important geochemical sink, acting as both a reservoir and a natural buffer for trace elements. Thus, soil characteristics (e.g. organic matter present in the soil) influence the transport of trace elements, their accumulation and availability to plants (Kabata-Pendias and Pendias, 1984; Sposito, 1989). In addition to trace elements associated with the organic components of soils, water borne trace elements exist in soluble forms for short periods of time, being present mainly as suspended colloids or particulates, and may become fixed to minerals or organic materials. (Kabata-Pendias and Pendias, 1984).

3. SOURCES OF METALS IN SOILS

As discussed in the preceding section, soils not influenced by anthropogenic input derive their metal content from the weathering of the parent material from which they evolved. In the case of South Florida which is underlain by limestone formations, the natural major mineral constituent is calcium carbonate in the form of calcite and aragonite. However, these minerals rarely occur naturally in compositionally pure phases, and the elements Mg, Fe, Sr, Ba, Mn, Co, Cd, Cu, Ni, Pb and Zn are frequently included in their mineralogy as a trace element (Brownlow, 1979; Sposito, 1989).

The redistribution of trace elements in soil results from leaching, adsorption onto soil surfaces, translocation, incorporation into plants and their products of decay or co-precipitation (Appendix G) of minerals

(FitzPatrick, 1979; Kabata-Pendias and Pendias, 1984; Bohn, McNeal and O'Connor, 1985; Sposito, 1989). For instance, soils that experience periods of water saturation may show mottling, as a result of the reduction of leached iron which produces soil colors characteristic of the valance state of iron. These color changes can be a helpful characteristic in identifying areas subject to periodic saturation, with reddish colors associated with Fe^{3+} and blue or grayish colors associated with Fe^{2+} .

Anthropogenic influences are chronicled by increasing levels of trace elements, not limited to those elements which are found in the parent material. The sources of these elements are numerous, including, but not limited to, input from fertilizer, pesticides, herbicides, sewage sludge, animal wastes, municipal refuse, waste and irrigation waters, fossil fuel combustion, mining and smelting operations, and auto emissions. Since trace elements are released into the atmosphere and hydrosphere and can be transported and deposited over great distances, the sources of increased levels of trace elements is not necessarily a localized or point-source phenomenon.

Dissolved constituents in soils are constantly being mobilized by meteoric waters which percolate downward and flow laterally carrying along different types of ions. The translocated ions can be sorbed by soils or sediments, or may be absorbed or adsorbed by plants. The uptake of trace elements by plants, along with the strong affinity humic substances have for certain trace elements can lead to the accumulation of trace elements at or near the soil surface. The primary method of trace element uptake by plants is through active and passive adsorption by roots. Trace elements are also adsorbed by foliar uptake through non-metabolic

cuticular penetration (passive adsorption from aerial sources through the leaves) and metabolic mechanisms accounting for element accumulations across a concentration gradient (active transport across the plasma membrane into the cell protoplast), as well as absorption by plant roots.

4. KNOWN GEOCHEMICAL BEHAVIORS OF ELEMENTS

Certain elements exhibit similar chemical behaviors that are reflected by their placement on the periodic table. The knowledge of elemental behavior provides a useful tool in the use of elements as tracers for other elements, materials or processes.

Twenty-two elements were selected for investigation in this study. This section and accompanying table (Table 1) summarize the known geochemical behaviors of the elements in this study.

Geochemical Behaviors of Main Elements in Soils

Aluminum

Aluminum occurs in soils as the stable ion Al^{3+} , and along with oxygen containing ligands forms in the solid phase hydroxide $Al(OH)_3$. This form and other Al hydroxides develop during weathering and form the structural components of clay minerals. Aluminum hydroxides are more mobile in acidic soils, and are not very soluble in the moderate range of pH (5-8), and their general solubility decrease with age. Aluminum is known to be associated with the trace elements beryllium, yttrium and chromium.

TABLE 1
A SUMMARY OF KNOWN GEOCHEMICAL BEHAVIORS OF THE
ELEMENTS IN THIS STUDY

1. Major soil constituents: Fe, Si, Al, Ca, Mg
2. Trace elements from carbonates: Sr, Mg, Ba, Mn, Fe, Cd, Pb, Zn, Co, Cu, Ni, Sc, Be
3. Trace elements from silicates/clays: Fe, Mn, Ti, Cr, Y, V, Co, Zn, Pb, Cu, Be, Sc, Sr
4. Toxic elements from anthropogenic sources: Cd, Cu, Pb, Co, Be, Ba, Mn, Zn, Ni, Fe, Cr, Sr, Sb
5. Elements from anthropogenic pollutants: Pb, Ni, P, Cd, Cr, Cu, Be, Ba, Mn, Zn, Fe, V, Co, Sb
6. Elements known to have a strong organic affinity: Be, Sb, Cd, Ni, Cu, Zn, Mn

Antimony

Antimony occurs usually as Sb^{3+} and infrequently as Sb^{5+} . Virtually nothing is known about its weathering reactions and behavior in soils. It is found in coal, peat and Fe hydroxides (Kabata-Pendias and Pendias, 1984), and if present in soils in a soluble form probably is substituting for P^{5+} in phosphates (Adriano, 1986).

Barium

Barium is most often associated with potassium bearing minerals because its ionic radius is so similar to K^{+} . Barium is released through weathering of potassium bearing minerals, but its mobility seems to be limited in soils due to the fact that it is concentrated into manganese and phosphorous concretions and minerals, and is easily precipitated into sulfates (Kabata-Pendias and Pendias, 1984).

Beryllium

Beryllium is an alkaline earth and may substitute for calcium, but it is not replaced by the other alkaline earth metals (Mg, Sr, Ba) due to its smaller atomic size. Beryllium forms complex organo-metallic compounds and accumulates in organic materials (plants and the humus of soils), thus coals in some cases may be enriched in this metal and combustion result in beryllium being released into the atmosphere (Adriano, 1986). The most common form in soils is Be^{2+} , but more complex forms also occur [$\text{Be}(\text{OH})\text{CO}_3$] (Kabata-Pendias and Pendias, 1984). Soluble salts of beryllium, BeCl_2 and BeSO_4 are fairly mobile in soils.

Cadmium

Cadmium like zinc and mercury, is a transition metal of group IIB of the periodic table and its natural concentration in soils is derived from the parent rock. The abundances of cadmium are generally low, less than 1.1 ppm on average (except for soils derived from shales or near cadmium bearing deposits or impacted by anthropogenic activity). Cadmium exists in a variety of forms in soils; incorporated as an oxide, hydroxide or hydrous oxide of Fe or Mn particulates, or as a coating on clays. It is adsorbed onto organic particulates, and forms chelates with organic matter as well as stable sulfides and ionic species in soil solutions. Anthropogenic impact in its abundance is significant by increased concentrations in humus enriched near surface layers. The largest anthropogenic sources of Cd are atmospheric fallout from smelting operations, application of sewage sludge and phosphatic fertilizers (Adriano, 1986).

Calcium

Calcium tends to form simple ionic species and coordinates with oxygen donors, e.g. CaCO_3 . The most common cation in solutions of most soils is Ca^{2+} , and a high concentration of this ion is an indication of a near neutral pH. The trace elements most commonly associated with calcium are magnesium, strontium and barium; also commonly found are iron, manganese, cobalt, cadmium, copper, nickel, lead, uranium, and zinc. Magnesium is the most prevalent as some calcitic skeletal materials contain abundant magnesium carbonate (Brownlow, 1979).

Chromium

Chromium in soils occurs in various oxidation states, with Cr^{3+} and Cr^{6+} being the most common. The III form is similar in geochemical properties and ionic size to Al^{3+} and Fe^{3+} , and is more stable than the more oxidized state. Chromium also forms complex ions, e.g. $\text{Cr}(\text{OH})^{2+}$, CrO_4^{2-} . Much chromium in soils occurs as Cr^{3+} in Fe or Cr oxides but also complexes with humic and fulvic acid (Adriano, 1986). In soils of pH greater than 5.5 Cr^{3+} exhibits limited mobility as it precipitates, except when organically complexed. The more soluble Cr^{6+} form is more readily sorbed by clays and oxides in acid conditions and more mobile in alkaline conditions. Chromium which is added to the soil as a result of anthropogenic activity is usually accumulated in the thin surface layer.

Cobalt

Cobalt follows the general distribution of iron, being found in many Fe-bearing minerals. Cobalt is not mobile as a soluble phase in soils except during weathering in an oxidizing acid environment. It forms Co^{2+} and Co^{3+} oxidation states and is sorbed easily by Fe and Mn oxides. The profile of Co in soils may resemble that of Fe, or Mn if enrichment of Mn minerals exists in that particular soil. Cobalt forms organic complexes and is mobile in soils in a chelated form.

Copper

Copper occurs in the oxidation state Cu^+ and Cu^{2+} , and can substitute for Fe^{2+} , Mg^{2+} , and Zn^{2+} . It exists as the native metal and in compounds

such as sulfides and oxides. The copper content of a pristine soil will reflect the Cu content of its parent material and will show a fairly uniform distribution in a soil profile. Copper is adsorbed onto Mn, Fe and Al oxides, and clays, and is adsorbed and complexed by organic matter. It is one of the more immobile trace elements when bound in soils. When delivered to a soil, e.g. from atmospheric fallout or direct application, it tends to remain in place because it is so strongly fixed by organic materials, the oxides and clays. Therefore, copper enrichment occurs within the first few centimeters at the top of the soil profile.

Iron

Iron is one of the most prevalent elements in the lithosphere, it occurs in soils primarily as small particulates of oxides and hydroxides or as surface coatings on other minerals. It also forms mobile organic complexes, and occurs primarily as chelates in organic rich soils allowing Fe to mobilize between horizons and be leached from the soil. In soils that are periodically water saturated increased solubility of iron occurs due to the reduction of Fe^{3+} to Fe^{2+} .

Lead

Lead exists primarily in the oxidation states Pb^{2+} and is known to occur less frequently as Pb^{4+} . It occurs in many different minerals with PbS , galena, being the most common. Lead also substitutes for K, Sr, Ba, Na, and Ca, so it is present as a trace element in other minerals as well. As lead is weathered out it is adsorbed onto Mn, Fe, and Al oxides. The natural lead concentration in soils is derived from the parent material, but lead

pollution (from industrial and automobile emissions) is so widespread now that soils are likely to be enriched. The accumulation of lead often observed at the surface of the soil profile is thought to result from its fixation by organic matter.

Magnesium

Magnesium occurs as a divalent cation, is adsorbed by Fe and Mn oxides, can substitute for calcium and be replaced by some of the same trace elements that replace Ca^{2+} , i.e. Sr, Ba, Pb.

Manganese

Manganese is one of the more abundant elements in the lithosphere. It is similar in behavior and natural occurrence to iron. Manganese exists commonly in three oxidation states, 2+, 3+ and 4+. It is widely distributed, forms oxide and hydroxide coatings on soil particles. The ionic size of Mn is similar to Fe, Ca and Mg, allowing substitution for these elements in a wide variety of minerals in igneous, sedimentary and metamorphic rocks. Higher concentrations of Mn have been noted for soils which contain large amounts of organic material. This reflects fixation of manganese by organic complexing, and may result in higher concentrations in surface soils where manganese has been added by anthropogenic means, e.g. sewage sludge. Manganese also concentrates in horizons where enrichment of iron oxides and hydroxides have occurred.

Nickel

Nickel distribution is similar to iron, as is its behavior. Nickel is mobile as Ni^{2+} , relatively stable in aqueous solution and may be transported over far distances. Nickel occurs as soluble chelates or other organic compounds in surface materials, and also co-precipitates with Fe and Mn oxides. Although widely distributed in the natural environment, Ni has become a pollutant as a result of atmospheric emissions from fossil fuel combustion, smelting operations and the surface applications of phosphate fertilizers and sewage sludge.

Phosphorus

Phosphorus exists in soils as the only stable oxidation state, phosphate (PO_4), and forms complex mixtures of iron, aluminum and calcium phosphates. It competes with arsenic for chemical binding sites in these mixtures. Some rock phosphates are enriched in trace elements, e.g. Cd, Ba, Cu, Mn, Pb, Sr, Zn and others. The application of phosphatic fertilizers can carry these trace elements into the environment.

Scandium

Scandium occurs as Sc^{3+} and can substitute for Al^{3+} , Fe^{3+} , Ti^{3+} , and Y^{3+} . It is found in ferromagnesian minerals, e.g. pyroxene and hornblende, and forms complexes with phosphates, and sulfates. It has been detected in ash residues of some coals, fuel oils and peat which could indicate future environmental enrichment due to atmospheric fallout from fossil fuels combustion (Kabata-Pendias and Pendias, 1984).

Silicon

Silicon is one of the most stable and abundant elements in soils occurring in quartz minerals and amorphous silicates.

Strontium

Strontium is a fairly common element in the lithosphere whose concentration in soils is dependent upon the parent rock and climate. It is biogenically precipitated as a trace element in the calcareous tests of invertebrates, and during weathering is readily incorporated into clays and forms chelates.

Titanium

Like silicon, titanium is also abundant in the lithosphere. It most commonly occurs as Ti^{4+} , may substitute for Al in igneous minerals (pyroxene, hornblende, biotite) and is associated with igneous rocks, silicates, titanites, and oxides. Titanium minerals are stable in soils, and its oxides and hydroxides are only weakly soluble in aqueous solutions.

Vanadium

In general not much information is available on the geochemistry of vanadium. It occurs in oxidation states of V^{2+} , V^{3+} , V^{4+} and V^{5+} and can replace Fe, Al, and Ti in parent rock mineral structures. Vanadium weathers out and is incorporated or sorbed onto Fe oxides and clays in soils. It is also found in crude oils and organic chelates. Vanadium frequently exhibits a high correlation with Fe in soil studies and can be expected to accumulate where soils are rich in Fe oxides and clays.

Yttrium

Yttrium is a fairly common element in the lithosphere and is distributed somewhat evenly among the different rock types. Geochemically its properties are like the lanthanides or rare earths (the trivalent form is most common and is concentrated in argillaceous sediments and phosphorites) but it is also associated with aluminum. Yttrium occurs as Y^{3+} and is found in silicates, oxides and phosphate minerals. Yttrium apparently does not accumulate in organic material as its abundances in coals is reported to be small.

Zinc

Zinc occurs only in the II oxidation state. It is a constituent of many igneous, metamorphic and sedimentary rock forming minerals, particularly those rich in iron. Weathering releases the zinc from the crystal lattices in the parent materials, in alkaline environments it precipitates into hydroxides on clay surfaces, in neutral or acid environments it exists as one of the Zn^{2+} ions. Zinc has been observed to accumulate in organic rich surface soils and in some peats. It forms organic complexes and chelates. It is known to substitute for Mg^{2+} in silicates, and is absorbed and coprecipitated in Fe, Al, and Mn oxides.

CHAPTER THREE

SAMPLE DESCRIPTIONS

The samples taken for the present study are from locations in South Florida (Fig 1). The sites are underlain by limestone of the Miami or Fort Thompson Formations. The soils which have developed over this limestone generally are shallow (less than 1 meter).

Twelve cores were obtained along with eleven surface samples from sites which were not suitable for coring (Appendix A). Five of the cores covering a broad area of South Florida were selected for this project analysis. Coring sites were chosen based on accessibility and depth of sediment present. Sediment thickness was determined by the insertion of a probe and if greater than 50.8 cm a core was collected adjacent to, but not including the path of the probe. Samples were collected using either the Wildco Hand Corer model 2420, or a rigid plastic tube which was covered with a board and hammered into the subsurface, or a hand operated piston corer. When the core was removed, it was capped both ends, labeled and transported upright to avoid disruption of the cored material and frozen upright to preserve any sedimentary structures which might be present. Appendix B has more details on sampling methods.

The division of cores into segments for analysis was based on three factors; the presence of stratigraphic features, the lack of features and packing. If the core contained stratigraphic features which could be used as a guide for segmentation, I followed the features when selecting the segments. In the cores which were laminated, but had no other obvious primary sedimentary structures, I tried to keep the segments as equal as

possible. In the instances in which the cores were loosely packed, I compensated for this by dividing slightly longer segments. In addition to these three factors an effort was made to divide the segments somewhat equally.

CORE DESCRIPTIONS

LOTI

Location:

Latitude: 26°42' N

Longitude: 80°42' W

Site description: Lake Okeechobee (see comments below)

Site condition: under 61 cm water

Map quadrangle: USGS topographic map, Belle Glade, Florida

Method of collection: Wildco Hand Corer

Length of core: 24.5 cm

Date collected: 9 July 1991

Comments: The sample was collected one meter north of the bank directly across from the Torry Island Campground in the southeastern quadrant of Lake Okeechobee (Fig. 1). This site was selected because it was under water and had sufficient depth to be sampled. The lake has been and is presently used for recreational purposes, boating, fishing, etc. The Wildco Hand Corer was used due to its weight, it was placed into the soft sediments and allowed to gradually sink downward, thus minimizing disturbance to the sediments.

DESCRIPTION:

Macroscopic

General: The upper 4.5 cm of the core was loosely packed with clumps of sediment and organic material separated from the sediment below. The sediments were fine grained

and thinly laminated throughout, the laminae are generally less than 1mm in thickness, and are not clearly visible in plate one.

- 0-4.5cm: Soft, water-saturated sediment, blackish red (5R 2/2), with visible roots.
- 4-24.5cm: Soft, water saturated sediment, grayish brown (4YR 3/2) roots visible to 5.5 cm.

Microscopic

- General: Sediment constituents are mostly micrite with rare quartz, ostracod, mollusk and gastropod fragments.
- Surface: Mostly micrite, mixed with rare quartz and very rare ostracods.
- 13 cm: Mostly micrite mixed with partially decayed plants, very rare quartz and very rare mollusk fragments.
- 22 cm: Micrite, some quartz, very rare gastropod.

Segmentation of core:

This core showed lamination, but no other primary sedimentary structure was visible. The core was divided into 4 segments.

- | | | |
|---|------------|--------|
| 1 | upper 8 cm | 8 cm |
| 2 | 8-13 cm | 5 cm |
| 3 | 13-18 cm | 5 cm |
| 4 | 18-24.5 cm | 6.5 cm |



Plate one: Core from Lake Okeechobee

WCA3B-2

Location:

Latitude: 25°46' N

Longitude: 80°30' W

Site description: Water Conservation Area 3B

Site condition: Dry at the time of sampling

Map quadrangle: USGS topographic map Coopertown, Florida

Method of collection: plastic tube

Length of core: 23 cm

Date collected: 29 March 1991

Comments: The site is located approximately .8 km north of the S-235 spillway on canal C-4 (Tamiami canal) within the Francis B. Taylor Preserve of the South Florida Water Management Water Conservation District 3B, approximately 2.4 km west of US 27 (Fig. 1). Usage of the conservation area is dependent upon seasonal conditions. This site was chosen because it was well within the confines of the water conservation area and high levels of mercury had previously been reported by the South Florida Water Management District (Richard Pfeuffer, personal communication, 1991). The site was accessible when sampled because the Water Conservation Area was dry. The plastic tube method was chosen as this had proven with my experience to be the best method in firm, dry sediments.

DESCRIPTION:

Macroscopic

General: The core consists of very dusky red (10R 2/2) peaty organic material with visible roots. No visible sedimentary structures present in this core (Plate 2).

Microscopic

General: Sediment constituents are mostly decayed organic matter and some spicules, which may be phytoliths due to their very small size, and some carbonized plant remains and micrite.

1-2 cm: Mostly decayed organic matter and some minute spicules (phytoliths) cemented with micrite.

15 cm: Mostly plant parts and decomposed organic matter cemented with micrite and very rare spicules as noted above.

22 cm: Partially decayed carbonized plant remains and micrite.

Segmentation of core:

Due to the fact that the core lacked sedimentary structures and was not tightly packed, it was divided into four even segments.

1	upper 6 cm	6 cm
2	6-12 cm	6 cm
3	12-17 cm	6 cm
4	17-23 cm	6 cm



Plate two: Core from Water Conservation Area 3B

FIU

Location:

Latitude: 25°45'30" N

Longitude: 80°23' W

Site description: Florida International University Nature Preserve

Site condition: dry, firm surface

Map quadrangle: USGS topographic map Hialeah, S.W., Florida

Method of collection: plastic tube

Length of core: 39.5 cm

Date collected: 9 March 1991

Comments: The core was collected from a slight depression approximately the center of the nature preserve, south of Tamiami Trail (US 41) and west of SW 104th Ave, approximately 13.7 meters from the perimeter road and from the edge of the preserve across from the runway parking area (Fig. 1). This site was selected because the preserve area exhibits topographical variations which appeared natural, soils follow the topography, with thicker accumulations in depressions. This area was once part of an airport and may have been disrupted by construction or other use activities prior to 1972. The nature preserve was established in 1972 and has not been disturbed since the airport was moved out, except in 1974 when a large number of non indigenous trees were removed. The plastic tube method was chosen because sediment at the site was firm and dry.

DESCRIPTION:

Macroscopic

- General: This core consists of layers of different colors and constituents (Plate 3).
- Surface to 19.5 cm: Dark grey (5YR 3 N3) loose clumps of mixed quartz and organic matter with visible roots to 9 cm. Gradational boundary from 18 to 19.5 cm.
- 19.5-29.5 cm Quartz sand, humus and sponge spicules in layered deposits of 1 to 7 mm thick, moderately brown (5YR 3/4) alternating with grayish yellow (5YR 8/4).
- 29.5-39.5 cm: Abrupt boundary, generally thicker lamination, very fine textured grayish yellow (5YR 8/4) micrite, with some 1 to 10 mm moderately brown (5YR 3/4) layers rich in decayed organic material.

Microscopic

- 0-19.5 cm: Clumps of quartz cemented with organic matter and spicules.
- 19.5-29.5 cm: Predominately quartz and sponge spicules, and humus.
- 29.5-39.5 cm: Mostly pure micrite, with some very decayed organic material and quartz (Miami Limestone).

Segmentation of core:

The division of this core was based on the presence of the sedimentary features. The first four segments were comprised of the upper layer of the core. The following two segments contained the middle, quartz sand enriched layer. The last two segments were the bottom layer, the Miami Limestone.

1	upper 5 cm	5 cm
2	5-10 cm	5 cm
3	10-15 cm	5 cm
4	15-19.5 cm	4.5 cm
5	19.5-24.5 cm	5 cm
6	24.5-29.5 cm	5 cm
7	29.5-34.5 cm	5 cm
8	34.5-39.5 cm	5 cm

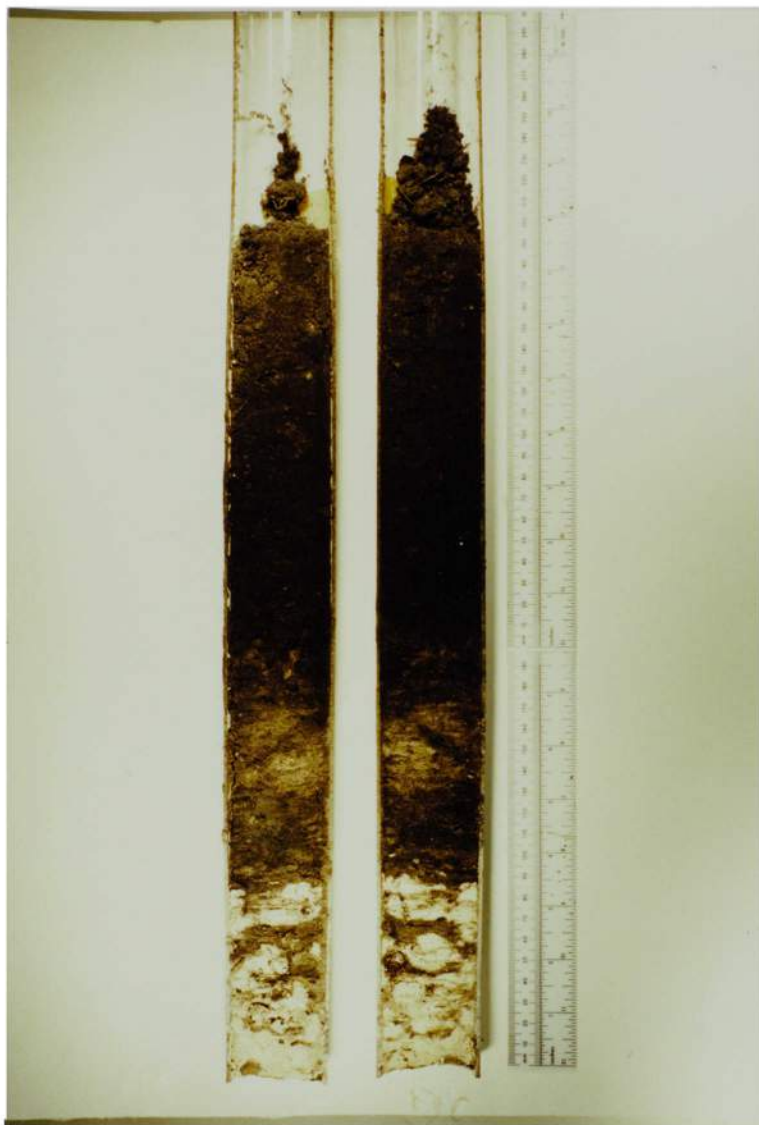


Plate three: Core from Florida International University

FCEG

Location:

Latitude: 25°43' N

Longitude: 80°36'30" W

Site description: Everglades, southwest of Frog City

Site condition: dry at time of sampling

Map quadrangle: USGS topographic map South of Coopertown, Florida

Method of collection: plastic tube

Length of core: 29.3 cm

Date collected: 5 July 1991

Comments: The site selected is on a hammock elevated above the surrounding flat, flooded terrain, approximately 2.8 km south of canal C-4 (at Frog City) and 1 km east of the Blue Shanty canal (Fig 1). The site is 25 meters southeast from the northwest bank of the hammock and is accessible only by airboat. When sampled, the site was dry and the sampling method selected was the plastic tube. The site was selected because it was well within the Everglades and because it was indicated to me by local inhabitants that there had once been a camp on this hammock and some dumping may have occurred there. The camp burned down in 1988 and was not rebuilt. There was little evidence of its having been there, (other than a clearing) no charred structure, supports or foundations were seen. Vegetation was plentiful. A boat slip had been dug out of the hammock. There was no refuse pile visible, and the only other sign of dumping was an old piece of furniture.

DESCRIPTION:

Macroscopic

- General: Laminae, less than 1 mm, are noted throughout the length of the core. Roots are present throughout (Plate 4).
- 0-16 cm: Mostly brownish black (5YR 2/1) soft sediment mixed with micrite.
- 11-23.5 cm: Mostly soft sediment and micrite with gradational color change from 11 to 16 cm. Light brown mottles (5YR 5/6) of 1 to 10 mm diameter in brownish black (5YR 2/1) matrix.
- 19.5-29.3 cm: Soft sediment and micrite with a gradational color change from 19 to 20.3 cm. Grayish orange (10 YR 7/4) sand sized grains in dark yellowish-brown (10YR 4/2) matrix. The matrix lightened with depth to moderate yellowish-brown (10YR 5/4).

Microscopic

- 1-2 cm: Predominately fine decayed organic matter with clumps of micrite aggregate and quartz. Occasional gastropod test fragments.
- 16-18 cm: Mostly micrite and organic matter mixed with Fe oxide and carbonized organic material. Some unidentified tiny mollusk fragments.
- 27-29 cm: Fine humic material mixed with micrite and unidentifiable shell fragments.

Segmentation of core:

The only primary sedimentary feature in the core was the presence of lamination. The core contained gradational color changes which were so diffuse that boundaries were not clearly identifiable.

1	upper 7 cm	7 cm
2	7-12 cm	5 cm
3	12 -17 cm	5 cm
4	17-23.5 cm	6.5 cm
5	23.5-30 cm	6.5 cm

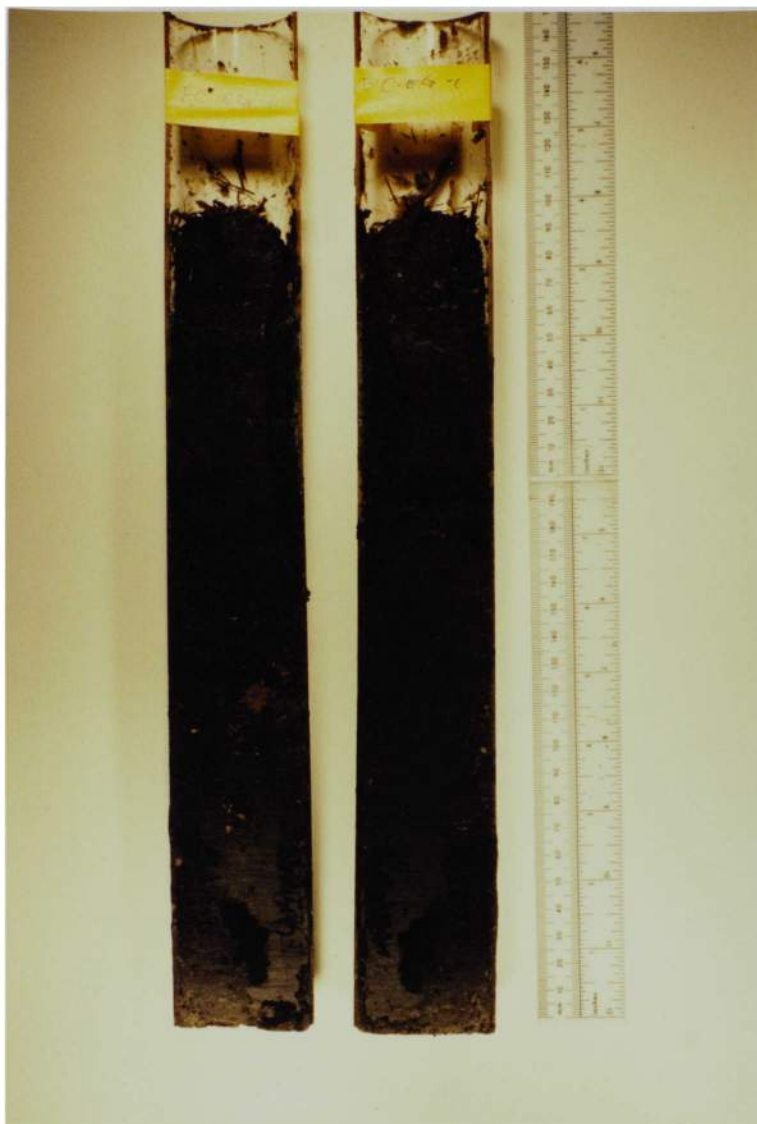


Plate four: Core from the Everglades

CSRA

Location:

Latitude: 25°37' N

Longitude: 80°37' W

Site description: Chekika State Recreation Area

Site condition: dry at the time of sampling

Map quadrangle: USGS topographic map Grossman Hammock, Florida

Method of collection: plastic tube

Length of core: 32.3 cm

Date collected: 11 July 1991

Comments: The site is located approximately 15.4 km west of Krome Ave, and west of SW 237 Ave (Fig. 1). The sample was collected approximately 2 meters north of the northernmost turn of the nature trail in the tropical hammock. Chekika had previously been the site of exploratory oil drilling operations. An illegal dumping area is located approximately 2 km north of the area where SW 237 Ave ends. The site was selected because of accessibility and depth of sediment. The plastic tube method was used because the site was dry at the time of sampling.

DESCRIPTION:

Macroscopic

- General: Consists of three visually identifiable layers. Roots present throughout the core (Plate 5).
- 0-11.5 cm: Dusky brown (5YR 2/2) soft muck mixed with pale yellowish-orange (10YR 8/6) micrite aggregates and clumps of quartz sand. Gradational boundary with layer two.
- 10.5-21 cm: Predominately pale yellowish-orange (10YR 8/6) quartz sand interfingered with pale yellowish-brown (10YR 6/2) marl.
- 18.5-32.3 cm: Mostly finely laminated (less than 2 mm) soft, grayish-black (O 2 N 2) muck lightening in color with depth to dusky brown (5YR 2/2). Also includes some yellowish-grey (5YR 8/1) clumped quartz and micrite aggregates.

Microscopic

- 1-2 cm: Mostly plant residue mixed with micrite and quartz with tiny unidentifiable fragments of mollusk tests.
- 14-15 cm: Predominately quartz and some tiny fragments of reworked shells, some foraminifera; marine, shallow water benthic, assigned to Elphidium or Cibicides, and little organic matter.
- 30-31 cm: Mostly quartz and humic material mixed with scant micrite.

Segmentation of core:

The division of this core was based on the presence of its sedimentary features. The first two segments contained the upper layer of the core. The next two segments were comprised of the middle layer. The last two segments were the organic rich bottom layer.

1	upper 6 cm	6 cm
2	6-10.5 cm	4.5 cm
3	10.5-15.5 cm	5 cm
4	15.5-21.5 cm	5 cm
5	21.5-26.5 cm	5 cm
6	26.5-32.3 cm	5.8 cm



Plate five: Core from Chekika Recreation Area

CHAPTER FOUR

CHEMICAL ANALYSIS

A flow chart containing a summary of the steps involved in sample preparation is included after this section, and the detailed procedure is found in Appendix C. Briefly, each section of each core was dried at 110°C, sieved and the samples of fine size fraction were split into 4 fractions: carbonate, organic (humic and fulvic acids) and residue. The carbonate and organic fractions were analyzed, the residue was reserved for future work. Each sample (except WCA3B2-1, 3 and 4) was also analyzed as a whole soil sample (not separated into the four fractional components). The four split fractions from each sample were analyzed by ICPEs (Inductively Coupled Plasma Emission Spectrometer) for major elements Fe, Si, Al, Ca, Mg and trace elements P, Ni, Ba, Mn, Cr, Ti, Sc, Sr, Sb, Zn, Pb, Cd, Co, V, Be, Cu and Y.

Since the relative proportions of organic and carbonate material from the samples could not be determined during the separation, a separate evaluation was done using volatile loss patterns (Appendix D). The samples which had been previously heated to 110°C, as noted above, were then heated to 550°C and 1000°C and weighed after each step. The percent weight lost at 550°C is proportional to the organic component. Mostly water bound in clays and hydroxides, and organic compounds are lost under 550°C, whereas 1000°C is the temperature of decarbonation of carbonate, since the samples were clay and hydroxide poor. Therefore, the weight lost at each temperature interval is an estimate of the organic and carbonate fractions of the sample.

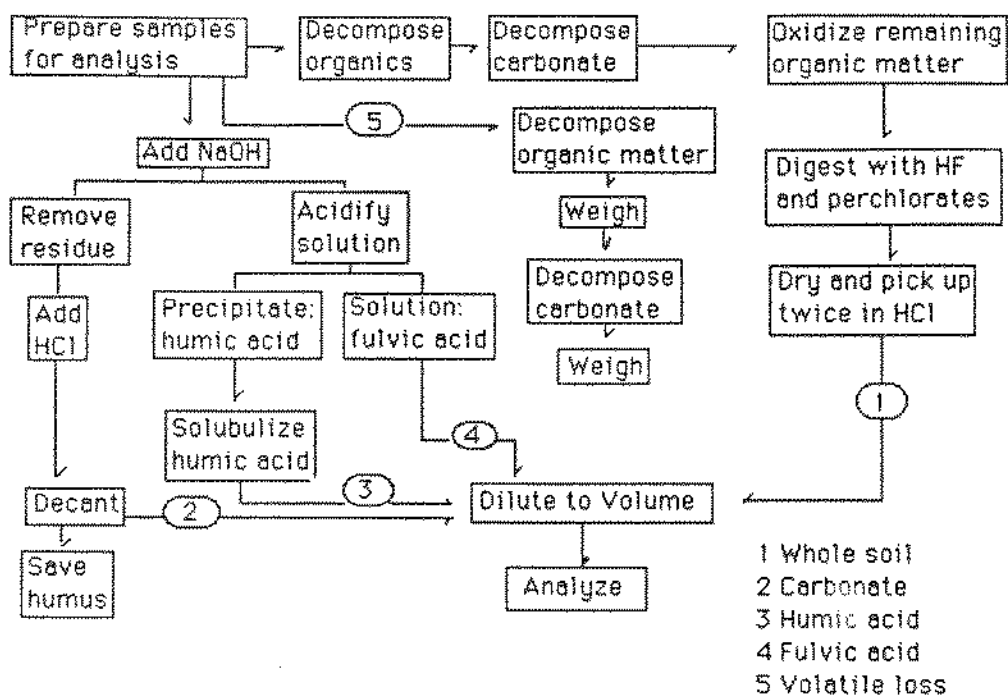


Fig. 3: Flowchart of chemical analysis procedure

CHAPTER FIVE

RESULTS AND INTERPRETATIONS

Results

The raw data with accompanying information on the reliability of the data may be found in Appendix E. Concentrations corrected for dilution are in Appendix F.

World and Florida Concentration Ranges

Background concentrations of soils and sediments accepted as normal and presumably safe (toxic elements) on a worldwide basis have been assembled from various works and are compared to the elemental concentrations determined in this study for South Florida. This information is presented in Table 2, World and Florida Ranges. The concentrations presented are for whole soil measurements and have been corrected for dilution. Most of the concentrations are within the ranges accepted as normal for soils on a world basis with the following exceptions: FCEG segments 1-4 enriched in cadmium, all FCEG segments enriched in phosphorus; CSRA segment 6 enriched in antimony, all CSRA segments enriched in phosphorus.

Data Analysis

I used several approaches to examine the data and assess the behavior of the elements:

- 1) whole soil element concentrations vs depth,

- 2) element concentrations in each fraction vs depth,
- 3) affinity of elements for the various fractions,
- 4) correlation coefficients for element vs element, and for element vs volatile loss in the whole soil, and
- 5) principal component analysis.

First Methodological Approach

In the first approach I constructed plots of the concentrations of the elements in the whole soil (not fractionated) in each segment vs the depths of the core segments. This indicates that elements are concentrating at a particular depth, and although this approach is the most direct, it does not address possible changes in whole soil composition through the depth of the core. Because the cores and depth segments were of different lengths, I developed a scale (Table 3) which allows the comparison between segments from each core based on their depths. I then recorded the segment in each core where the peak abundances of each element occurred, and compared this information with the depth scale from Table 3. Table 4 summarizes this approach by showing at what depth the peak abundances of each element occurs within each core. This permits a rough comparison between all the cores and highlights on the depths where the elements are concentrated.

Table 2
Ranges of Element Concentrations for the World and Florida
Sites

Ranges in element concentration commonly accepted worldwide, along with those determined for South Florida. Values are ppm except where indicated.

	World	FOEG	CSRA	LOTH	FIU	WCA3B2-2
Sb	.05-4	1.16-3.65	.29-13.73	1.18-3.32	.53-3.61	0.6
Pb	2-200	44.9-1016	5.2-22.4	7.6-13.5	2.1-10.3	4.9
Zn	10-300	12.6-25.7	4.4-50.9	14.6-34	1.1-19.7	1.3
Cd	.01-7	4.15-18.57	.30-5.9	2.21-3.94	.14-1.90	1.1
Co	1-50	1.02-2.13	.70-8.77	2.21-3.62	.38-2.29	0.4
V	20-500	3.5-10.3	4.5-58.3	15.2-25.2	5.4-14.9	15.9
Be	1-40	0	0-1.73	.21-.44	.03-.19	0.0
Cu	2-100	19.6-35.3	6.3-83.5	8.1-33.4	2.0-9.4	4.7
Y	20-200	.8-1.2	5.5-29.9	6.1-14.4	1.5-5.4	0.2
P	100-1000	19980-37990	1555-3315	472-785	51-167	143.0
Ni	10-100	1.0-3.2	1.3-34.6	6.9-12	1.3-8.7	4.5
Ba	84-838	113-154	42-142	15-24	5-30	74.0
Mn	200-3000	129-171	15-40	216-392	6-55	90.0
Fe	10-300K	12798-50K	696-20.1K	6525-12.1K	567-637	4168.0
Cr	5-3000	2.9-6.1	8.9-165.2	24.7-52.3	9-32.9	4.6
Mg	.03%-.84%	1.7%-2.52%	11.3%-30.9%	12.47%-19.9%	.39%-.39%	0.0
Ca	.07%-1.7%	3.8%-34.3%	3.5%-19.3%	2.97%-3.2%	.22%-32.16%	0.3
Ti	1000-10K	118-243	162-4438	831-1502	146-1077	59.0
Sc	.5-45	.43-.60	.51-14.03	1.63-4.42	.53-2.5	0.1
Al	10K-200K	2383-3926	3139-77.8K	13.6K-32K	2571-15.2K	632.0
Sr	18-3500	12.1-1811	371-662	600-707	16-1746	1331.0

TABLE 3

DEPTH COMPARISON BETWEEN CORES

This scale provides a rough comparison between the depths at which the various segments from different cores are located. For example, any core segment which falls predominantly between 10 and 20 cm is included in the third segment.

Depth		FIU	LOTI	FCEG	CSRA
< 5 cm	(1)	1	1	1	1
5-10 cm	(2)	2	2	2	2
10-20 cm	(3)	3,4	3	3	3,4
20-30 cm	(4)	5,6	4	4,5	5,6
30-40 cm	(5)	7,8			

TABLE 4

Peak Abundances of Elements Within the Cores

This table shows the depth at which the peak abundances of each element occurs within each core. Depth scale is from Table 3. The greatest abundances of phosphorus is found in the first depth segment (upper 5 cm) in FIU, LOTI, and CSRA. In the FCEG core the peak abundance of P is in the fourth depth segment (20-30 cm).

Elements	FIU	LOTI	FCEG	CSRA
P	1	1	4	1
Ni	2	4	2	4
Ba	2	1	2	4
Mn	1	1	2	1
Fe	1	4	4	4
Cr	4	4	4	4
Mg	5	4	1	4
Ca	5	4	4	1
Ti	1	4	1	4
Sc	2	4	2	4
Al	2	4	1	4
Sr	5	1	4	3
Sb	2	2	2	4
Zn	1	1	4	1
Pb	1	1	1	4
Cd	1	4	2	4
Co	1	4	2	4
V	1	4	2	4
Be	3	4	-	4
Cu	1	1	1	1
Y	1	4	2	4

Certain patterns of behavior were noted in Table 4. The greatest concentrations of Cu always occurred near the top of the cores less than 5 cm depth. The greatest abundances of Mn were in the upper 10 cm of the cores. Conversely, Ni, Sc, Sb and Be never displayed a peak abundance in the upper 5 cm of the cores. Their greatest concentrations were always in the segments greater than 5 cm. The peak concentrations of Cr were always greater than 20 cm depth.

These patterns do not necessarily reflect processes occurring at the site(s). Manganese is always found in the upper 10 cm of the cores. It is known to accumulate in top soils by complexing with organic matter, and may fixate on the surfaces of CaCO_3 . Its concentration in the upper 10 cm of the cores would likely be due to the abundance of organic matter associated with these depths. As detailed in the less than 550° C volatile loss study (Appendix D) these levels contain the highest percent estimates of surficial organic fraction. However, when the Mn from all five sites are plotted against both the less than 550° C and greater than 550° C volatile loss estimates, very little correlation is found. This indicates that concentrations are related to other factors, and highlights the need for pursuit of other avenues of investigation, as were discussed above.

The plots of element concentrations in the whole soil vs depth are included as part of figures 6 to 85, (ref. p. 52-91) and when considered along with the peak element concentrations reveal trends which possibly illustrate the impact of changes in the bulk composition of the whole soil within a core.

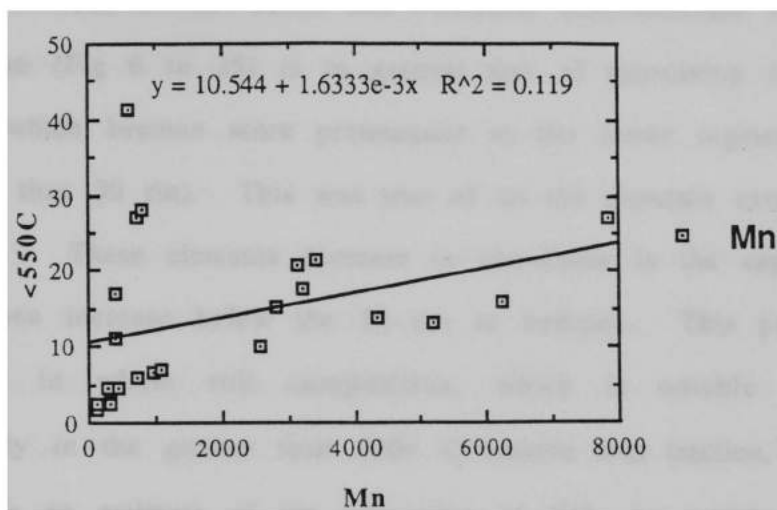


Fig. 4: Mn vs less than 550° C volatile loss

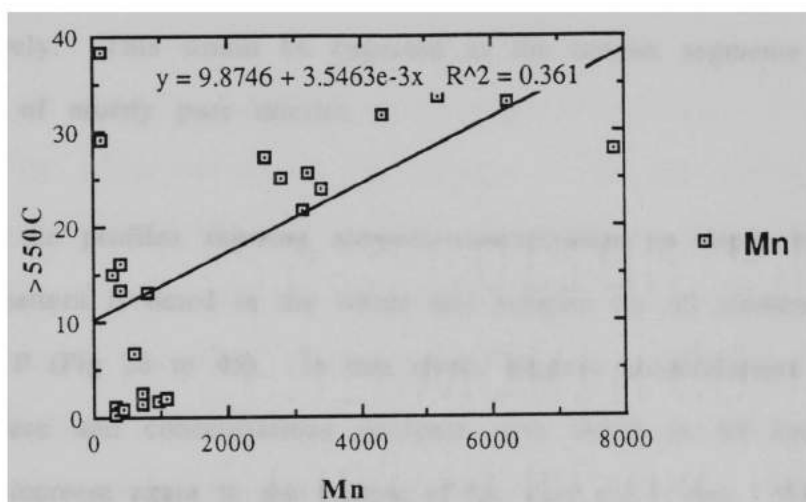


Fig. 5: Mn vs greater than 550° C volatile loss

FIU

The trend of the whole soil elemental concentrations vs depth in the FIU core (Fig 6 to 25) is in general that of decreasing abundances with depth, which become more pronounced in the lower segment of the core (greater than 30 cm). This was true of all the elements except Ca, Mg, P, and Sr. These elements decrease in abundance in the upper part of the core, then increase below the 30 cm to bedrock. This probably reflects changes in whole soil composition, which is notable in this core, especially in the greater than 550° C volatile loss fraction. This fraction, which is an estimate of the proportion of CO₂ by sample, is 2% in the surface segment of the core, decreases to less than .5% in the subsurface and then sharply increases in segments 7 and 8 to 29% and 38% respectively. This would be expected as the bottom segments of this core consists of mostly pure micrite.

CSRA

In the profiles showing element concentration vs depth for the CSRA core a pattern is noted in the whole soil samples for all elements except Ca, Sr, and P (Fig 26 to 45). In this trend, element accumulations are noted at the surface and concentrations decrease with depth to 30 cm where they start to increase again to the bottom of the core (32.3 cm). When compared to the less than 550° C percent volatile loss (Appendix D) a similar pattern is seen where the percent volatile loss is 28% at the surface, decreases with depth (17%, 5%, 11% respectively), and then demonstrates a large increase below 30 cm depth (41%, 27% respectively). This is related to changes in composition, corresponding to the organic rich lower layer of the core.

LOTI

In the Lake Okeechobee core, little change is noted to occur in the whole soil in element abundance with depth (Fig 46 to 65). Most of the concentrations vary less than 1 ppm, with the following exceptions: 1) Al, Ca, Fe, Mg, and Ti, which vary by more than 10 ppm, 2) P, which varies by 6 ppm, 3) Mn, which varies by 3.5 ppm, and 4) Sr which varies by 3 ppm. The less than 550° C % volatile loss estimate indicates the greatest proportion of organic matter (28%) is in the upper segment of the core, followed by 16%, 13% and 14% respectively with depth. The greater than 550° C % volatile loss varies little, being 28%, 33% and 34% respectively with depth. No clear patterns are detected when comparing the changes in element concentrations with depth and volatile loss patterns.

FCEG

In the FCEG core (Fig 66-85) the major soil elements (Al, Ca, Fe, Mg) vary in the whole soil by at least 10 ppm. The trace elements show less variation. Strontium varies by 12.2 ppm and phosphorus by 360 ppm. The other trace elements vary by less than 2 ppm through the core (Appendix E). When the variations of elemental abundances with depth are compared to the changes in the whole soil contents of the core as determined by the volatile loss study, no clear pattern emerges. In this core, there is a relatively small variation in the volatile loss for each segment.

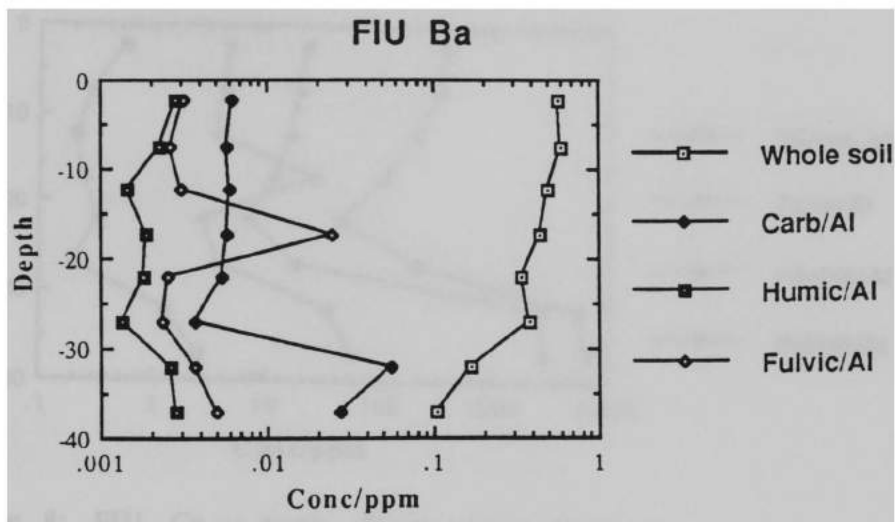


Fig. 6: FIU Ba vs depth. Average standard deviations, sigma values, are: whole soil 2.7%; carbonate 1.7%; humic acid 26%; fulvic acid 8.3%.

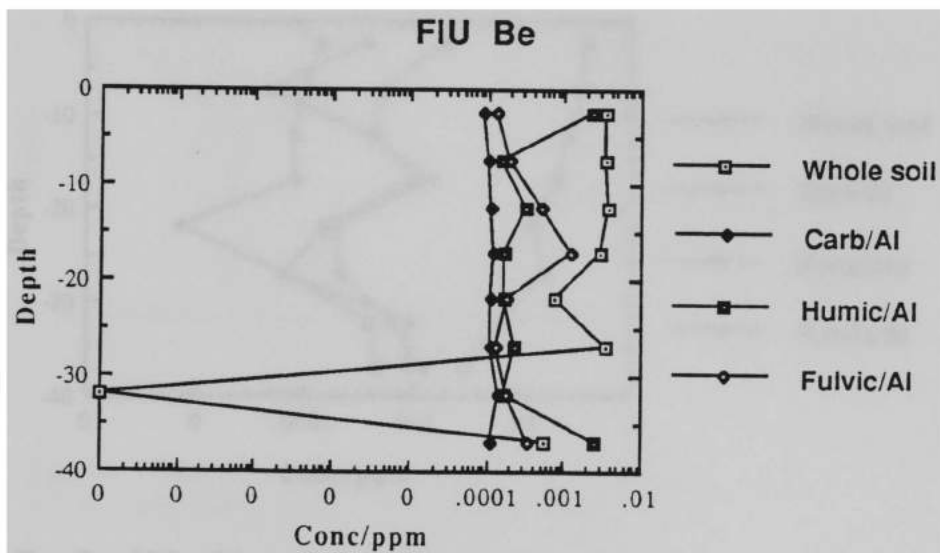


Fig. 7: FIU Be vs depth. Sigma values are w.s. 4.1%; carb 160%; humic 310%; fulvic 360%.

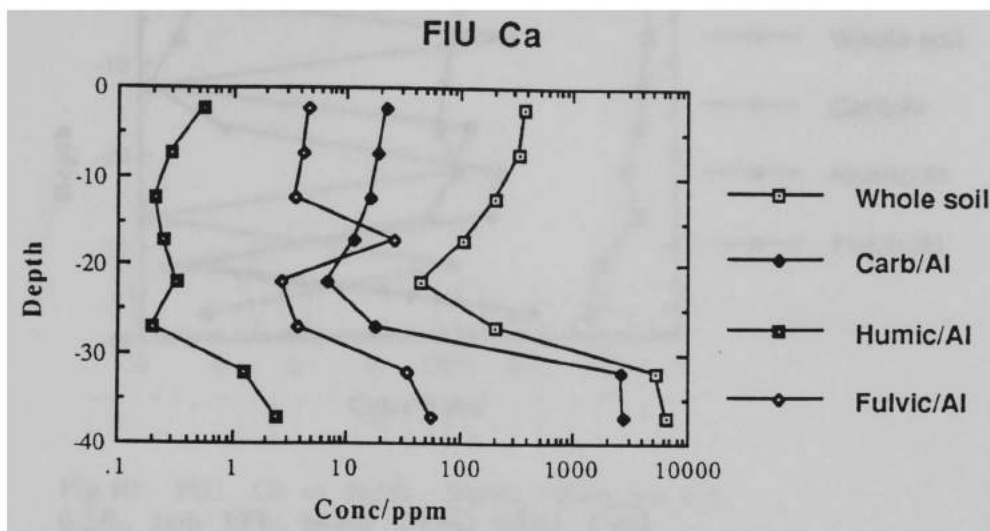


Fig. 8: FIU Ca vs depth. Sigma values are w.s. 1.5%; carb 2.3%; humic 1.0%; fulvic 1.1%.

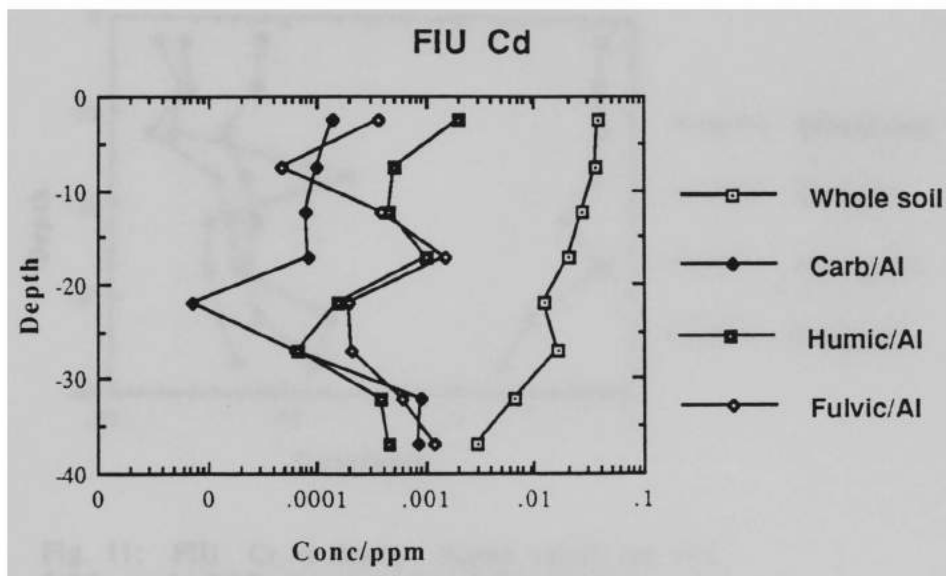


Fig. 9: FIU Cd vs depth. Sigma values are w.s. 4.5%; carb 82%; humic 79%; fulvic 130%.

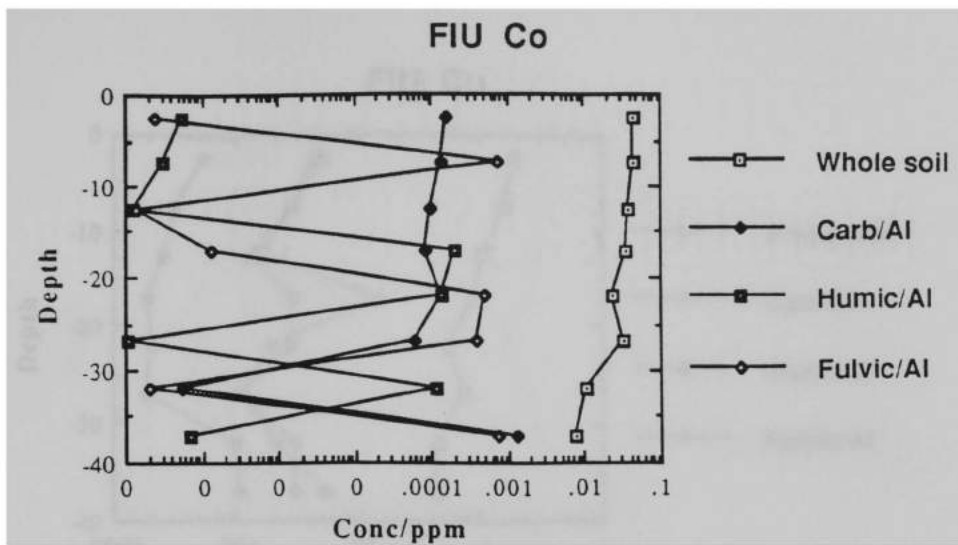


Fig.10: FIU Co vs depth. Sigma values are w.s. 6.5%; carb 59%; humic 250%; fulvic 170%.

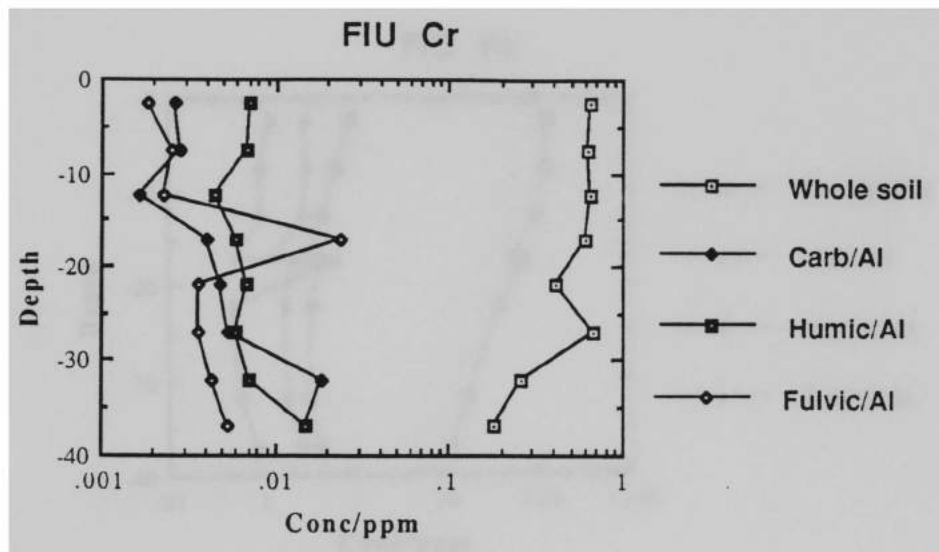


Fig. 11: FIU Cr vs depth. Sigma values are w.s. 3.4%; carb 7.0%; humic 16%; fulvic 28%.

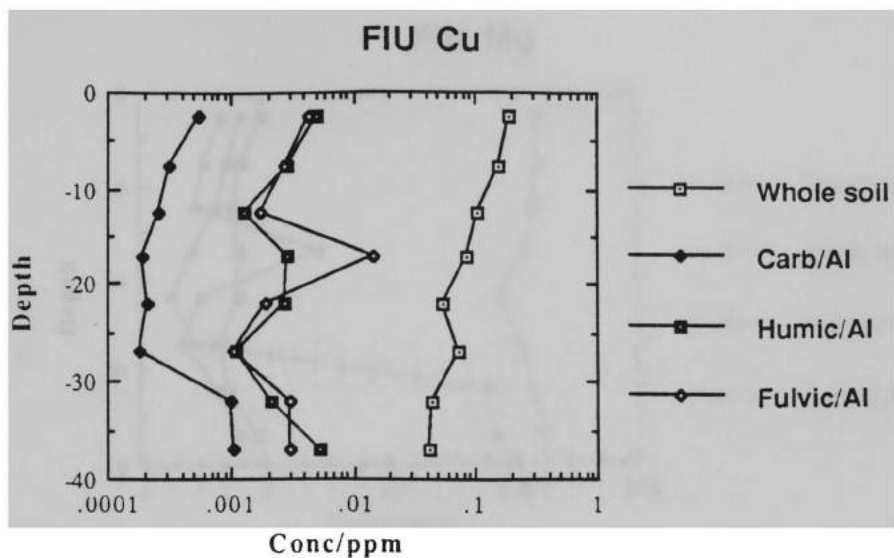


Fig. 12: FIU Cu vs depth. Sigma values are w.s. 2.8%; carb 12%; humic 16%; fulvic 25%.

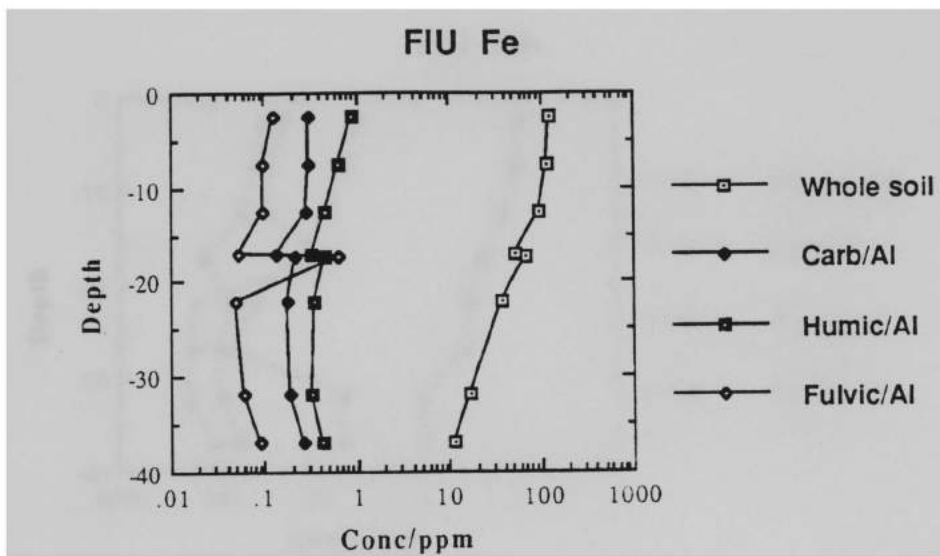


Fig. 13: FIU Fe vs depth. Sigma values are w.s. 1.7%; carb 2.5%; humic 1.1%; fulvic 1.9%.

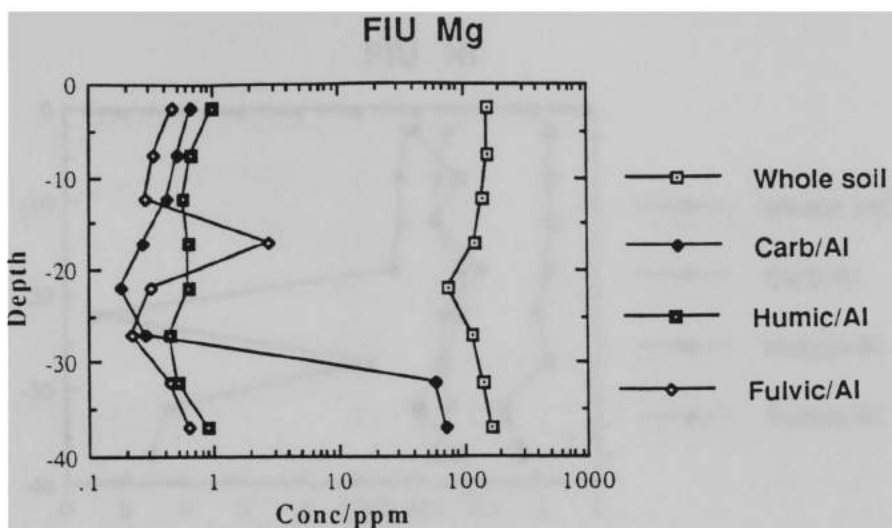


Fig. 14: FIU Mg vs depth. Sigma values are w.s. 1.6%; carb 1.3%; humic 1.1%; fulvic 1.2%.

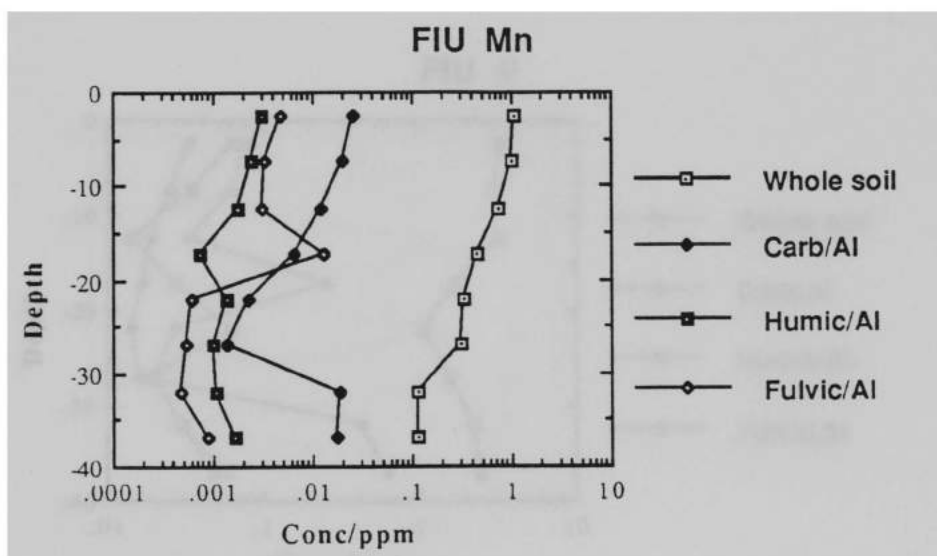


Fig. 15: FIU Mn vs depth. Sigma values are w.s. 2.2%; carb 1.3%; humic 4.2%; fulvic 4.5%.

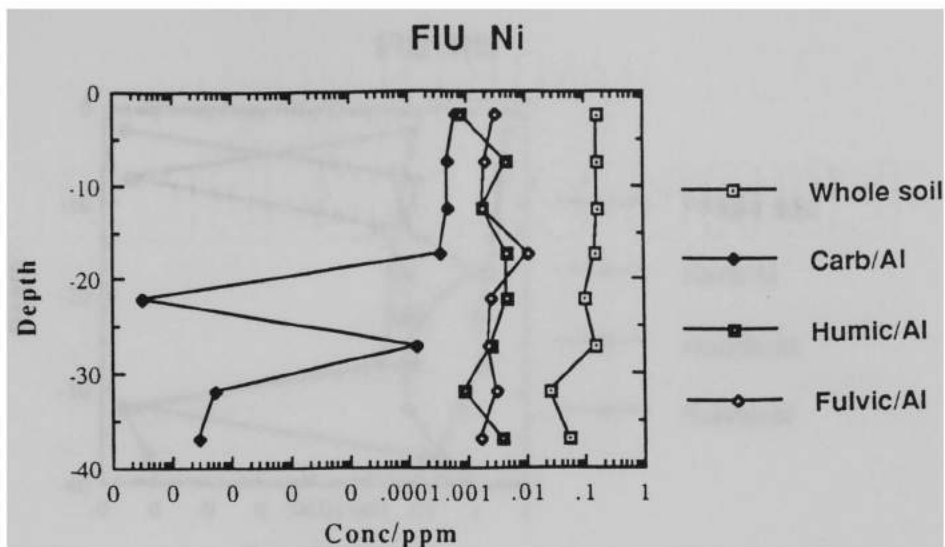


Fig. 16: FIU Ni vs depth. Sigma values are w.s. 13%; carb 40%; humic 96%; fulvic 47%.

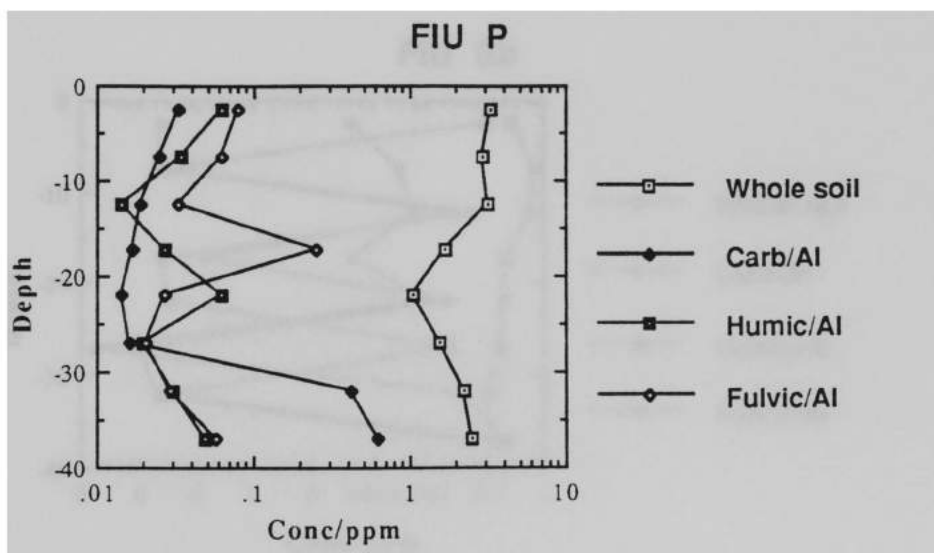


Fig. 17: FIU P vs depth. Sigma values are w.s. 7.7%; carb 8.2%; humic 51%; fulvic 34%.

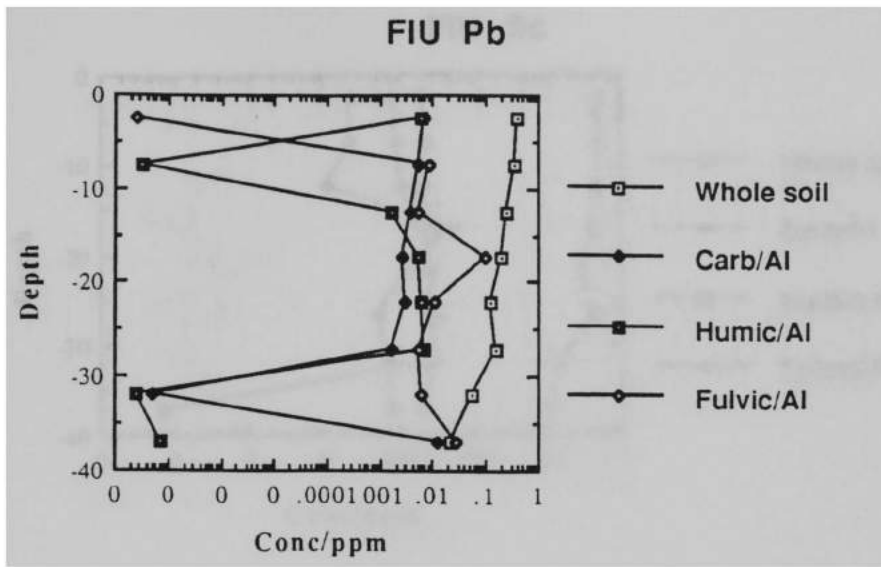


Fig. 18: FIU Pb vs depth. Sigma values are w.s. 8.8%; carb 16%; humic 120%; fulvic 56%.

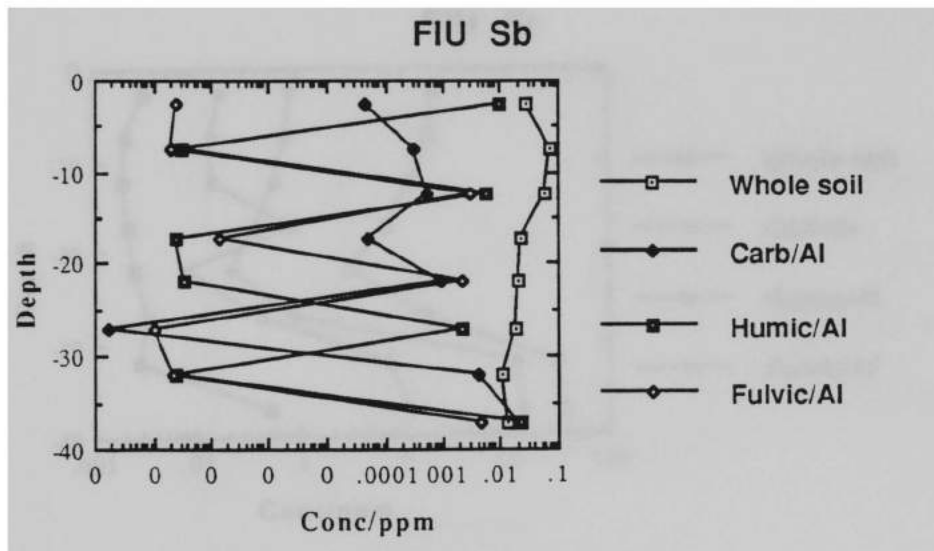


Fig. 19: FIU Sb vs depth. Sigma values are w.s. 56%; carb 240%; humic 94%; fulvic 200%.

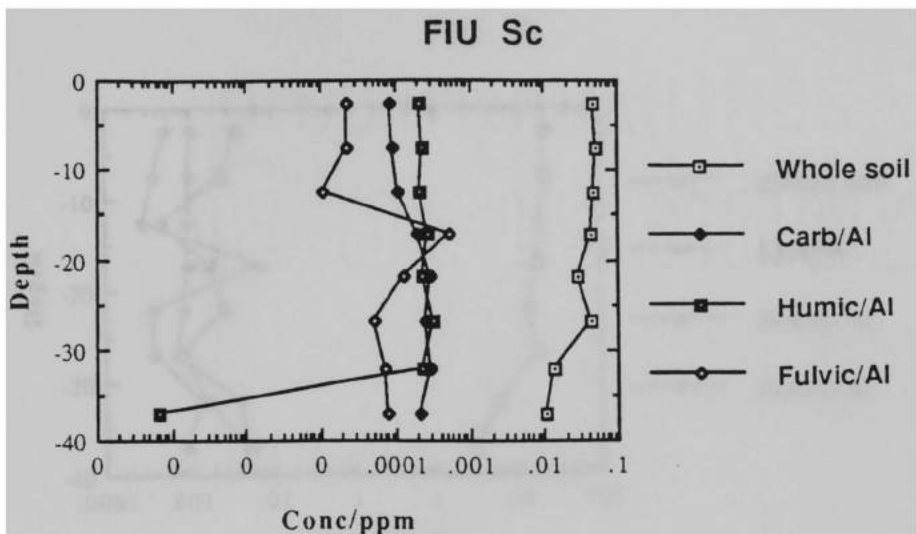


Fig. 20: FIU Sc vs depth. Sigma values are w.s. 2.2%; carb 16%; humic 23%; fulvic 140%.

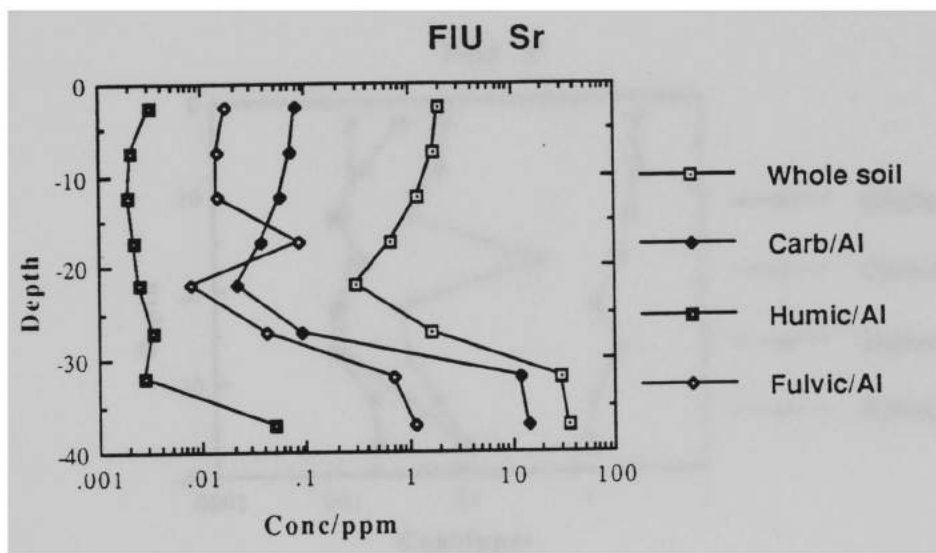


Fig. 21: FIU Sr vs depth. Sigma values are w.s. 2.2%; carb 1.3%; humic 1.3%; fulvic 1.2%.

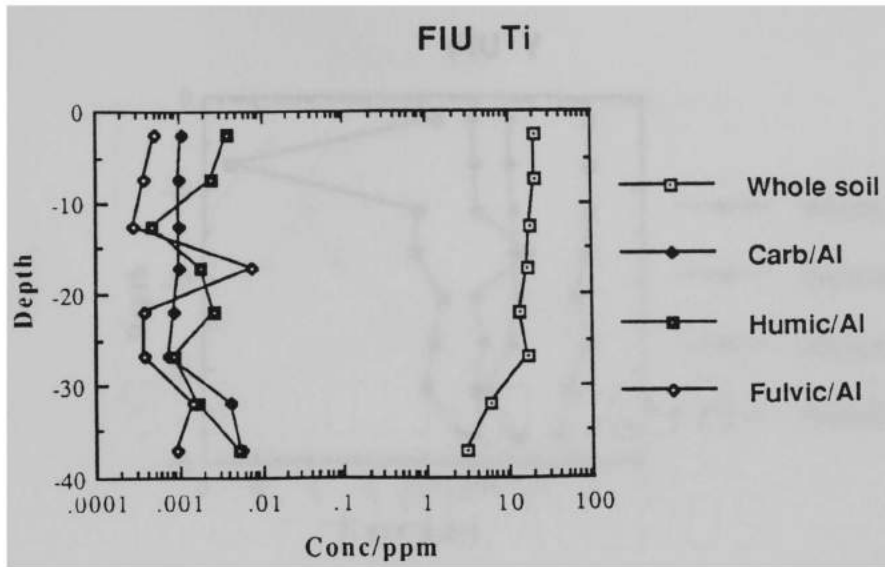


Fig. 22: FIU Ti vs depth. Sigma values are w.s. 2.0%; carb 2.5%; humic 13%; fulvic 54%.

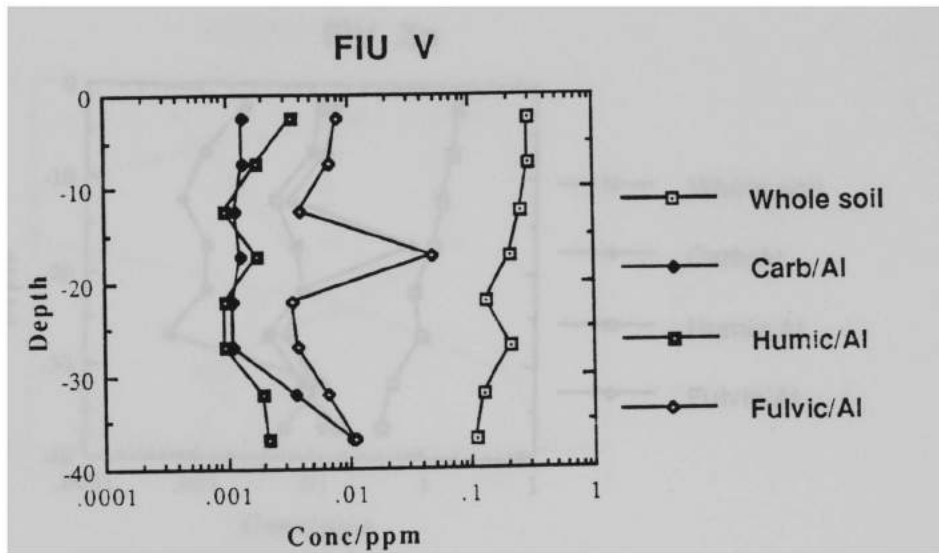


Fig. 23: FIU V vs depth. Sigma values are w.s. 1.5%; carb 46%; humic 32%; fulvic 9.6%.

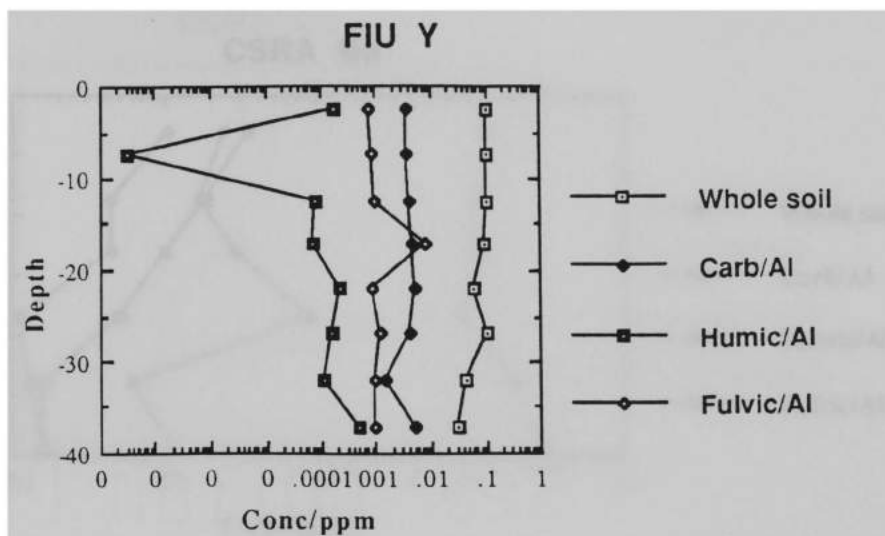


Fig. 24: FIU Y vs depth. Sigma values are w.s. 1.6%; carb 1.8%; humic 130%; fulvic 8.7%.

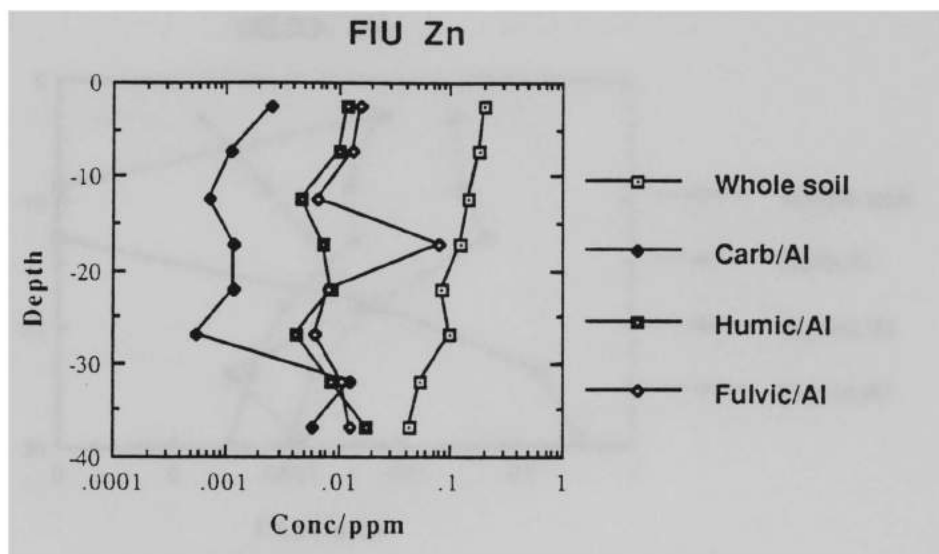


Fig. 25: FIU Zn vs depth. Sigma values are w.s. 1.7%; carb 3.5%; humic 5.9%; fulvic 5.8%.

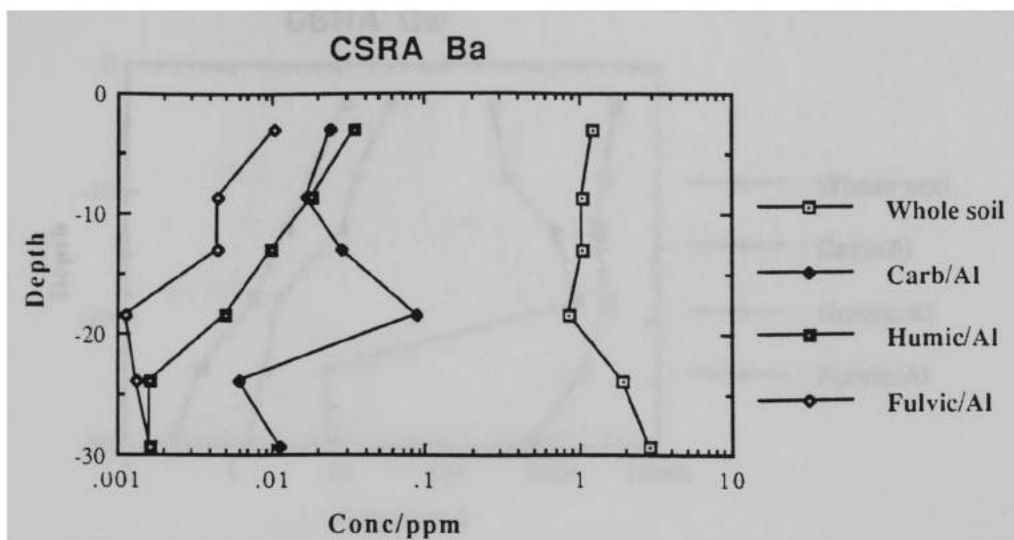


Fig. 26: CSRA Ba vs depth. Sigma values are w.s. 1.4%; carb 1.8%; humic 23%; fulvic 12%.

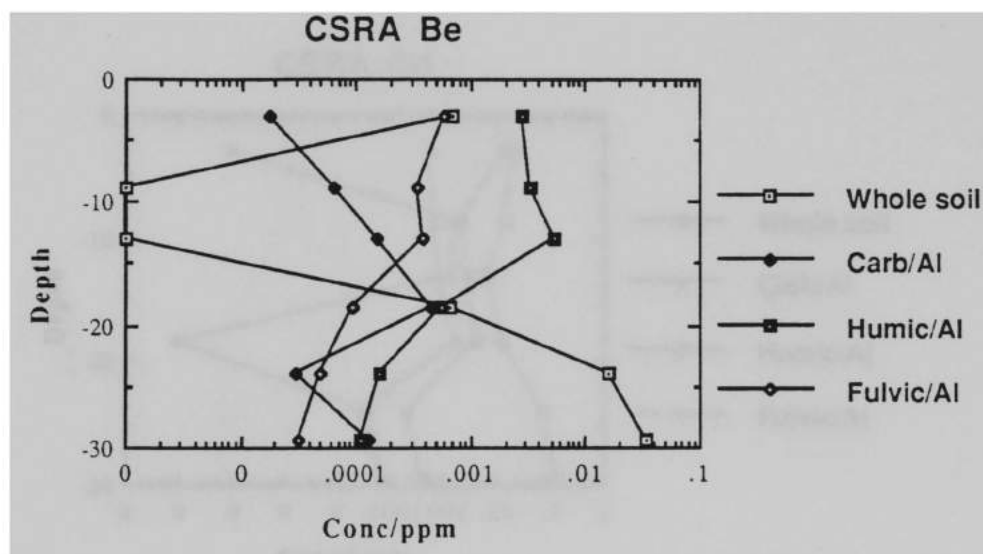


Fig. 27: CSRA Be vs depth. Sigma values are w.s. 3.3%; carb 250%; humic 190%; fulvic 510%.

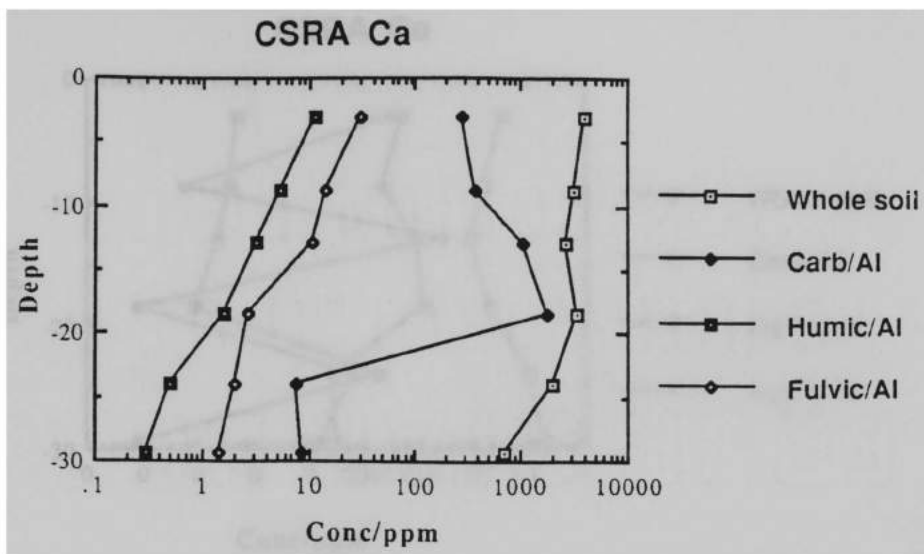


Fig. 28: CSRA Ca vs depth. Sigma values are w.s. 1.1%; carb 2.5%; humic 1.5%; fulvic 1.0%.

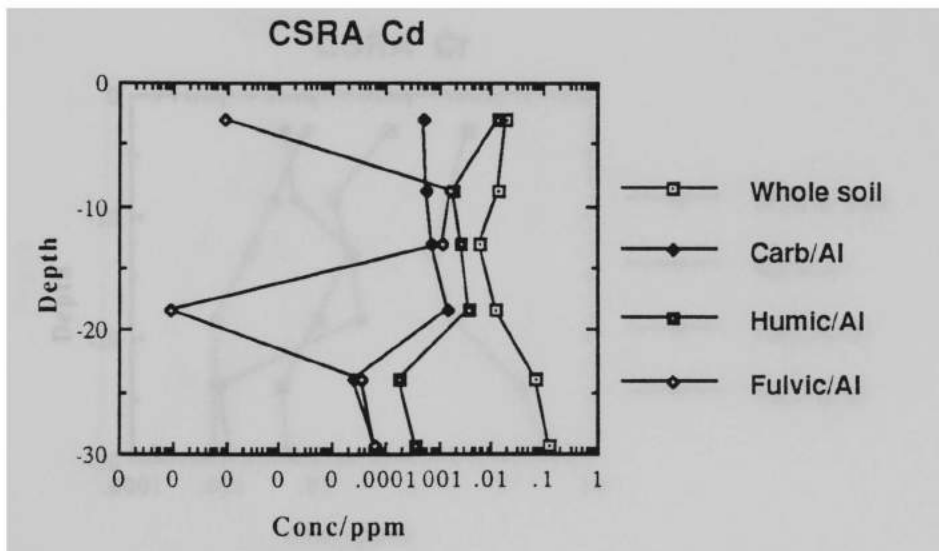


Fig. 29: CSRA Cd vs depth. Sigma values are w.s. 5.3%; carb 21%; humic 170%; fulvic 100%.

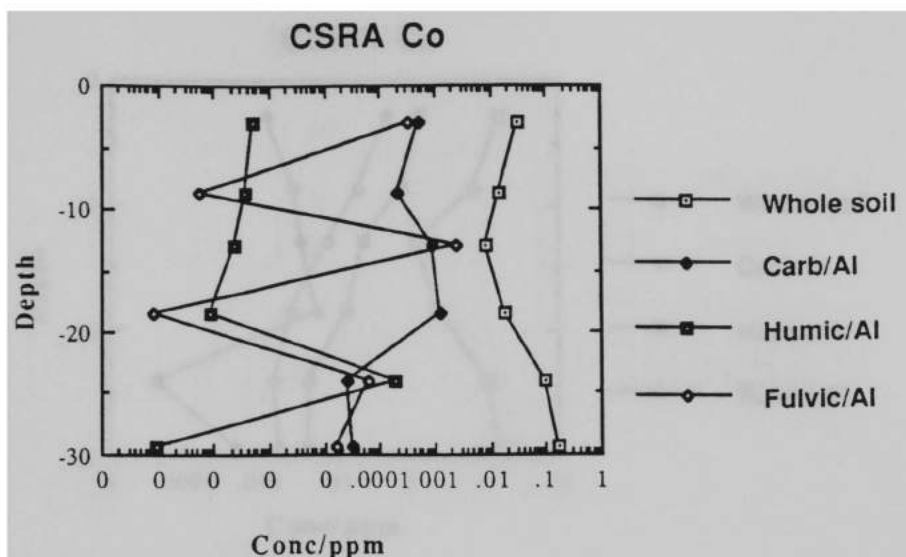


Fig. 30: CSRA Co vs depth. Sigma values are w.s. 4.8%; carb 32%; humic 210%; fulvic 370%.

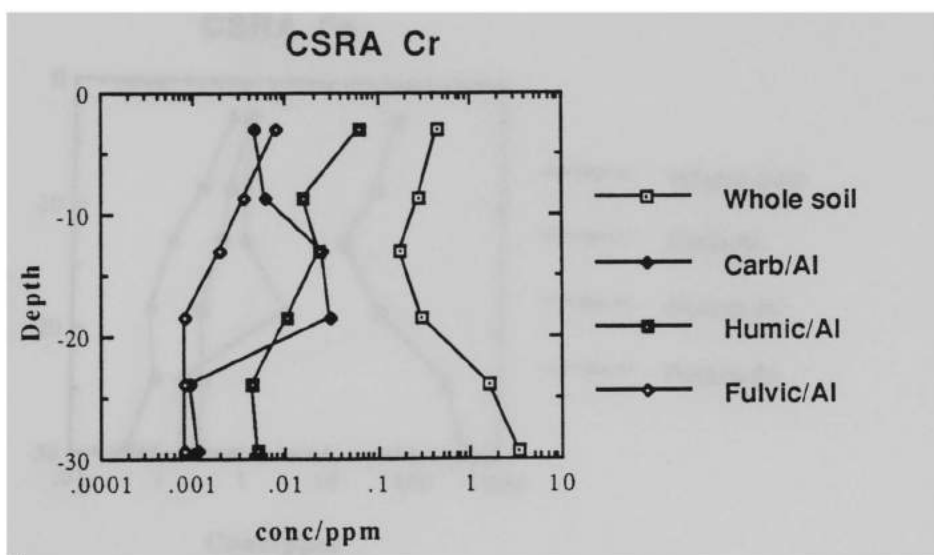


Fig. 31: CSRA Cr vs depth. Sigma values are w.s. 2.9%; carb 2.8%; humic 25%; fulvic 63%.

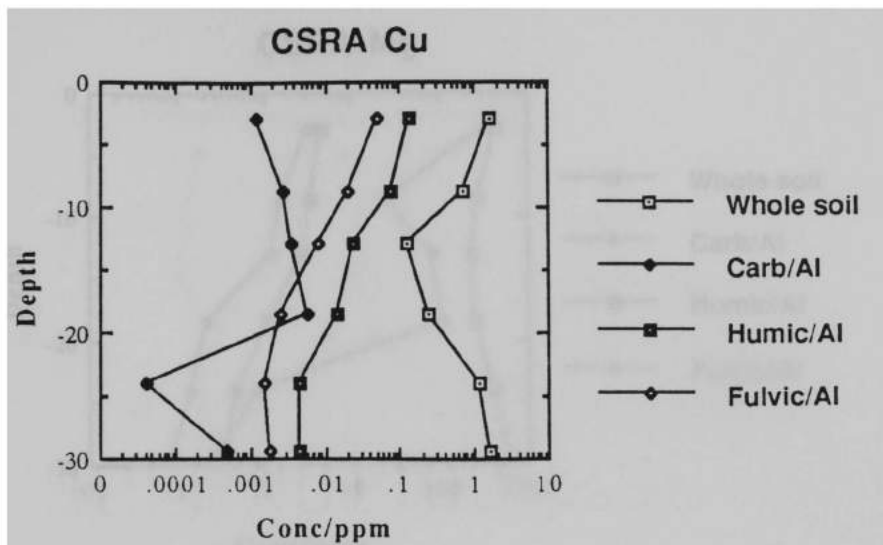


Fig. 32: CSRA Cu vs depth. Sigma values are w.s. 1.4%; carb 7.4%; humic 8.8%; fulvic 4.0%.

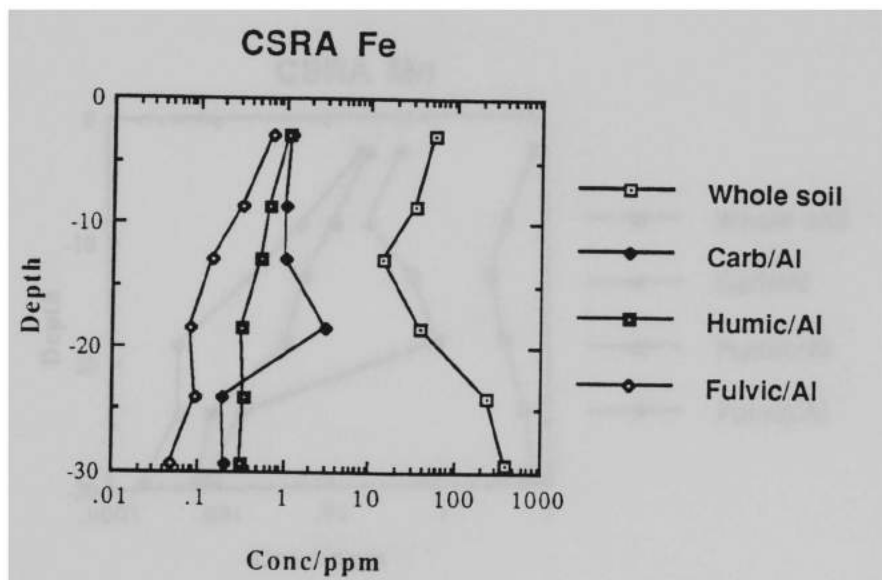


Fig. 33: CSRA Fe vs depth. Sigma values are w.s. 1.6%; carb 1.5%; humic 1.9%; fulvic 1.1%.

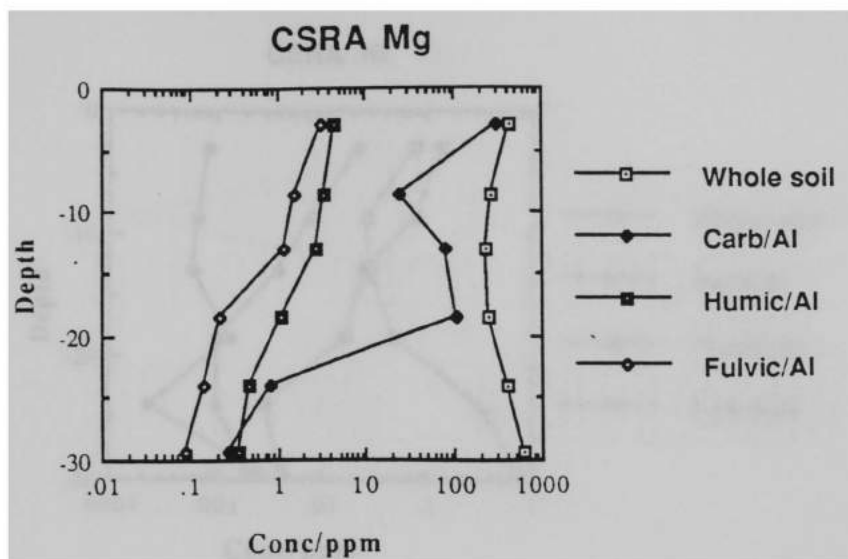


Fig. 34: CSRA Mg vs depth. Sigma values are w.s. 1.6%; carb 1.4%; humic 1.2%; fulvic 1.1%.

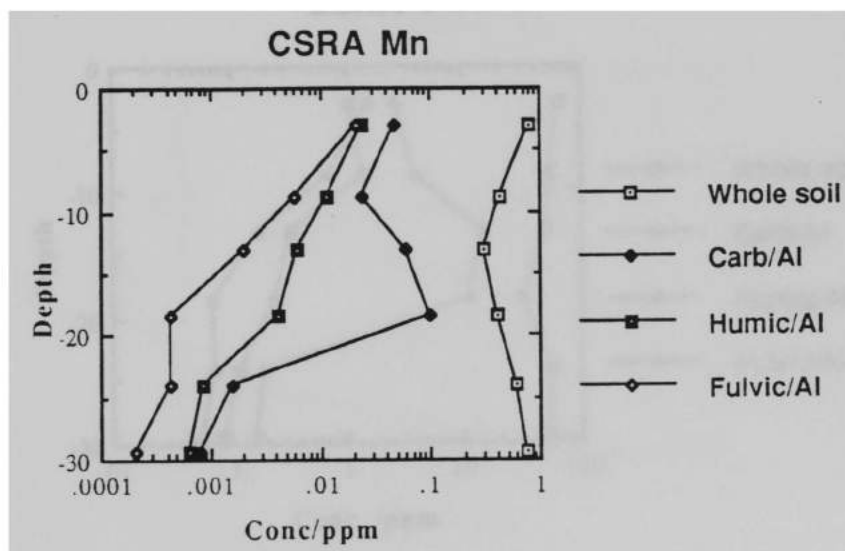


Fig. 35: CSRA Mn vs depth. Sigma values are w.s. 1.6%; carb 1.4%; humic 9.2%; fulvic 11%.

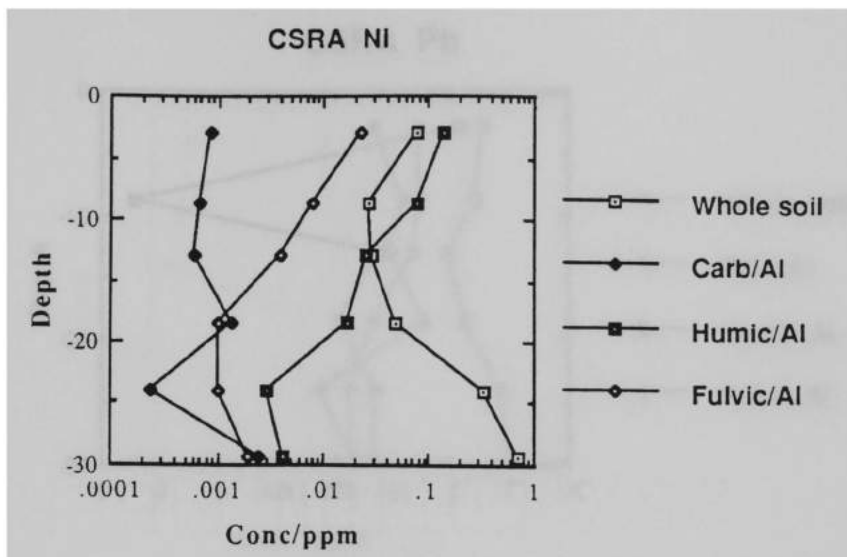


Fig. 36: CSRA Ni vs depth. Sigma values are w.s. 19%; carb 36%; humic 30%; fulvic 71%.

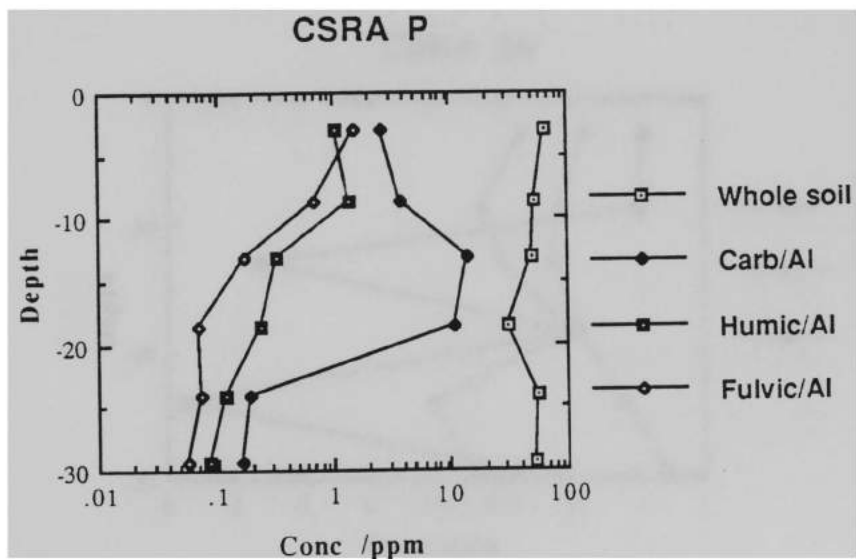


Fig. 37: CSRA P vs depth. Sigma values are w.s. 1.4%; carb 1.8%; humic 23%; fulvic 8.6%.

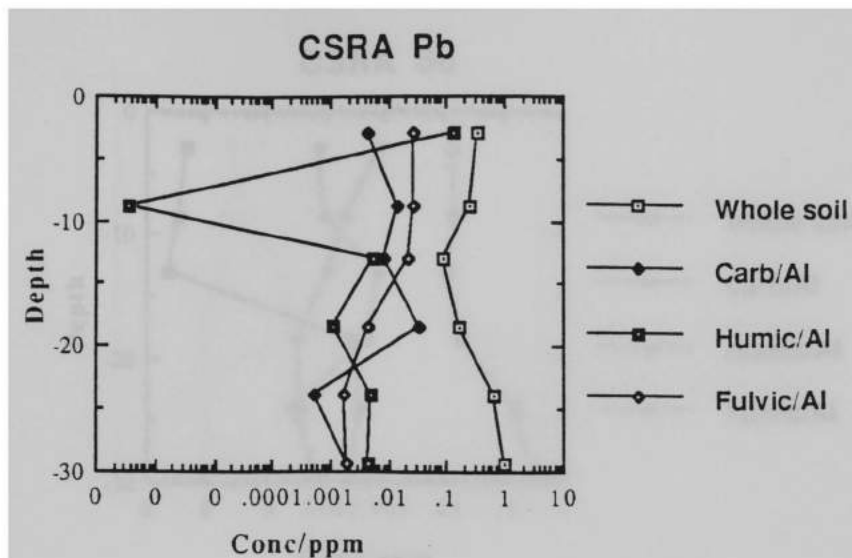


Fig. 38: CSRA Pb vs depth. Sigma values are w.s. 4.2%; carb 2.8%; humic 25%; fulvic 60%.

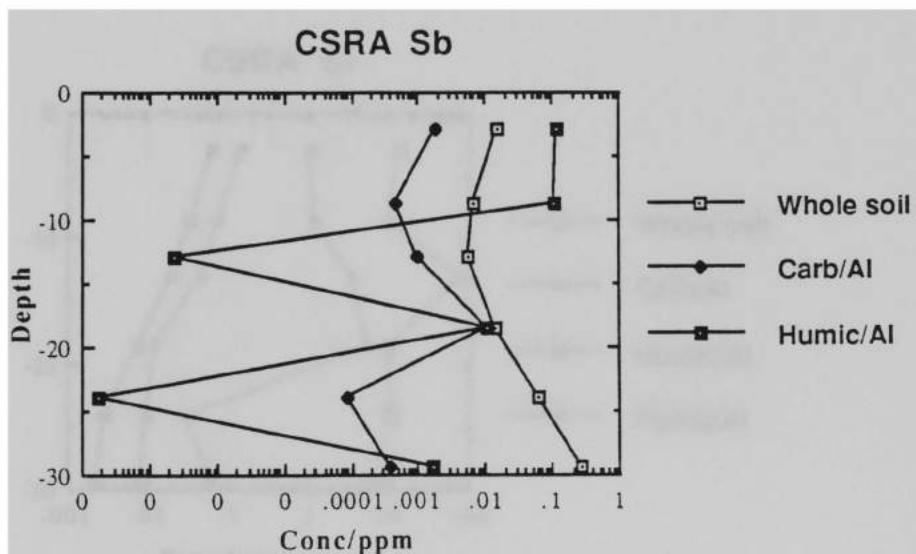


Fig. 39: CSRA Sb vs depth. Sigma values are w.s. 64%; carb 110%; humic 81%. Sb not detected in the fulvic acid.

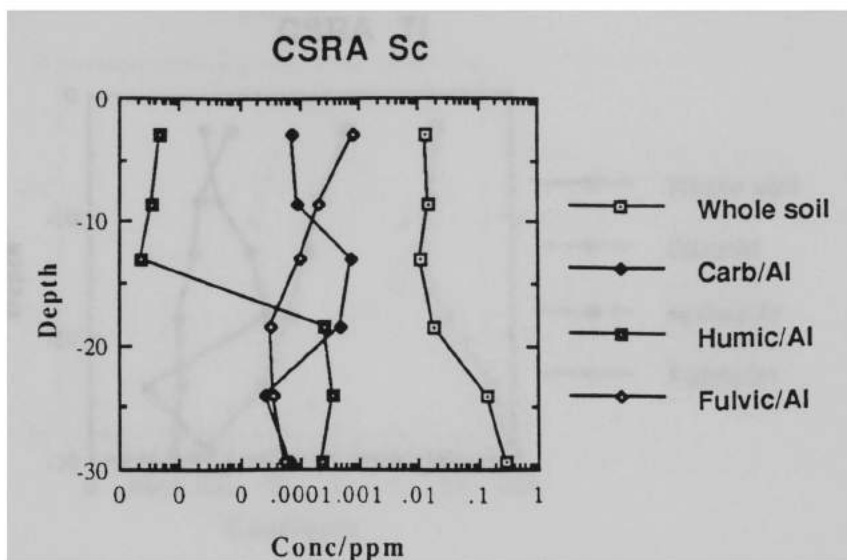


Fig. 40: CSRA Sc vs depth. Sigma values are w.s. 2.7%; carb 6.9%; humic 18%; fulvic 59%.

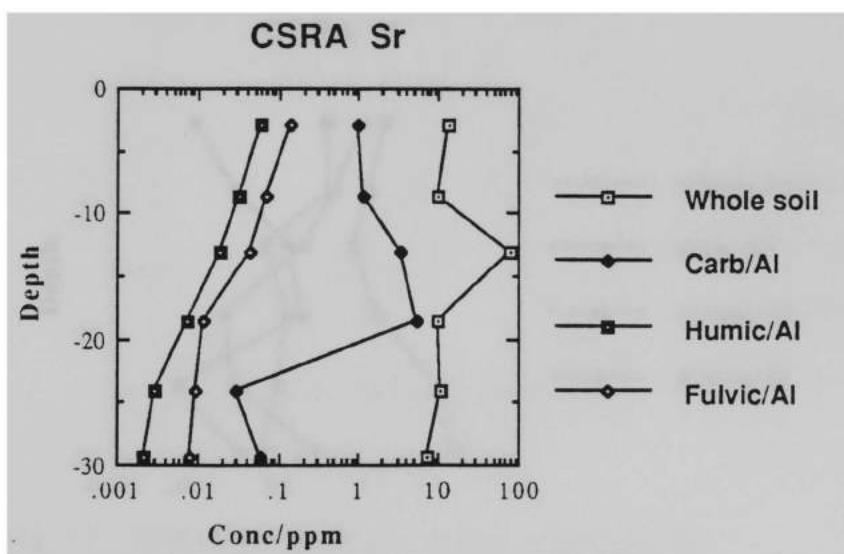


Fig. 41: CSRA Sr vs depth. Sigma values are w.s. 2.5%; carb 1.4%; humic 1.0%; fulvic 1.1%.

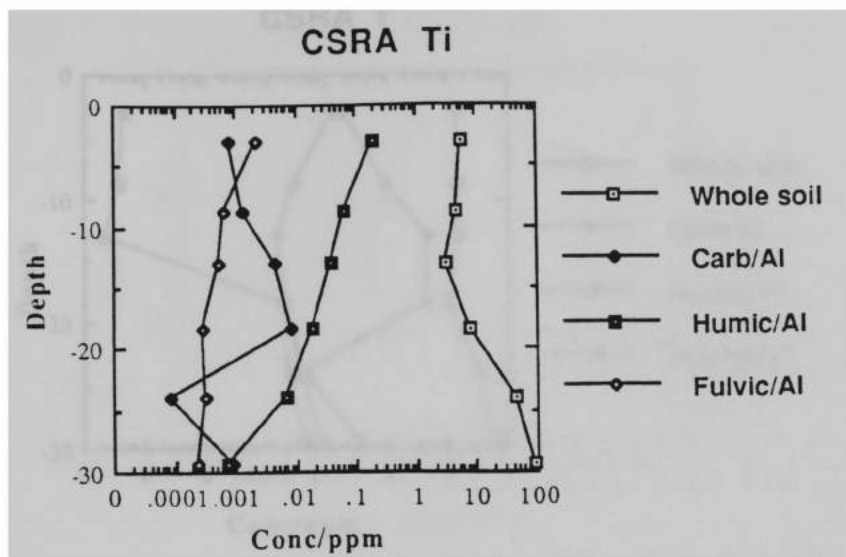


Fig. 42: CSRA Ti vs depth. Sigma values are w.s. 2.2%; carb 1.7%; humic 8.8%; fulvic 30%.

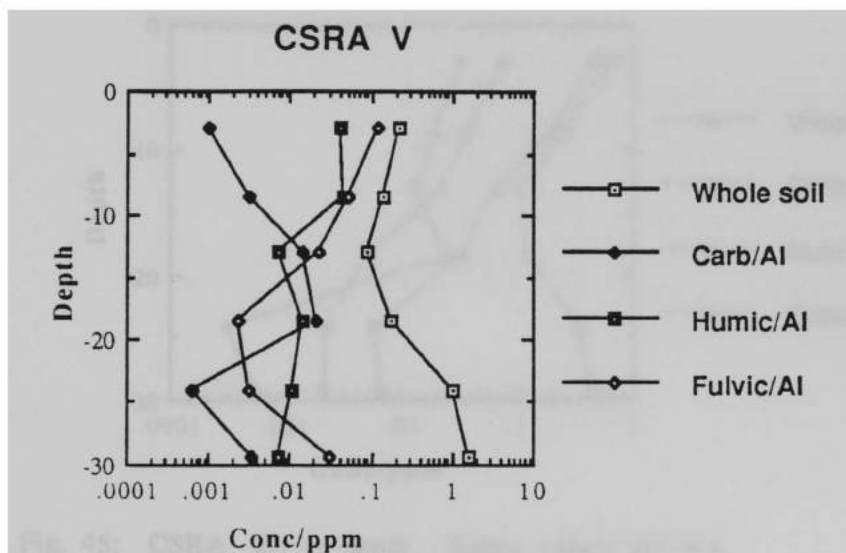


Fig. 43: CSRA V vs depth. Sigma values are w.s. 2.1%; carb 80%; humic 22%; fulvic 2.5%.

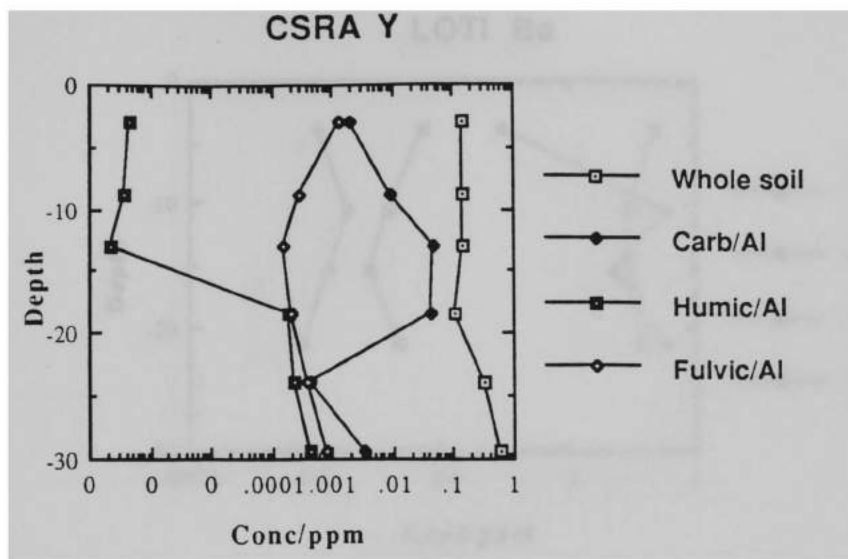


Fig. 44: CSRA Y vs depth. Sigma values are w.s. 1.2%; carb 3.1%; humic 10%; fulvic 3.6%.

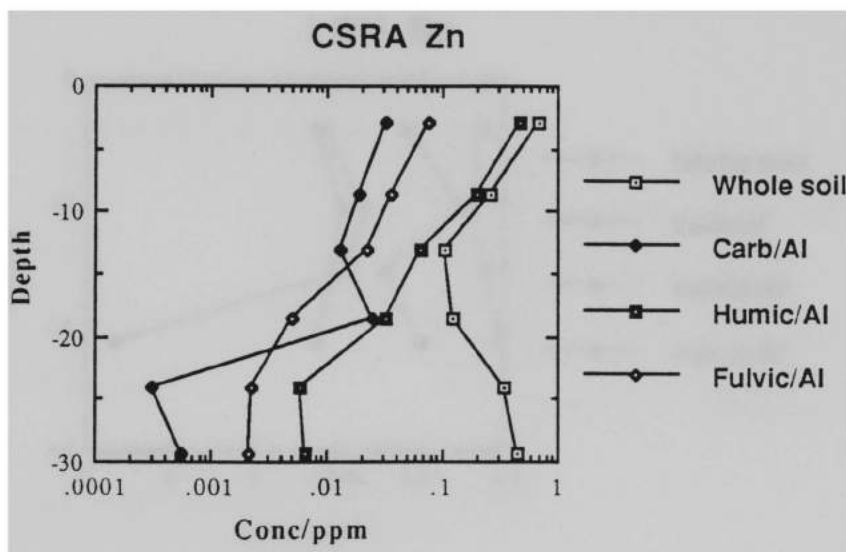


Fig. 45: CSRA Zn vs depth. Sigma values are w.s. 1.8%; carb 2.0%; humic 5.1%; fulvic 4.3%.

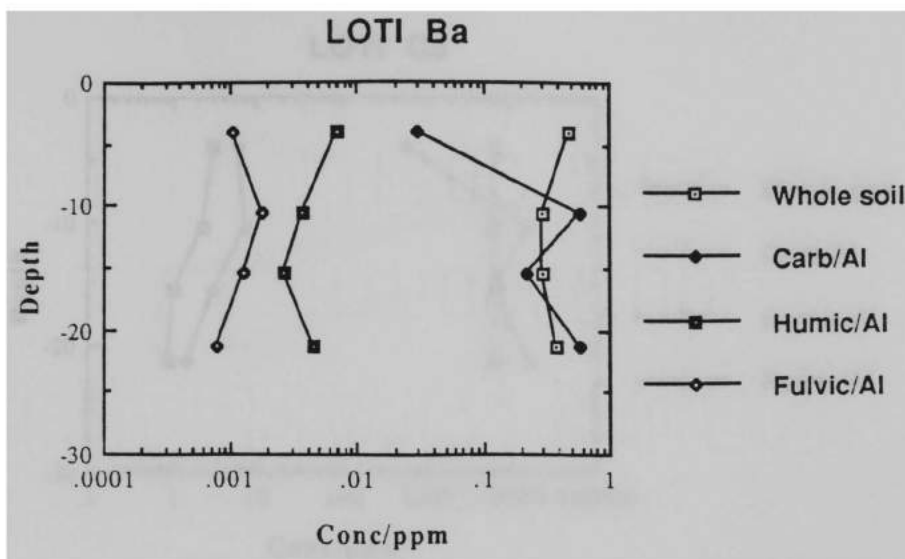


Fig. 46: LOTI Ba vs depth. Sigma values are w.s. 2.5%; carb 1.3%; humic 47%; fulvic 27%.

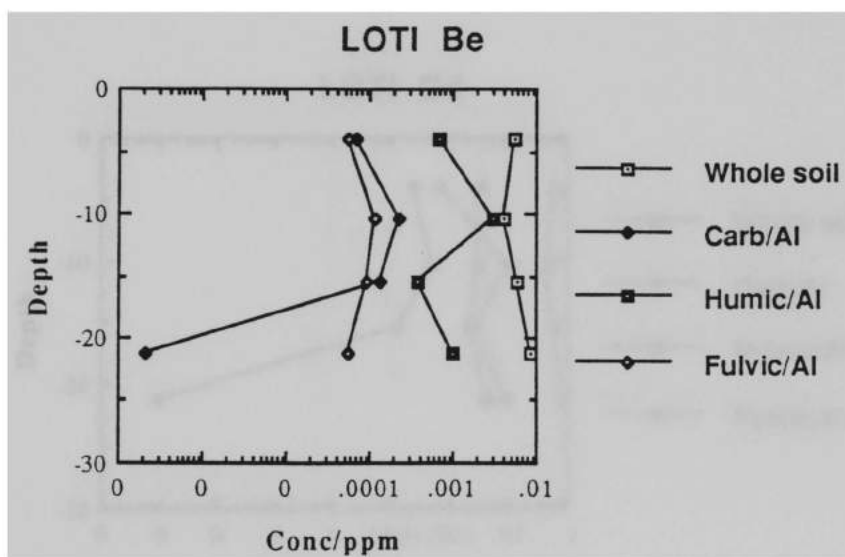


Fig. 47: LOTI Be vs depth. Sigma values are w.s. 2.9%; carb 88%; humic 260%; fulvic 590%.

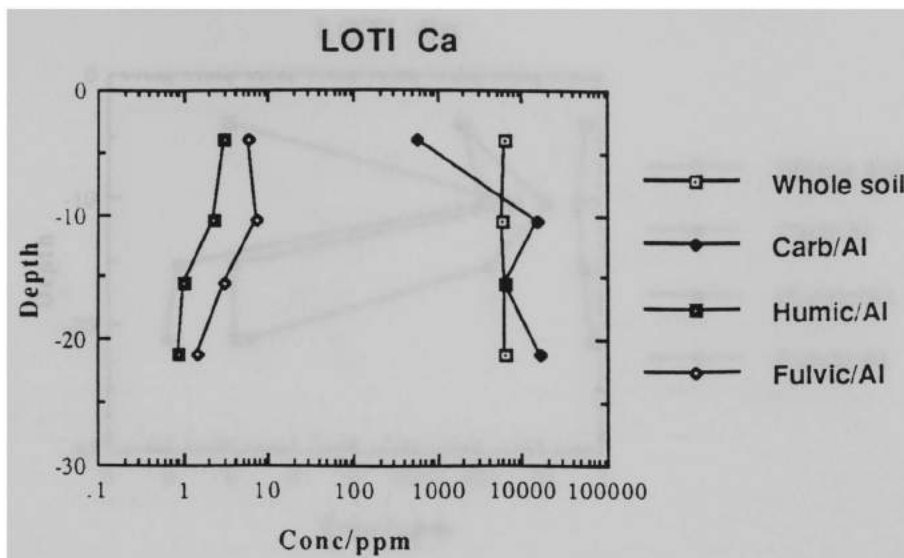


Fig. 48: LOTI Ca vs depth. Sigma values are w.s. 1.3%; carb 2.0%; humic 2.7%; fulvic 1.5%.

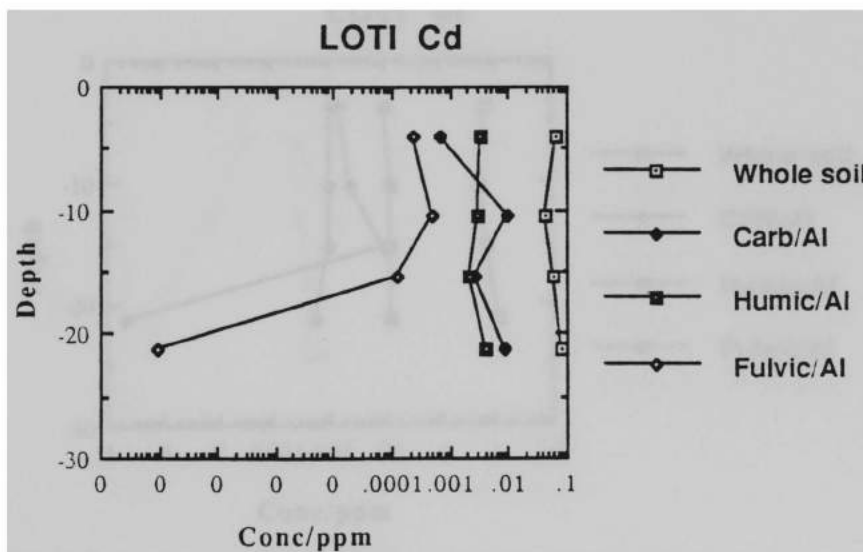


Fig. 49: LOTI Cd vs depth. Sigma values are w.s. 2.0%; carb 35%; humic 68%; fulvic 85%.

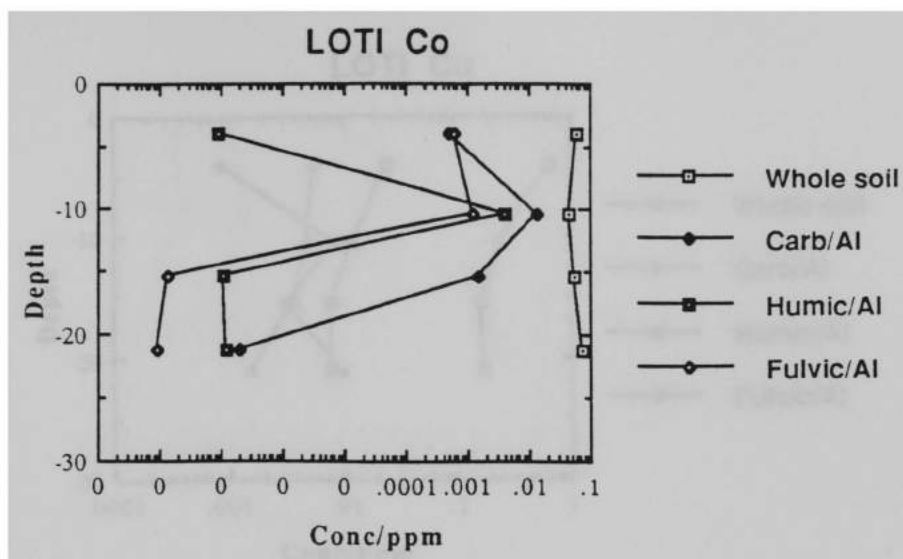


Fig. 50: LOTI Co vs depth. Sigma values are w.s. 2.9%; carb 47%; humic 66%; fulvic 69%.

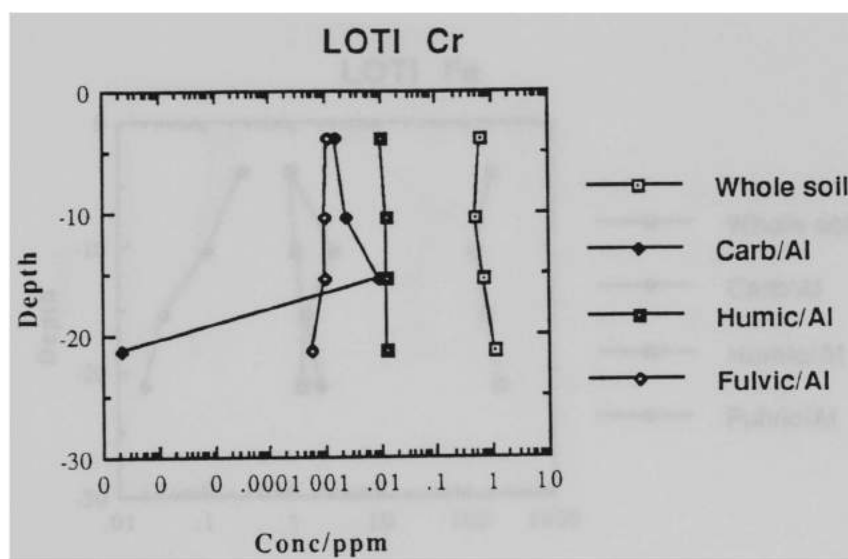


Fig. 51: LOTI Cr vs depth. Sigma values are w.s. 4.0%; carb 190%; humic 28%; fulvic 71%.

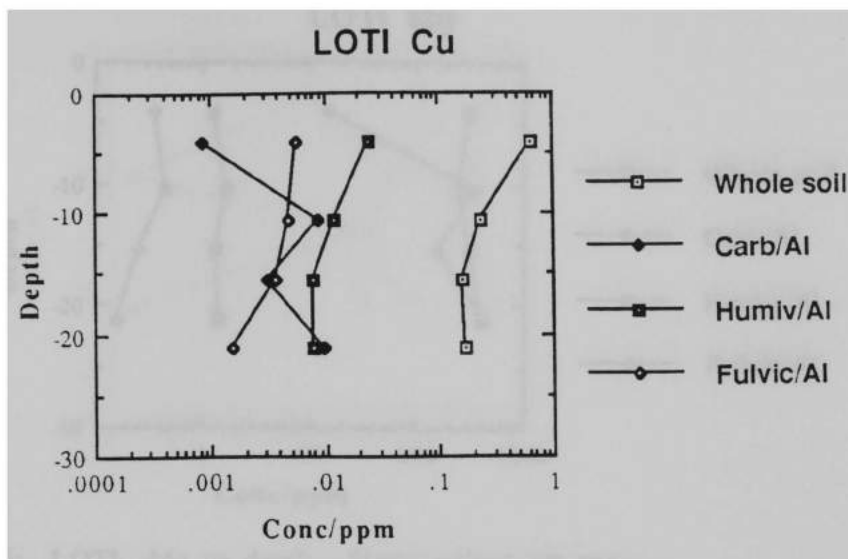


Fig. 52: LOTI Cu vs depth. Sigma values are w.s. 1.8%; carb 28%; humic 15%; fulvic 7.8%.

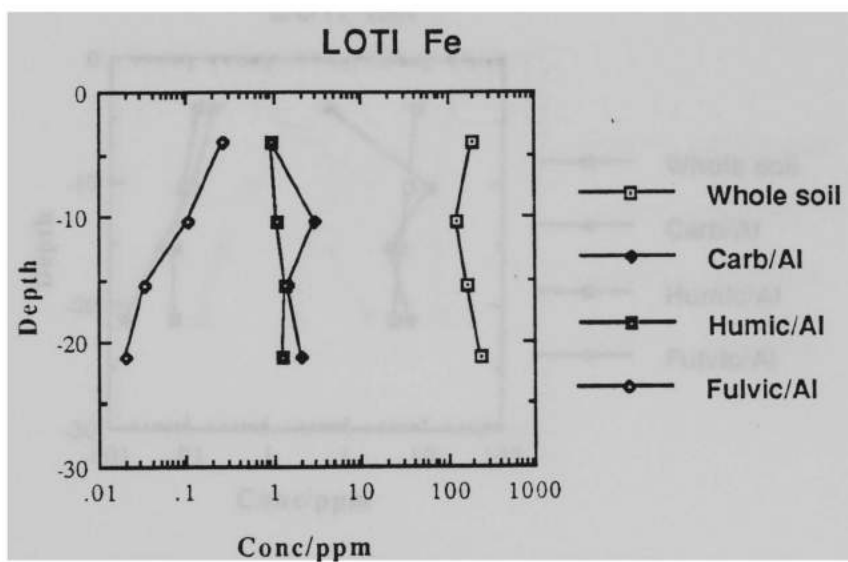


Fig. 53: LOTI Fe vs depth. Sigma values are w.s. 1.4%; carb 1.8%; humic 2.1%; fulvic 2.5%.

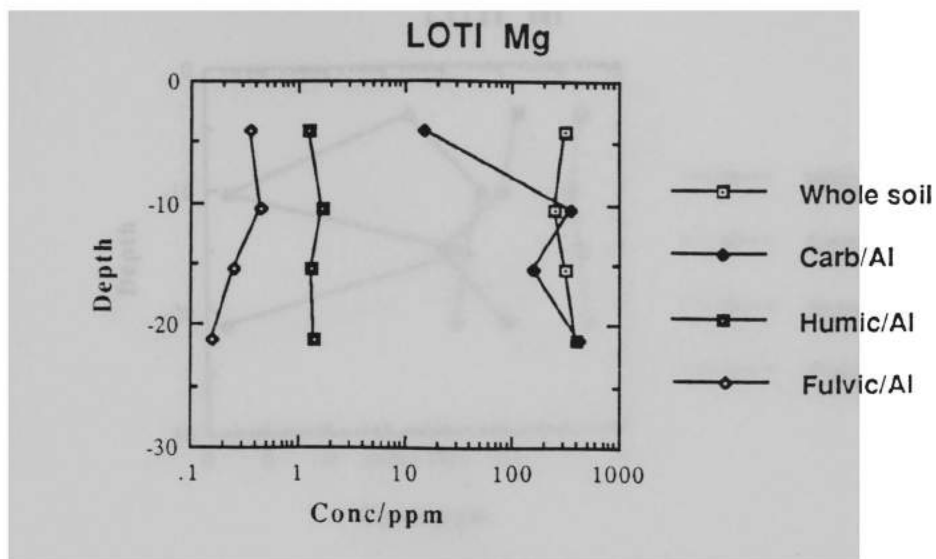


Fig. 54: LOTI Mg vs depth. Sigma values are w.s. 1.3%; carb 1.0%; humic 2.3%; fulvic 1.6%.

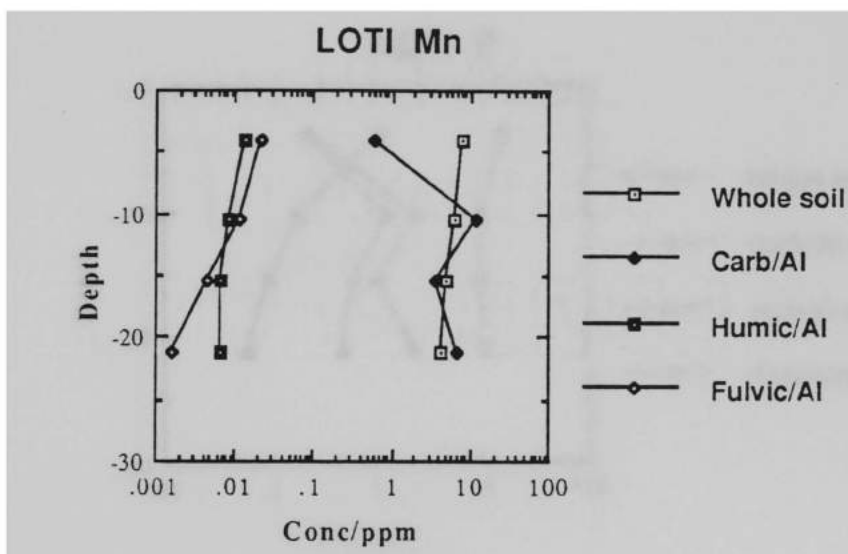


Fig. 55: LOTI Mn vs depth. Sigma values are w.s. 1.7%; carb 1.1%; humic 7.9%; fulvic 2.2%.

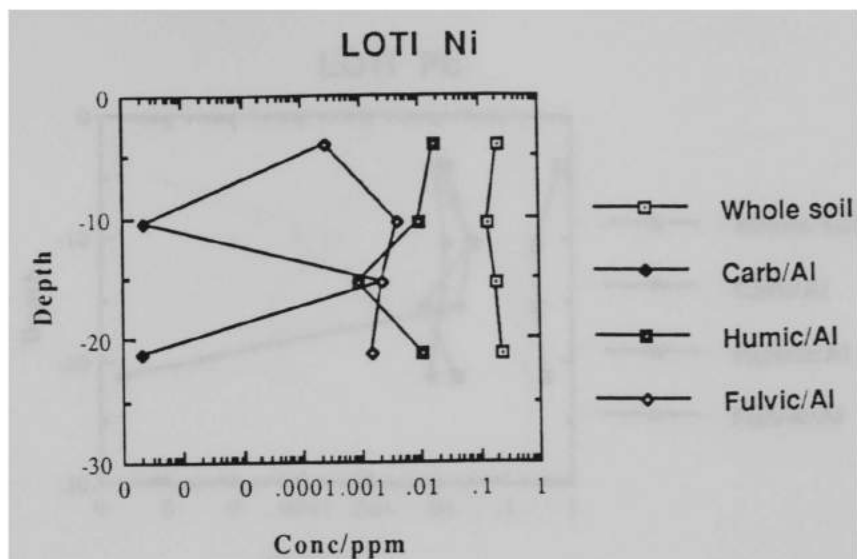


Fig. 56: LOTI Ni vs depth. Sigma values are w.s. 5.7%; carb 170%; humic 52%; fulvic 210%.

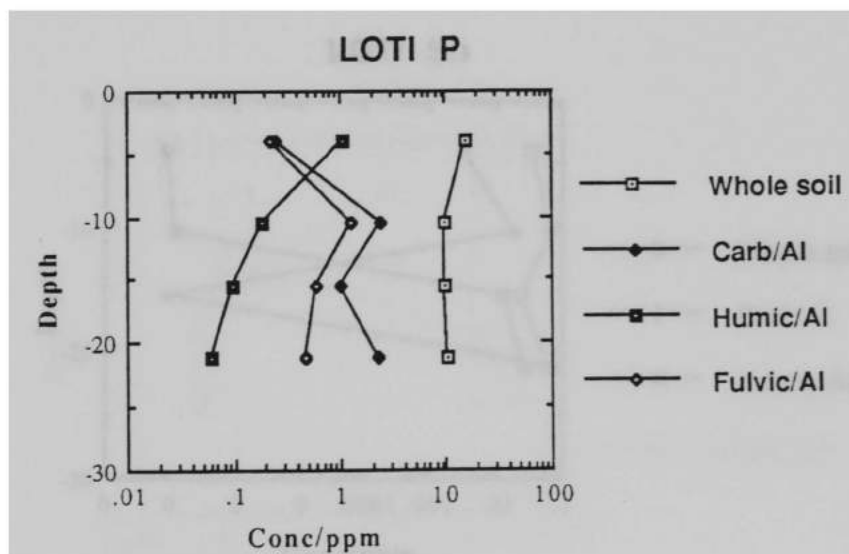


Fig. 57: LOTI P vs depth. Sigma values are w.s. 2.5%; carb 9.7%; humic 40%; fulvic 5.5%.

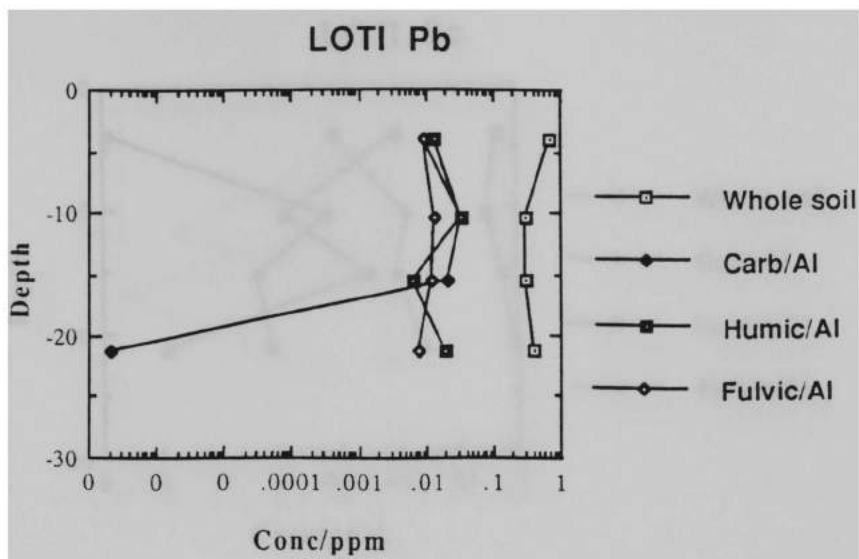


Fig. 58: LOTI Pb vs depth. Sigma values are w.s. 3.5%; carb 98%; humic 200%; fulvic 32%.

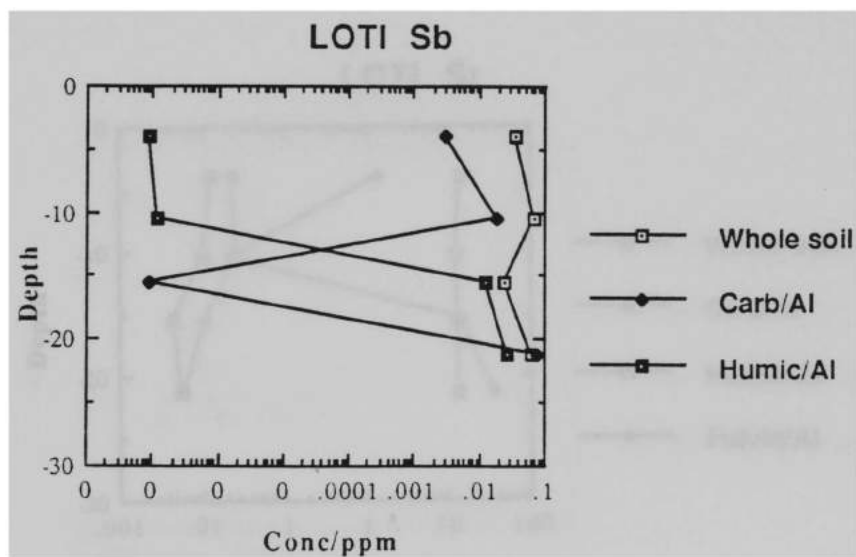


Fig. 59: LOTI Sb vs depth. Sigma values are w.s. 30%; carb 130%; humic 77%. Sb not detected in the fulvic acid.

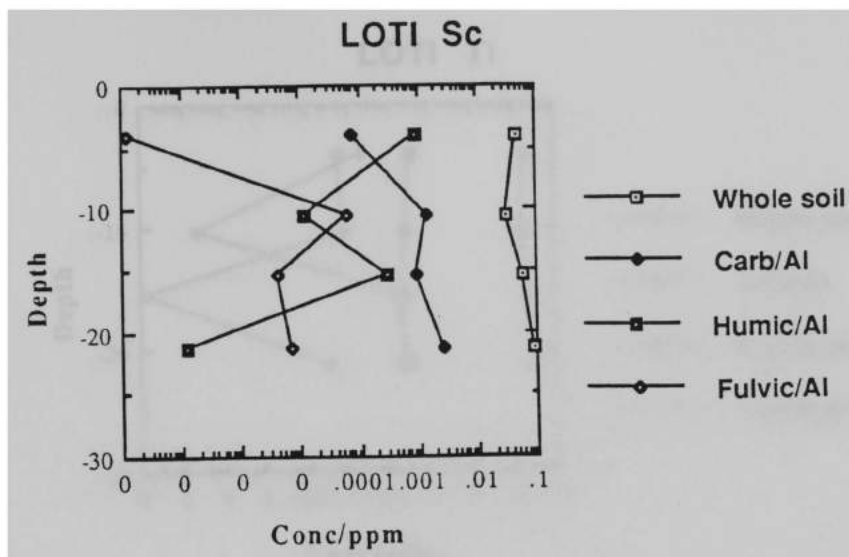


Fig. 60: LOTI Sc vs depth. Sigma values are w.s. 1.9%; carb 35%; humic 180%; fulvic 220%.

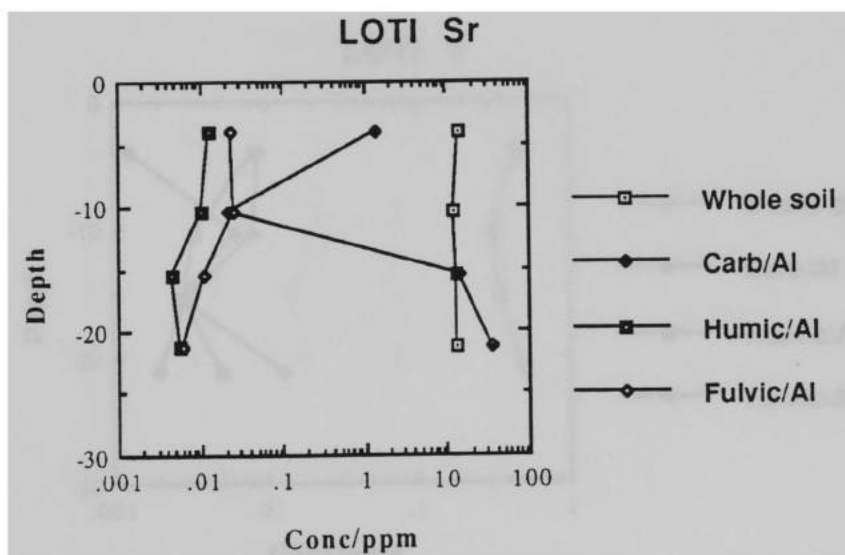


Fig. 61: LOTI Sr vs depth. Sigma values are w.s. 2.0%; carb 5.2%; humic 2.5%; fulvic 1.5%.

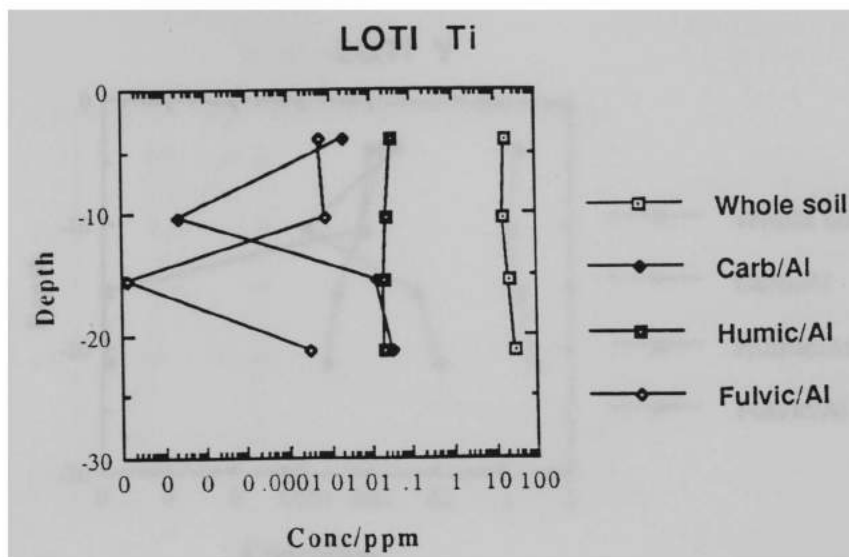


Fig. 62: LOTI Ti vs depth. Sigma values are w.s. 1.7%; carb 3.2%; humic 4.4%; fulvic 50%.

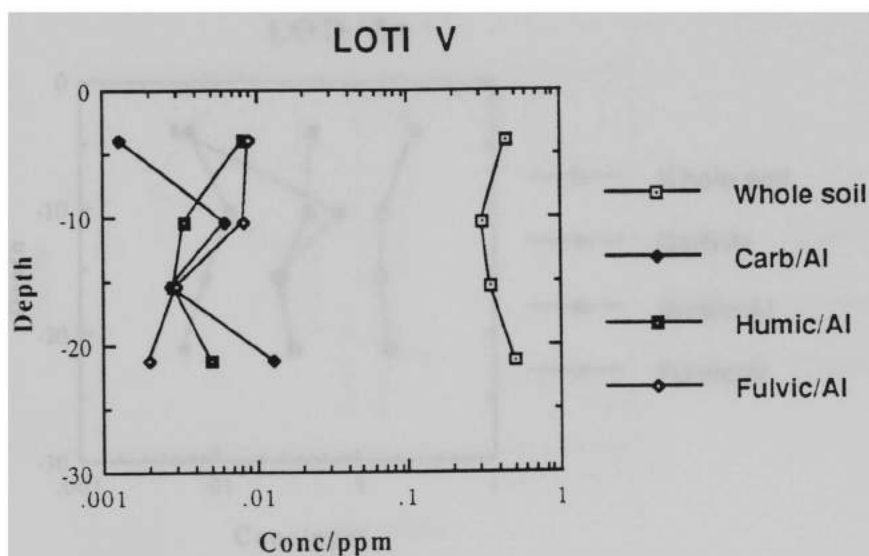


Fig. 63: LOTI V vs depth. Sigma values are w.s. 1.8%; carb 23%; humic 44%; fulvic 11%.

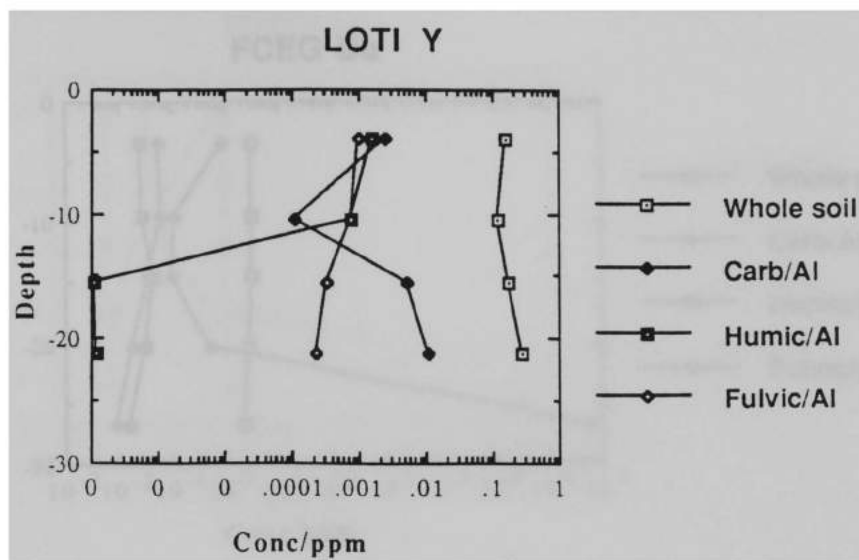


Fig. 64: LOTI Y vs depth. Sigma values are w.s. 2.1%; carb 9.2%; humic 170%; fulvic 12%.

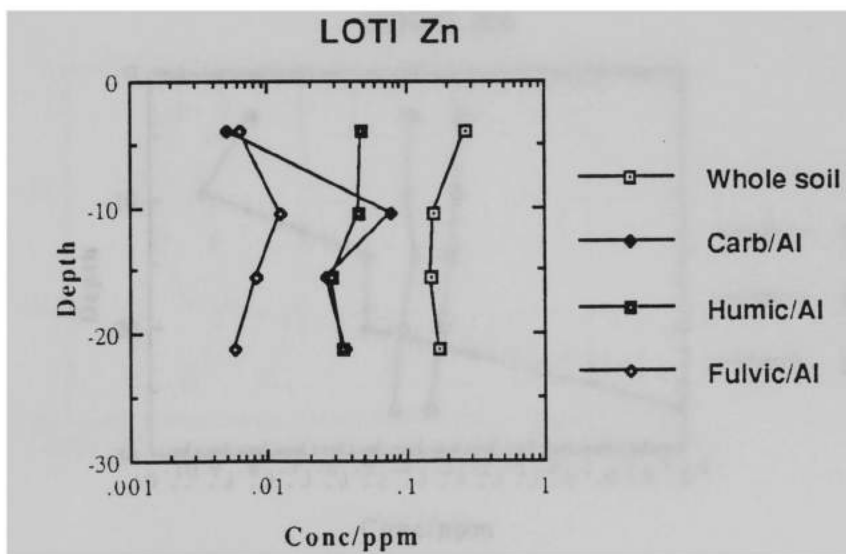


Fig. 65: LOTI Zn vs depth. Sigma values are w.s. 1.8%; carb 2.7%; humic 6.9%; fulvic 4.3%.

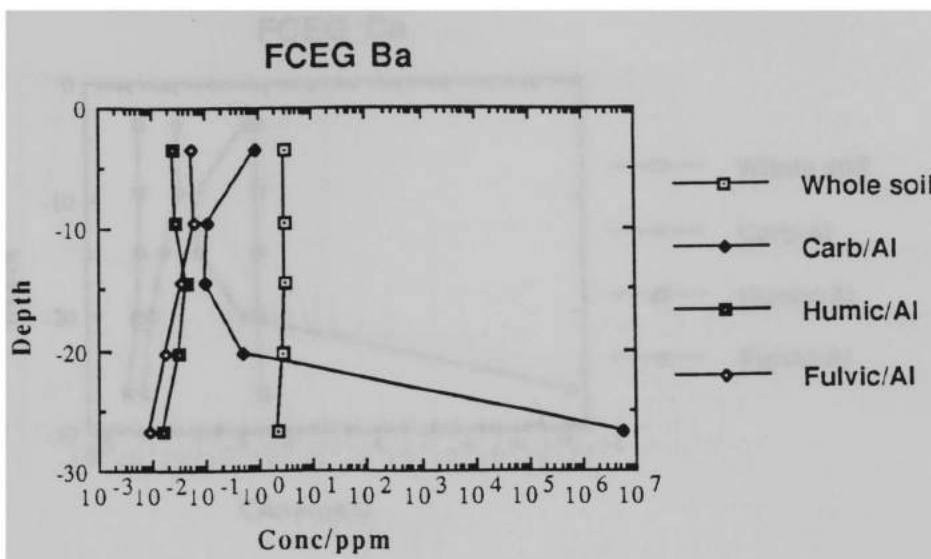


Fig. 66: FCEG Ba vs depth. Sigma values are w.s. 2.3%; carb 3.3%; humic 22%; fulvic 4.6%.

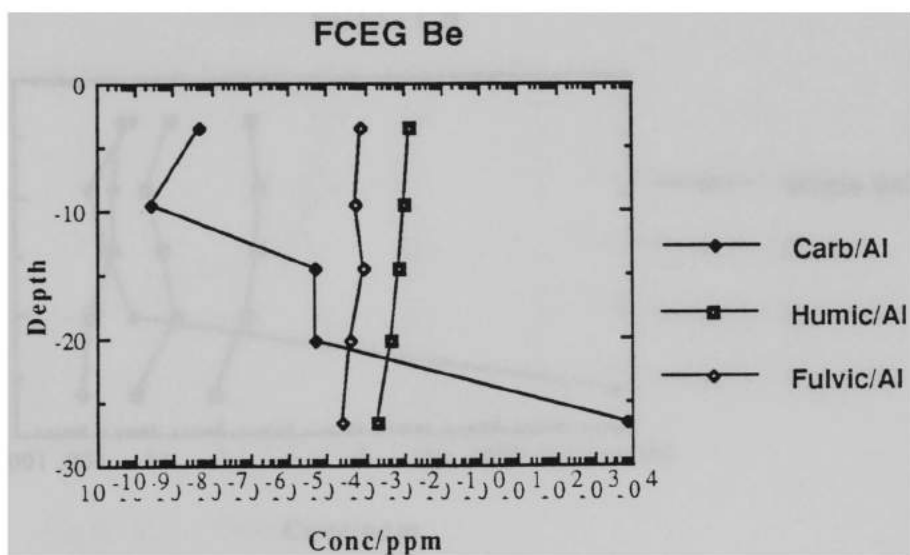


Fig. 67: FCEG Be vs depth. Sigma values are carb 88%; humic 320%; fulvic 570%. Be not detected in the whole soil.

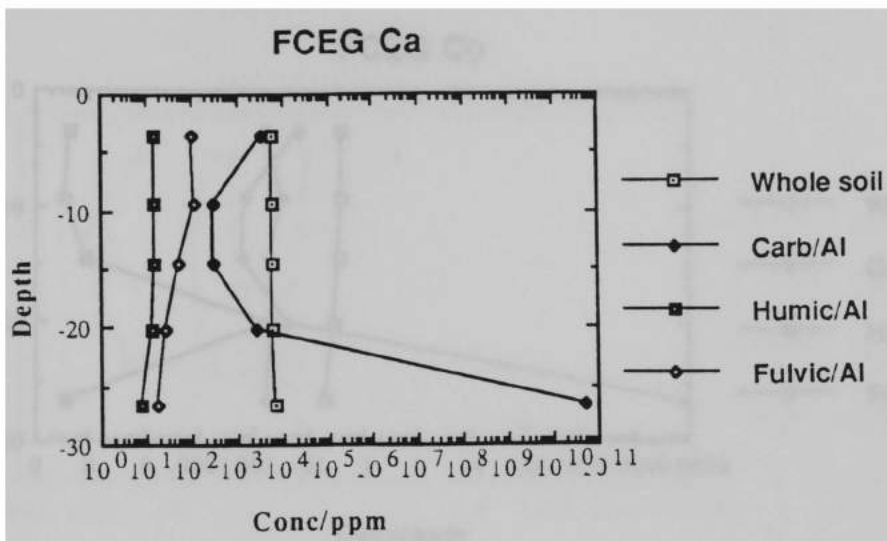


Fig. 68: FCEG Ca vs depth. Sigma values are w.s. 1.4%; carb 2.5%; humic 2.7%; fulvic 1.5%.

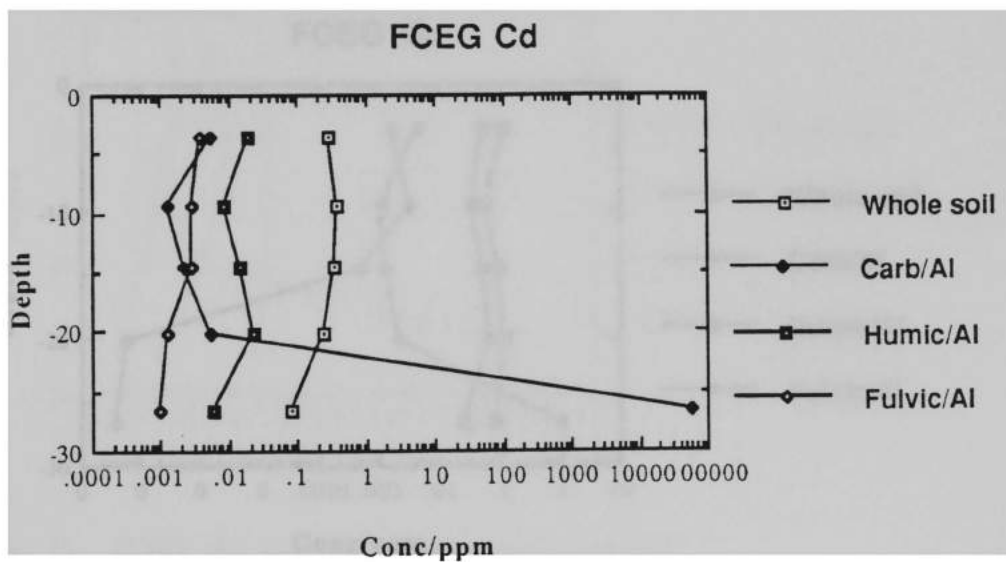


Fig. 69: FCEG Cd vs depth. Sigma values are w.s. 1.7%; carb 14%; humic 90%; fulvic 63%.

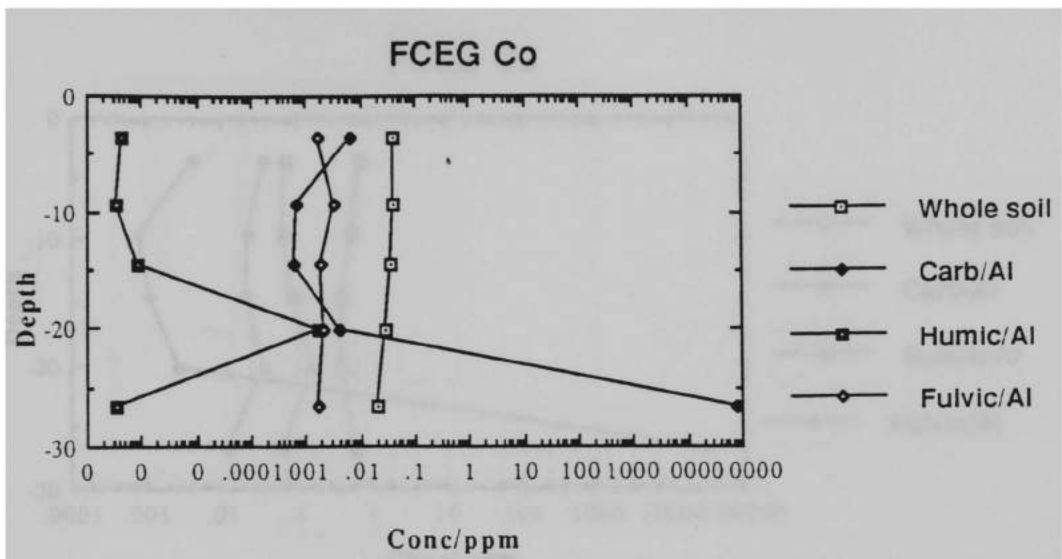


Fig. 70: FCEG Co vs depth. Sigma values are w.s. 5.8%; carb 30%; humic 520%; fulvic 100%.

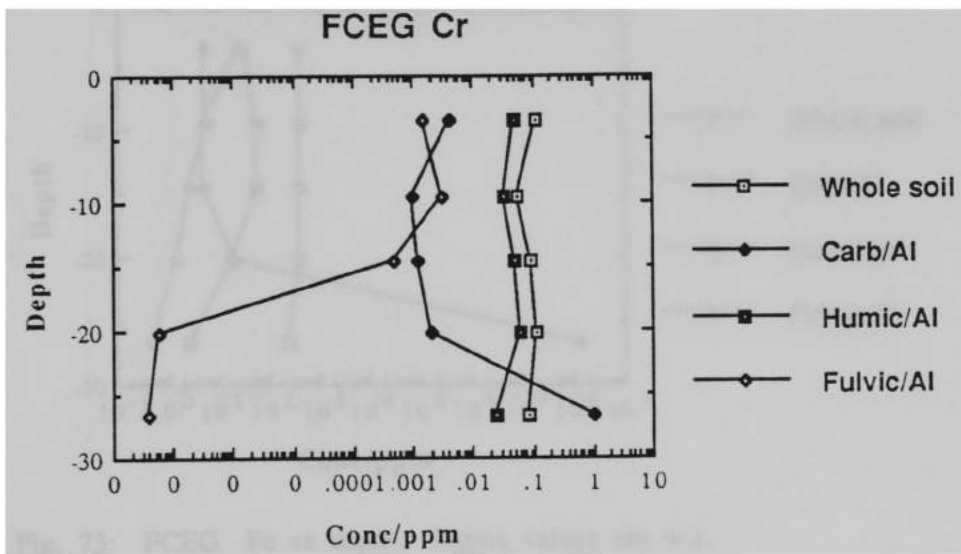


Fig. 71: FCEG Cr vs depth. Sigma values are w.s. 18%; carb 46%; humic 49%; fulvic 100%.

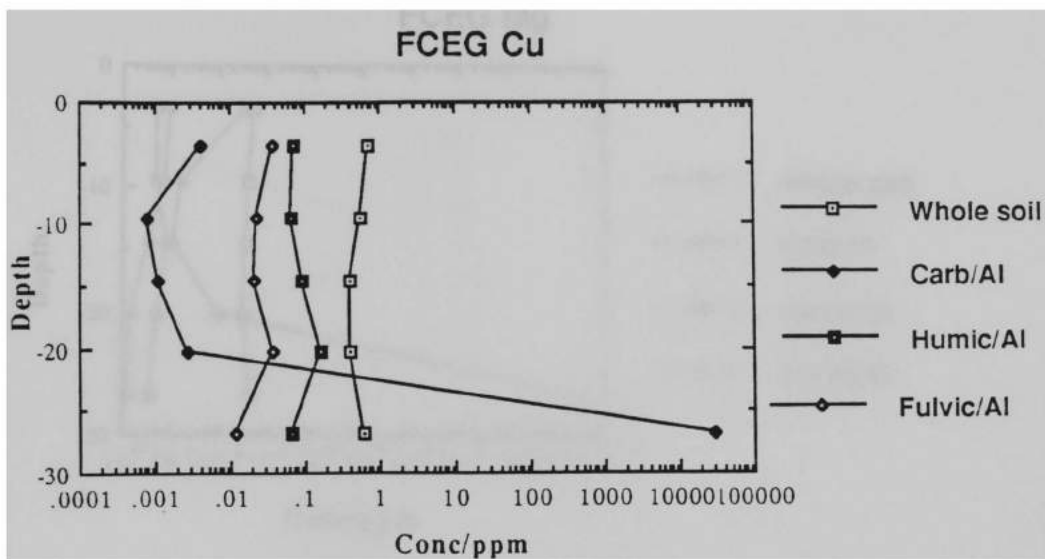


Fig. 72: FCEG Cu vs depth. Sigma values are w.s. 1.4%; carb 24%; humic 7.2%; fulvic 10%.

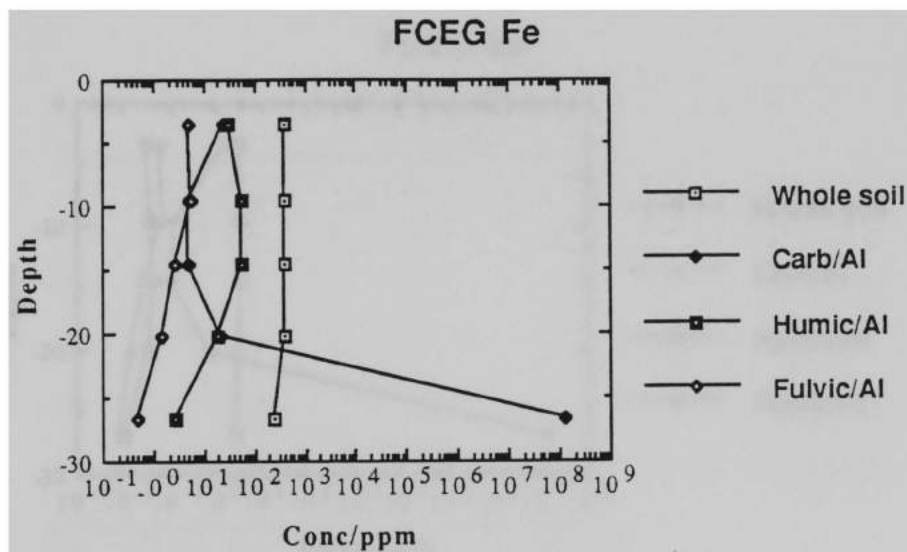


Fig. 73: FCEG Fe vs depth. Sigma values are w.s. 0.3%; carb 2.3%; humic 1.5%; fulvic 1.0%.

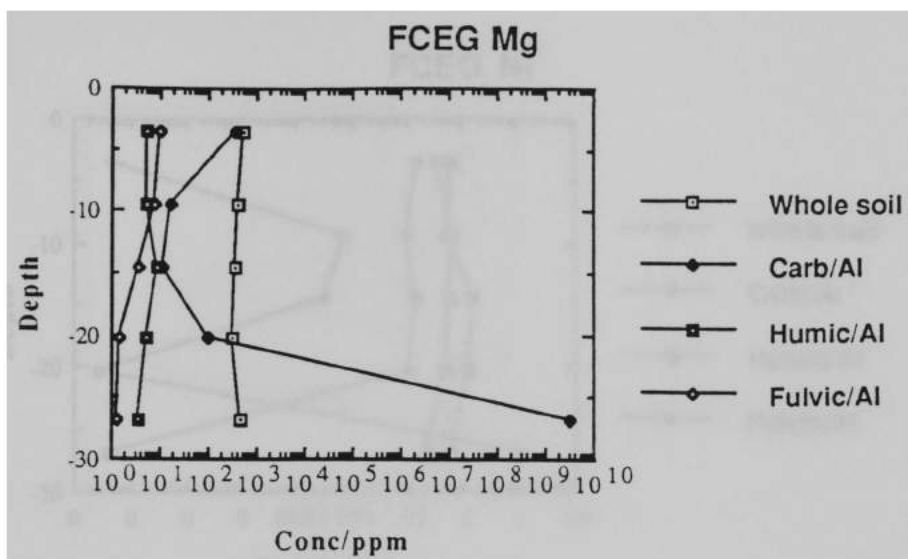


Fig. 74: FCEG Mg vs depth. Sigma values are w.s. 1.3%; carb 1.5%; humic 1.4%; fulvic 0.7%.

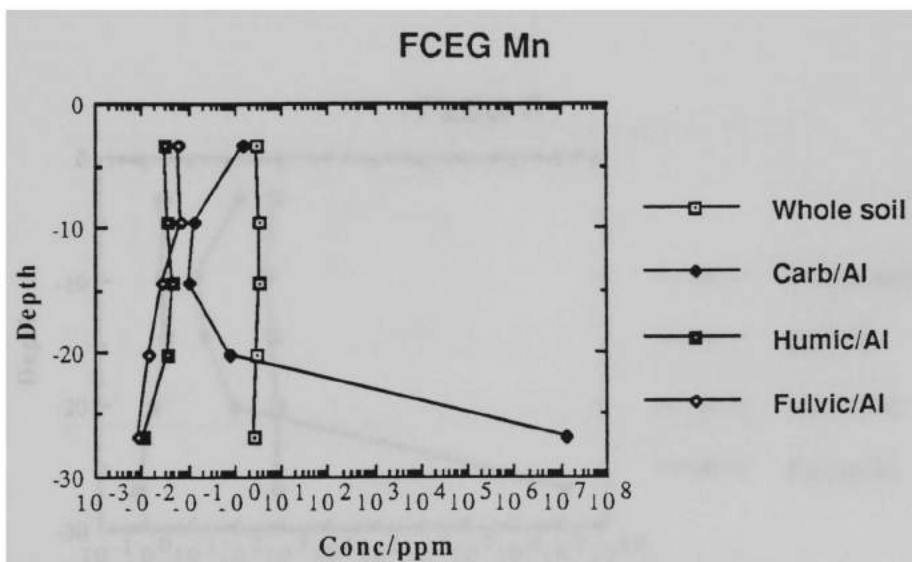


Fig. 75: FCEG Mn vs depth. Sigma values are w.s. 1.8%; carb 1.6%; humic 4.3%; fulvic 1.6%.

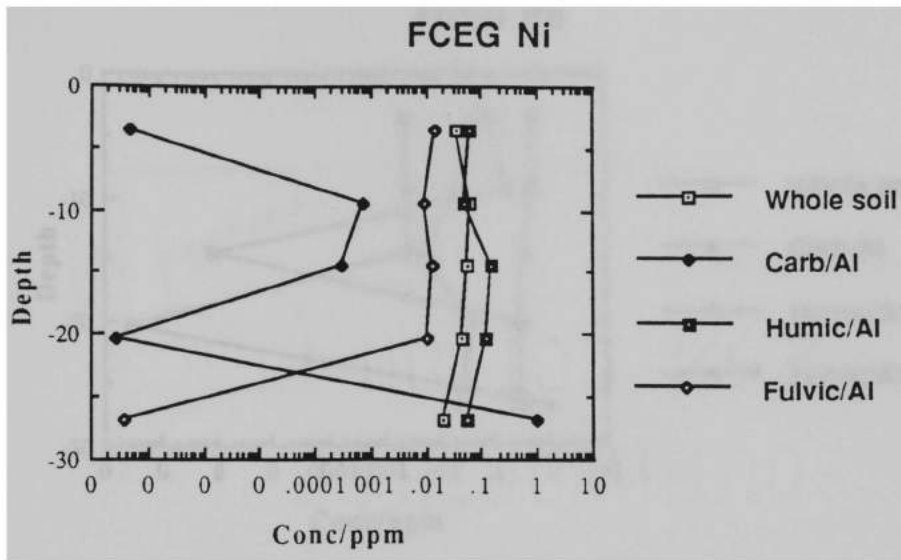


Fig. 76: FCEG Ni vs depth. Sigma values are w.s. 46%; carb 36%; humic 40%; fulvic 88%.

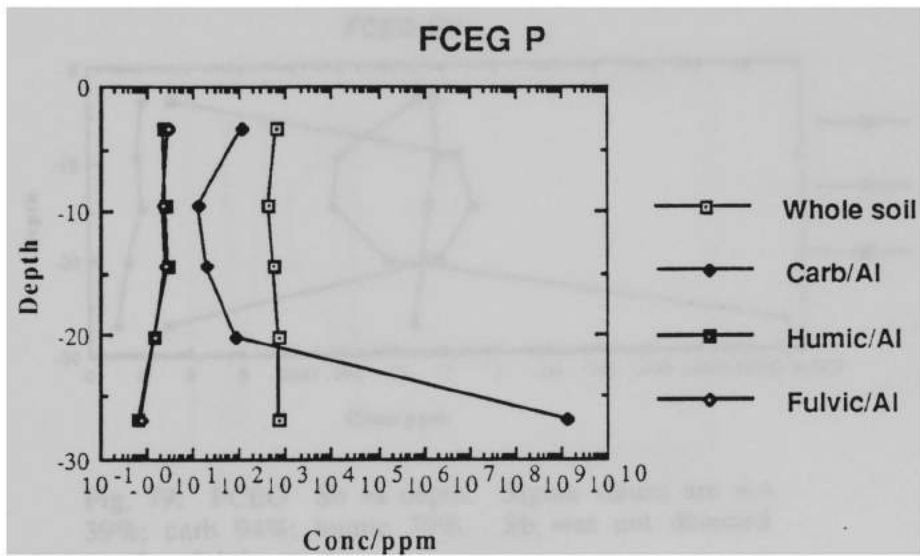


Fig. 77: FCEG P vs depth. Sigma values are w.s. 1.5%; carb 1.9%; humic 26%; fulvic 37%.

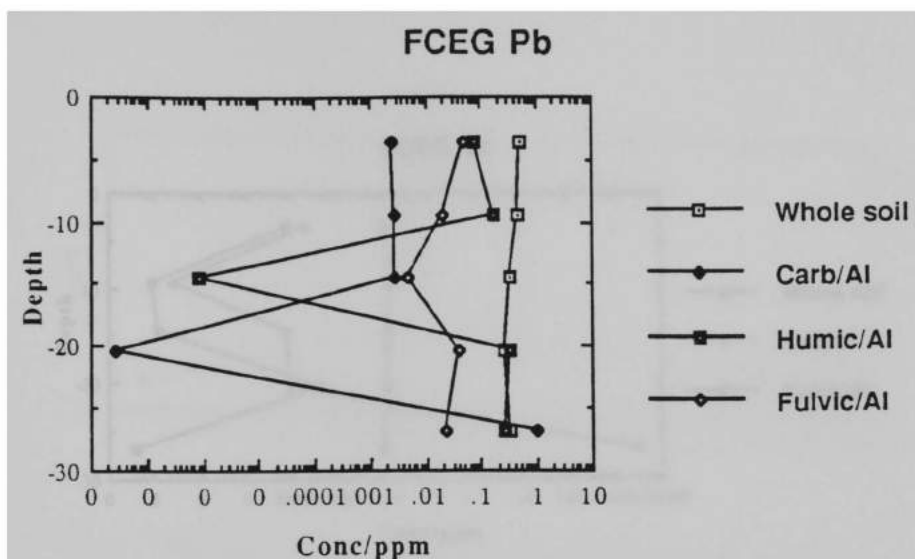


Fig. 78: FCEG Pb vs depth. Sigma values are w.s. 3.5%; carb 120%; humic 84%; fulvic 160%.

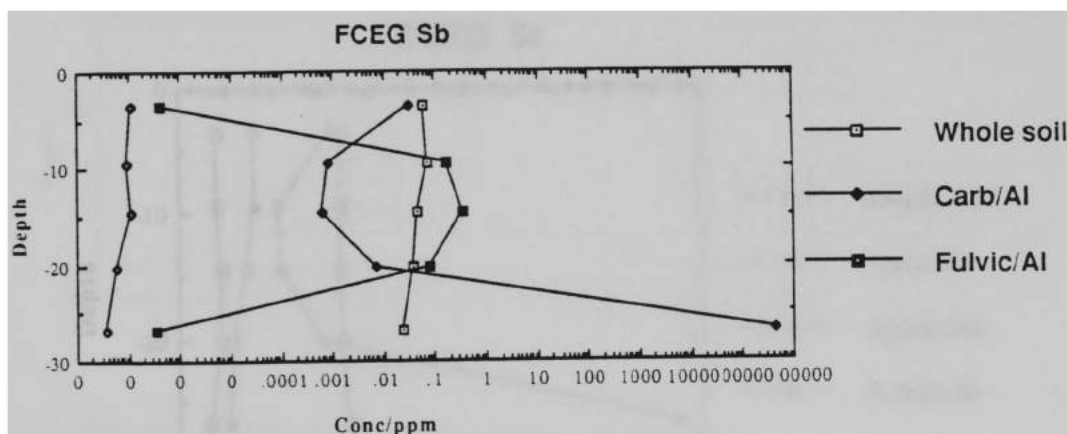


Fig. 79: FCEG Sb vs depth. Sigma values are w.s. 39%; carb 94%; humic 79%. Sb was not detected in the fulvic acid.

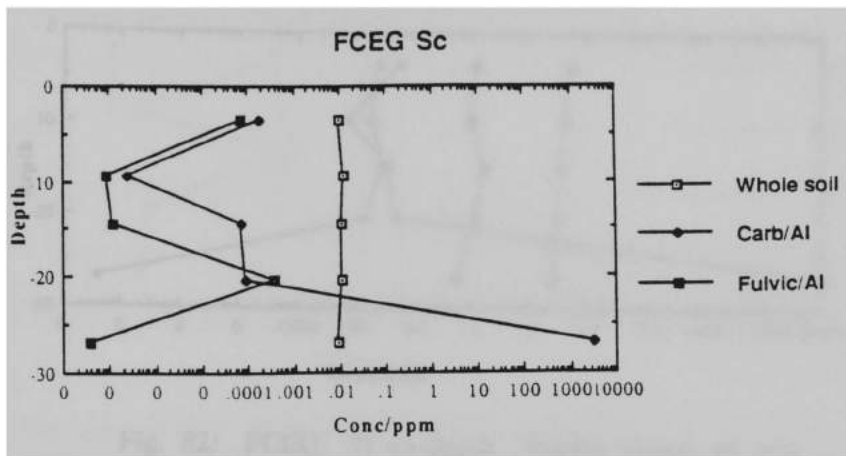


Fig. 80: FCEG Sc vs depth. Sigma values are w.s. 4.9%; carb 77%; fulvic 245%. Sc was not detected in the humic acid.

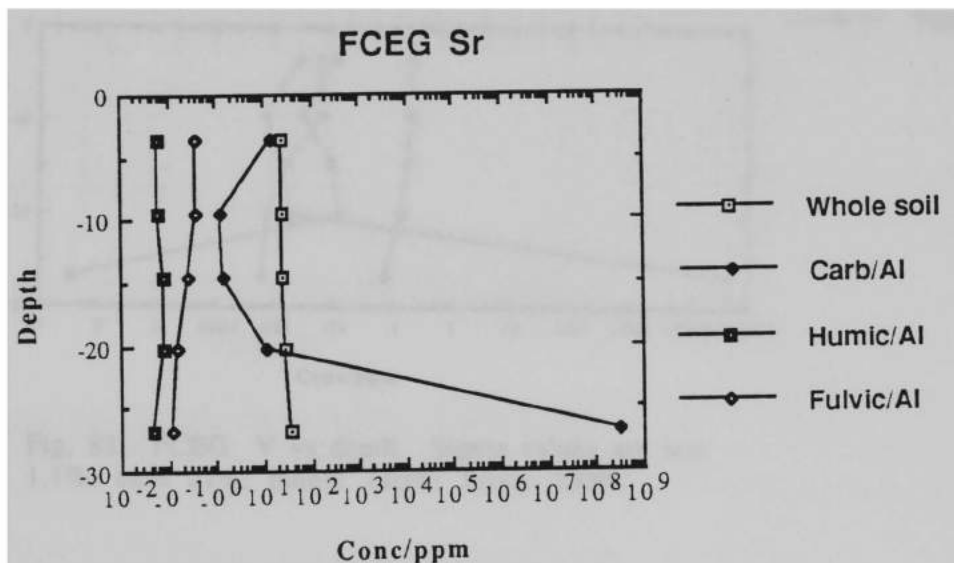


Fig. 81: FCEG Sr vs depth. Sigma values are w.s. 1.5%; carb 1.3%; humic 1.6%; fulvic 0.8%.

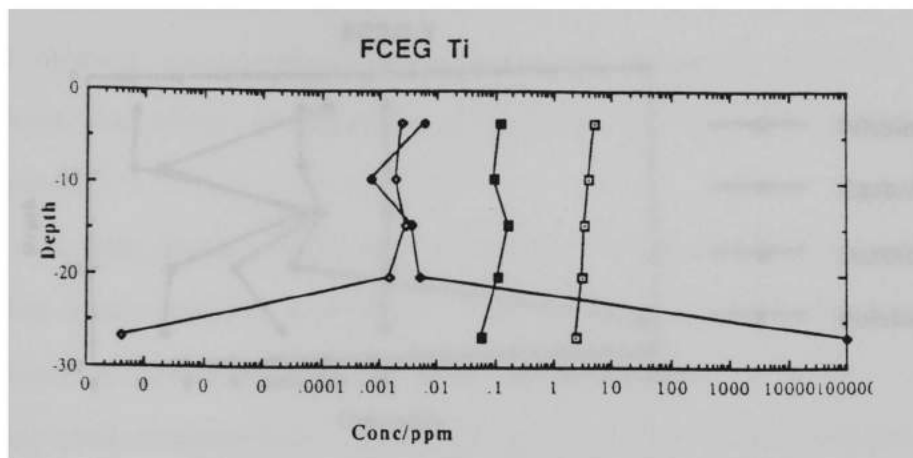


Fig. 82: FCEG Ti vs depth. Sigma values are w.s.
1.5%; carb 5.2%; humic 4.1%; fulvic 56%.

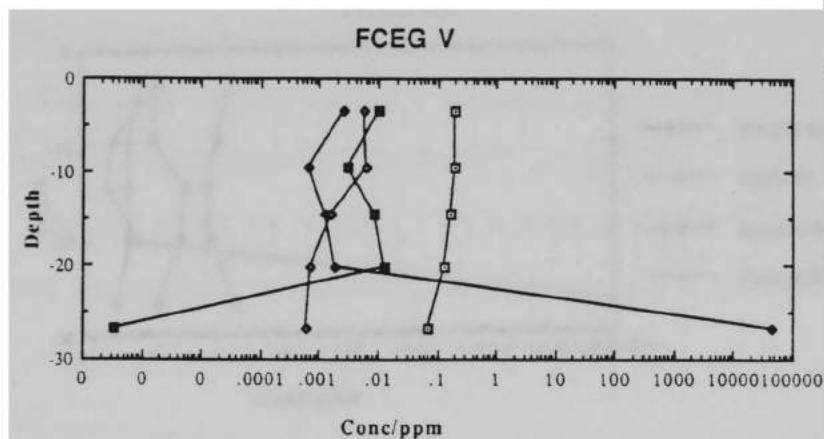
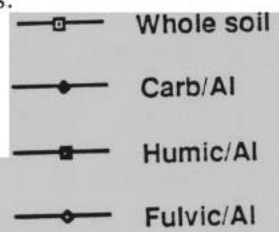


Fig. 83: FCEG V vs depth. Sigma values are w.s.
1.1%; carb 21%; humic 210%; fulvic 180%.

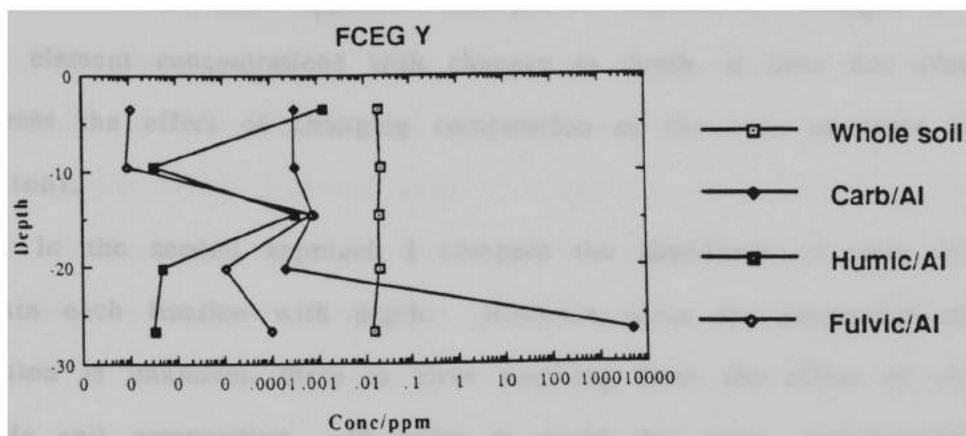


Fig. 84: FCEG Y vs depth. Sigma values are w.s. 1.8%; carb 120%; humic 1000%; fulvic 332%.

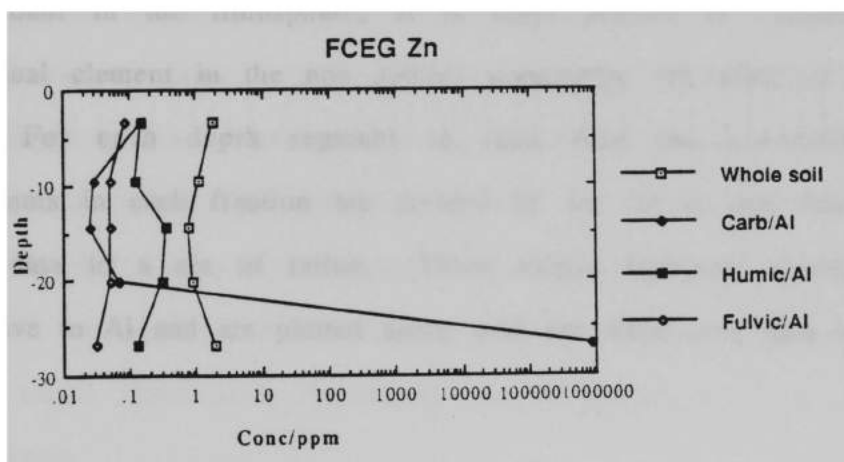


Fig. 85: FCEG Zn vs depth. Sigma values are w.s. 1.8%; carb 2.0%; humic 4.7%; fulvic 3.9%.

Second Methodological Approach

While the above approach attempts to characterize changes in whole soil element concentrations with changes in depth, it does not adequately address the effect of changing composition of the core on trace element content.

In the second approach I compare the abundance of trace elements within each fraction with depth. However, since the proportion of each fraction is unknown, there is error resulting from the effect of changing whole soil composition. In order to avoid this error, concentrations are normalized to a single element within each fraction. The single element chosen is Al because it is one of the major soil forming elements, is abundant in the lithosphere, is in clay, present in limestone and is a residual element in the non soluble component left after its weathering.

For each depth segment in each core the concentrations of the elements in each fraction are divided by the Al in that fraction, reducing the data to a set of ratios. These values represent element abundances relative to Al and are plotted along with the whole soil data in figures 6 to 85.

Third Methodological Approach

In the third approach, I attempt to assess the affinity of elements for the different fractions, regardless of the depth. I divide the normalized carbonate and organic fractions by the ratio of the whole soil to Al (whole soil/Al) and plot the elements against the log of the normalized concentrations (Fig 86 to 112). The approach for WCA3B2 is slightly

different. Whole soil was available only for segment two of that core, so all depths are normalized to that soil/Al ratio.

The patterns of these plots show that the abundances of Ba, Ca, Mn and P in the carbonate fraction display values always greater than 1 (with the exception of the WCA3B2 plots, 1, 3 and 4). These values indicate that these elements are relatively more abundant when compared to the Al in the carbonate fraction. None of the elements in the carbonate fraction in any of the cores studied had a value consistently less than 1. In the FCEG core the apparent increased carbonate abundances for segment 5 plotted in the figures is an artifact resulting from the normalization to Al, which was essentially not detected in that segment of the core.

In the humic acid fraction the elements Be, Cd, Cr, Cu and Zn always show values greater than 1, indicating a greater relative abundance compared to Al. None of the elements in the humic acid fraction have values consistently less than 1.

In the fulvic acid fraction, Be always shows values greater than 1, and Ti consistently shows values less than 1, indicating relatively greater and lesser abundances respectively as compared with the abundances of aluminum.

Although these patterns represent the general affinity of elements for a particular fraction it needs to be further quantified. I define values for enrichment and depletion of the elements as greater than 10X and less than 0.1X respectively as compared to Al. I look at the concentrations of each element compared to the Al in each fraction and note the frequency of occurrence divided by the possible number of occurrences. This

information is included in Table 5. Elements which were enriched or depleted in a particular fraction in at least 12 of the 24 segments were:

Carbonate fraction

Enriched: Be, Ca, Sr, Mg and Sb

Depleted: Ti

Humic fraction

Enriched: Be, Ni and Zn

Depleted: Co and Sc

Fulvic fraction

Enriched: Be and Zn

Depleted: Sb and Ti

Fourth Methodological Approach

In the fourth approach, correlation coefficients in the whole soil are determined for element vs element (Table 6, Fig 113, 114) and the element concentrations in the whole soils are plotted against the less than 550°C and the greater than 550°C % volatile loss. The correlation coefficients for these plots are determined (Table 7). This approach highlights similar behavior between the major and trace elements which indicates that the trace elements are sited in predictable minerals or phases (i.e. Al and Ti; Fe and Cd) and demonstrates the correlations between changes in the composition of the whole soil and element concentrations (Fig 115 and 116).

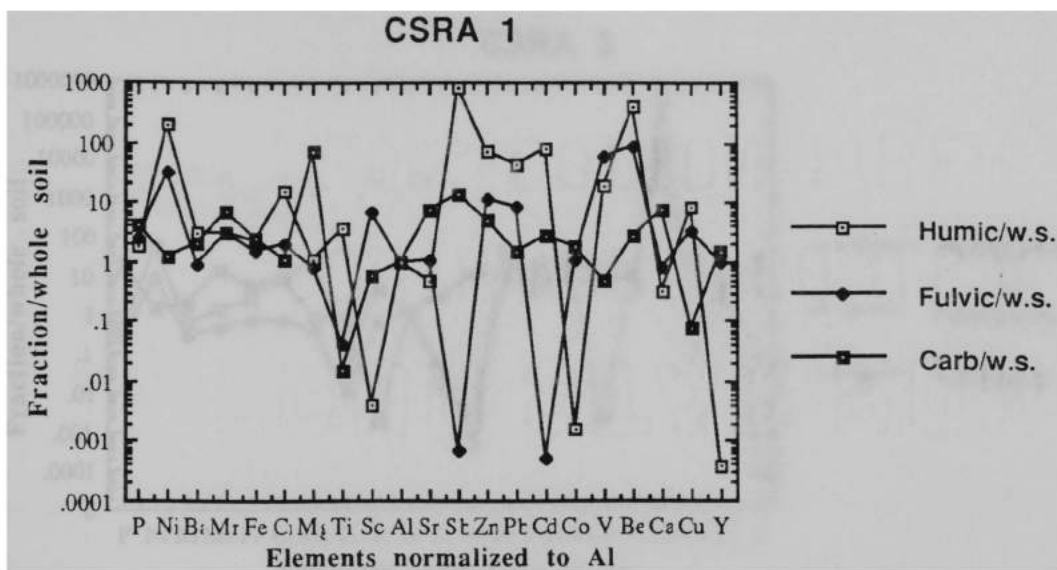


Fig. 86: CSRA 1: Enrichment/depletion of organic and carbonate fractions relative to Al.

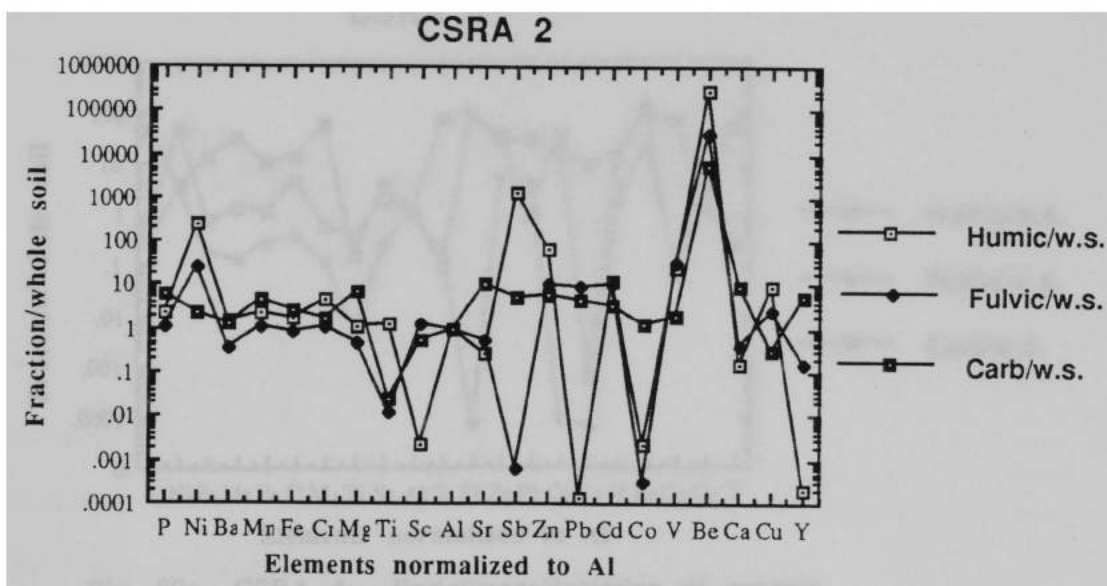


Fig. 87: CSRA 2: Enrichment/depletion of organic and carbonate fractions relative to Al.

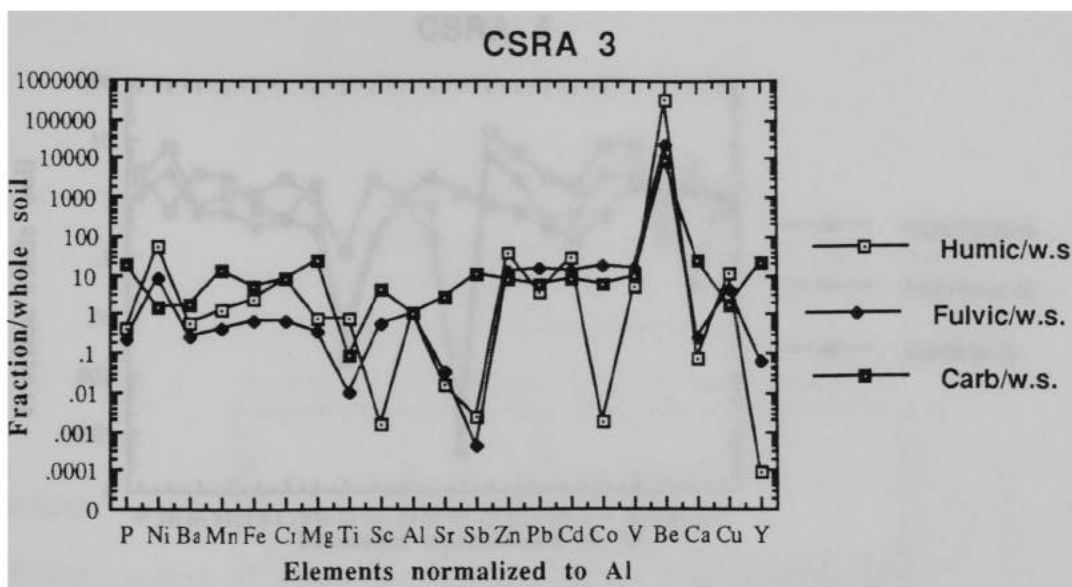


Fig. 88: CSRA 3: Enrichment/depletion of organic and carbonate fractions relative to Al.

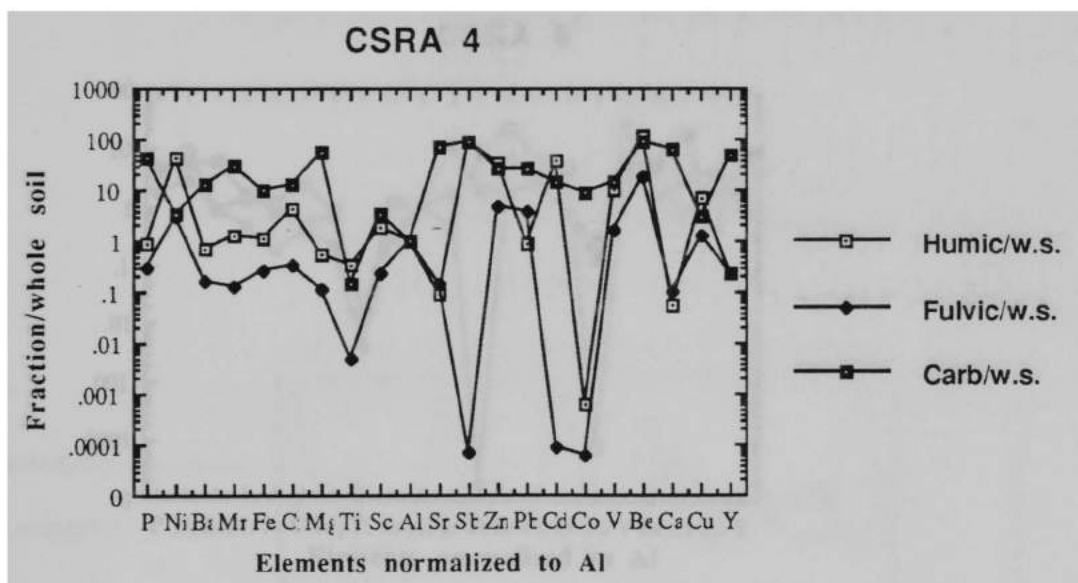


Fig. 89: CSRA 4: Enrichment/depletion of organic and carbonate fractions relative to Al.

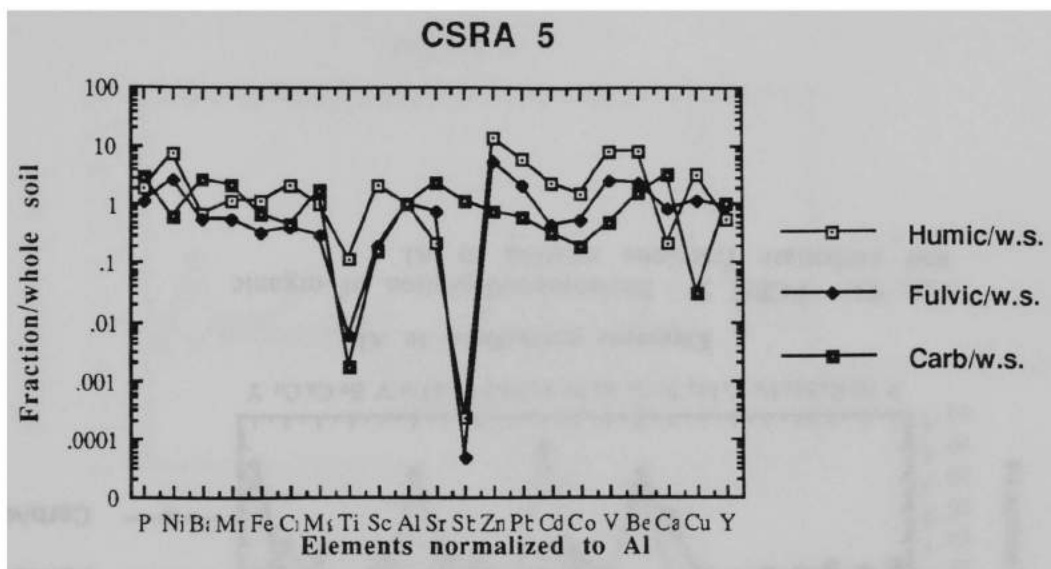


Fig. 90: CSRA 5: Enrichment/depletion of organic and carbonate fractions relative to Al.

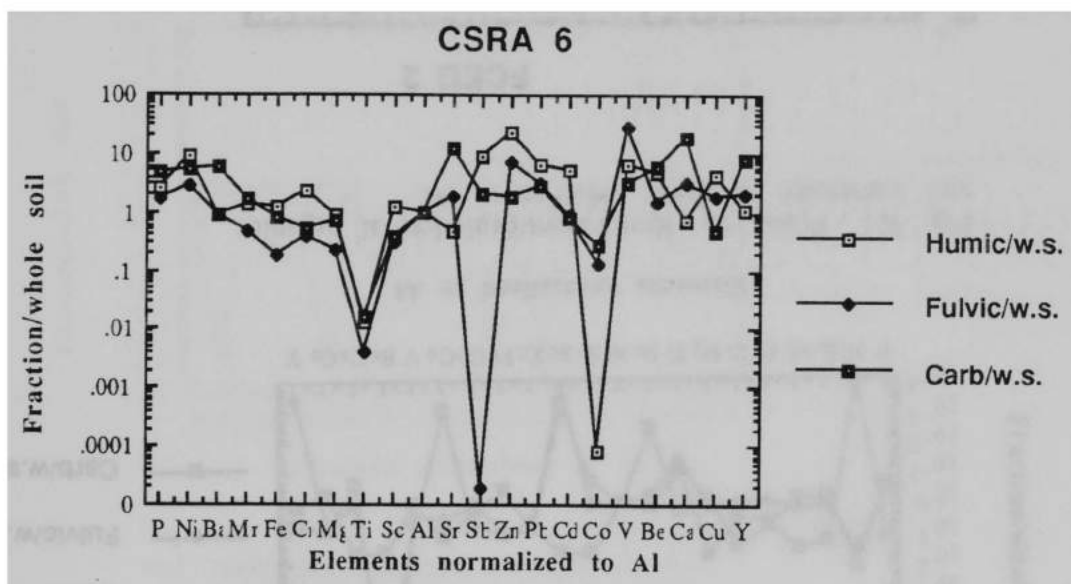


Fig. 91: CSRA 6: Enrichment/depletion of organic and carbonate fractions relative to Al.

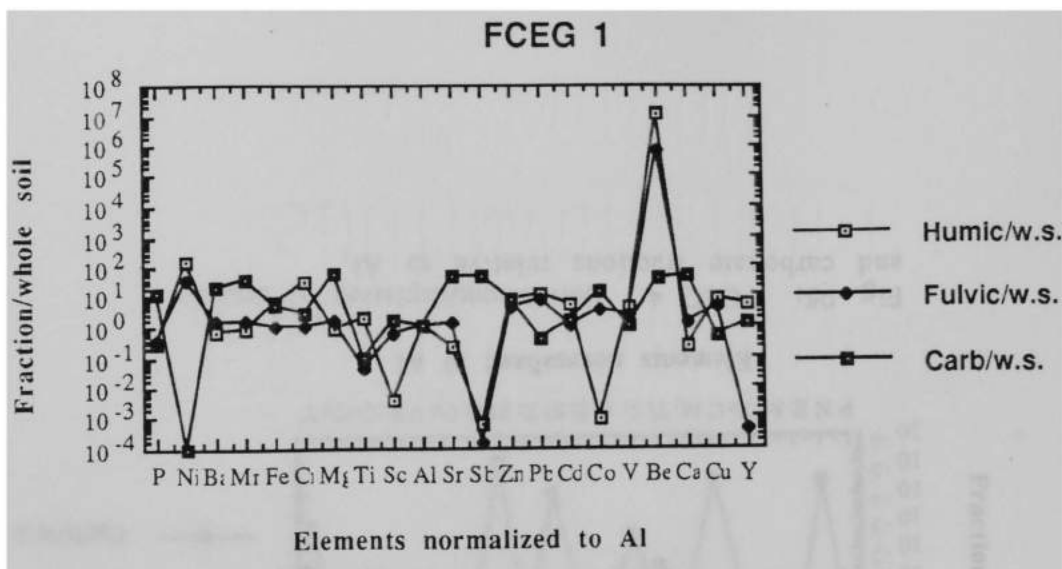


Fig. 92: FCEG 1: Enrichment/depletion of organic and carbonate fractions relative to Al.

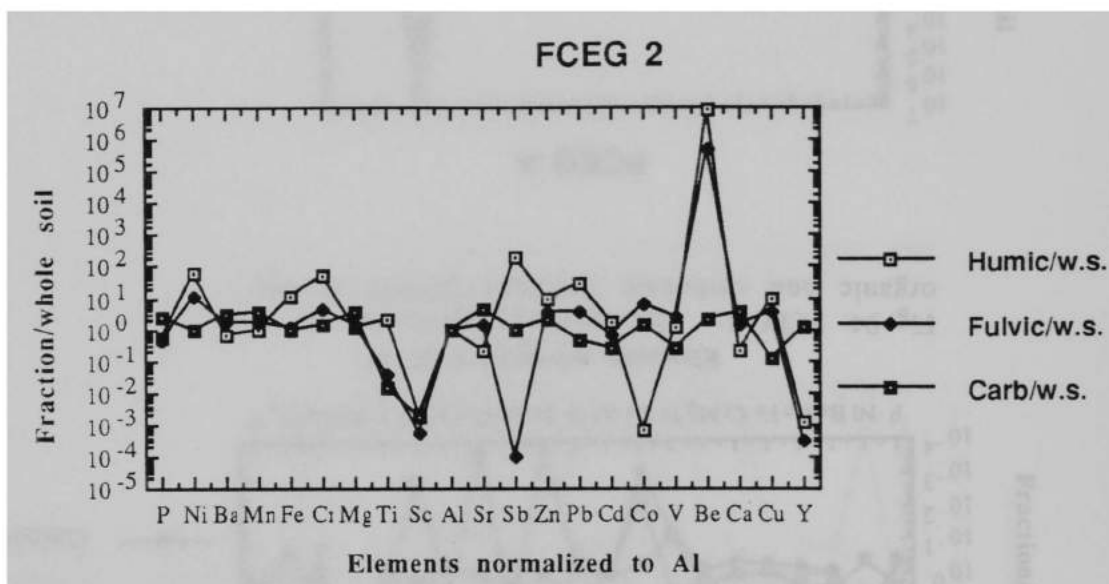


Fig. 93: FCEG 2: Enrichment/depletion of organic and carbonate fractions relative to Al.

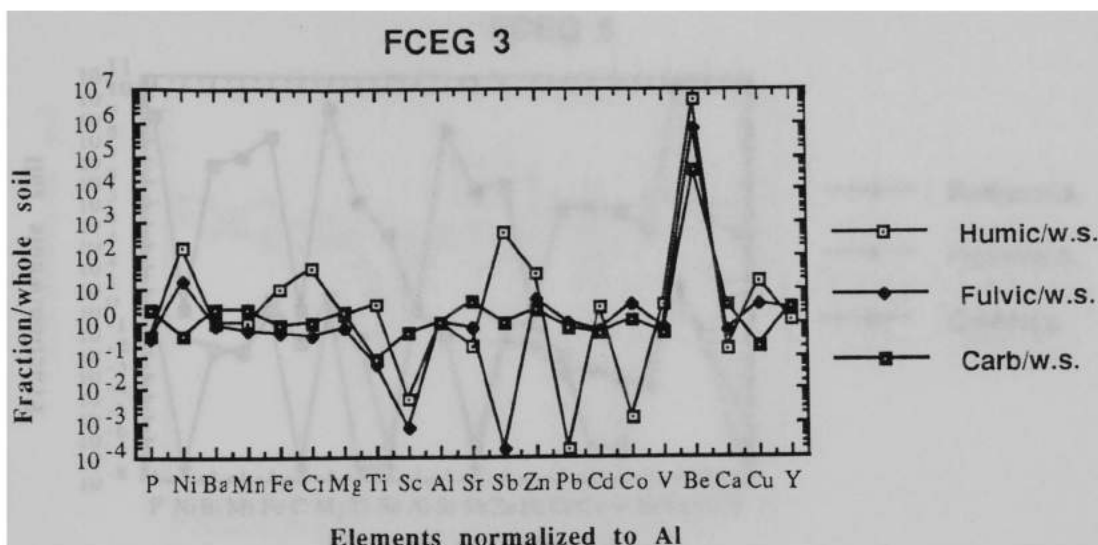


Fig. 94: FCEG 3: Enrichment/depletion of organic and carbonate fractions relative to Al.

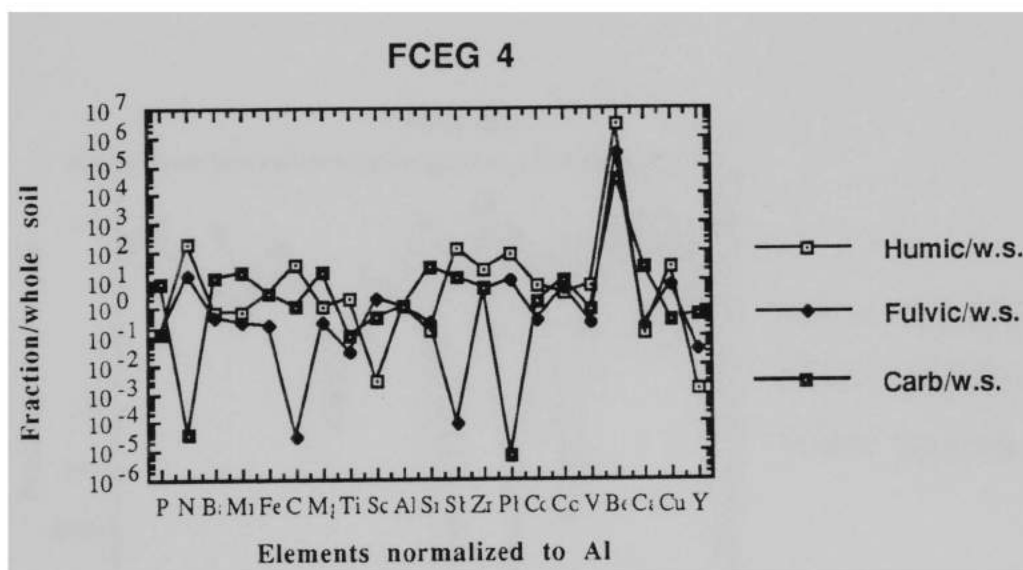


Fig. 95: FCEG 4: Enrichment/depletion of organic and carbonate fractions relative to Al.

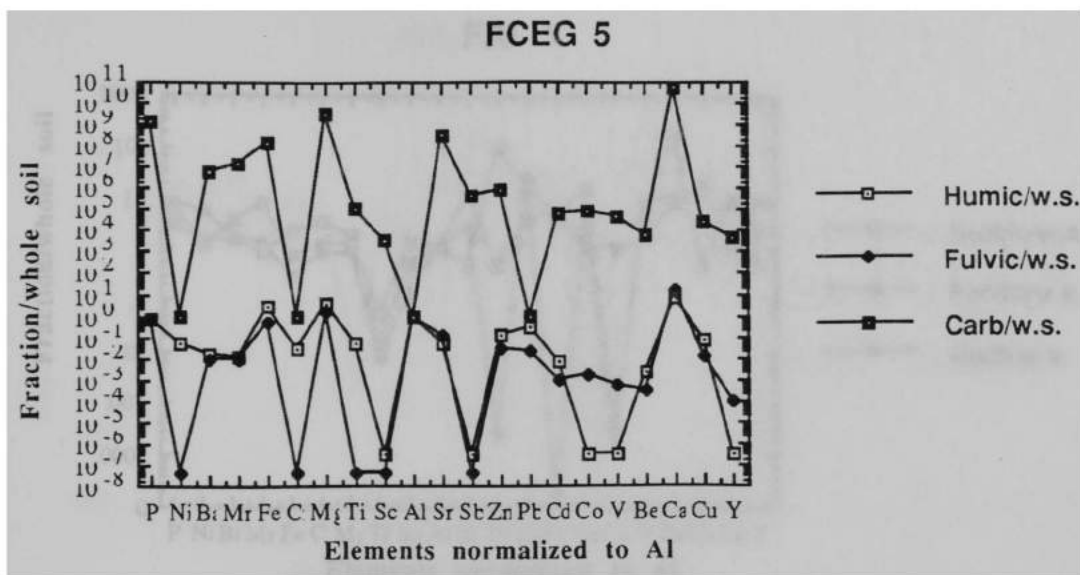


Fig. 96: FCEG 5: Enrichment/depletion of organic and carbonate fractions relative to Al.

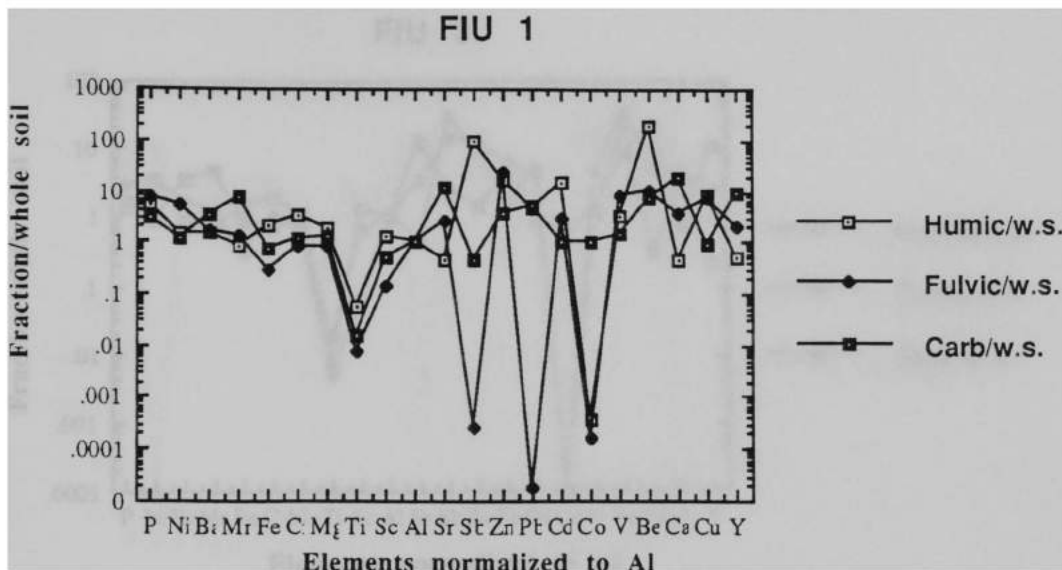


Fig. 97: FIU 1: Enrichment/depletion of organic and carbonate fractions relative to Al.

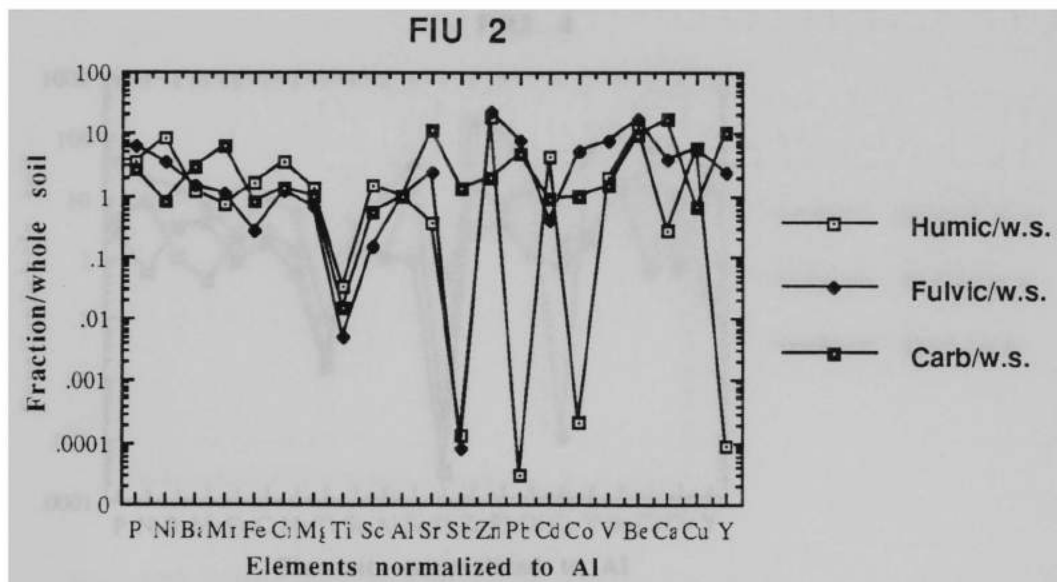


Fig. 98: FIU 2: Enrichment/depletion of organic and carbonate fractions relative to Al.

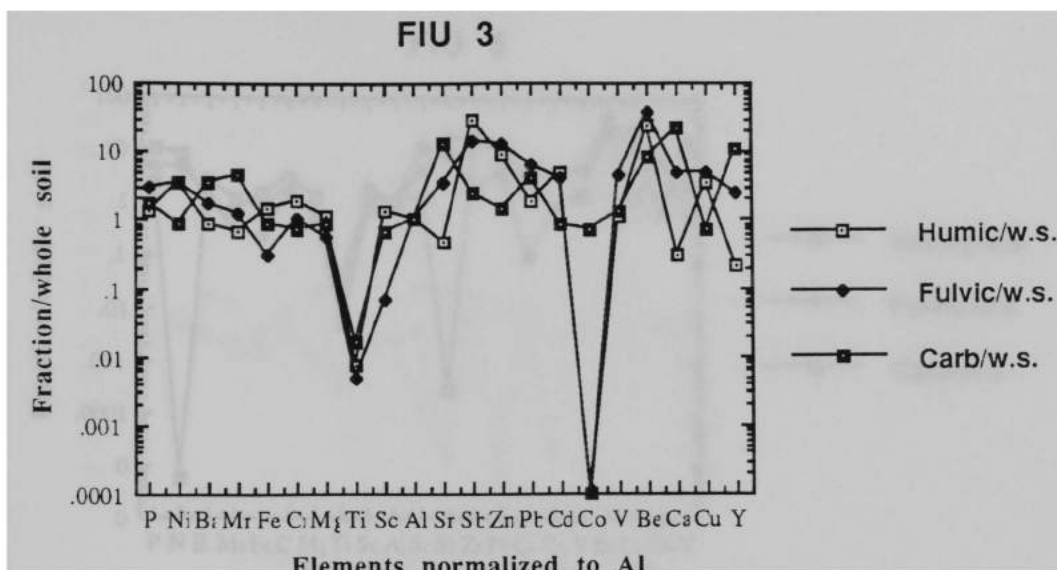


Fig. 99: FIU 3: Enrichment/depletion of organic and carbonate fractions relative to Al.

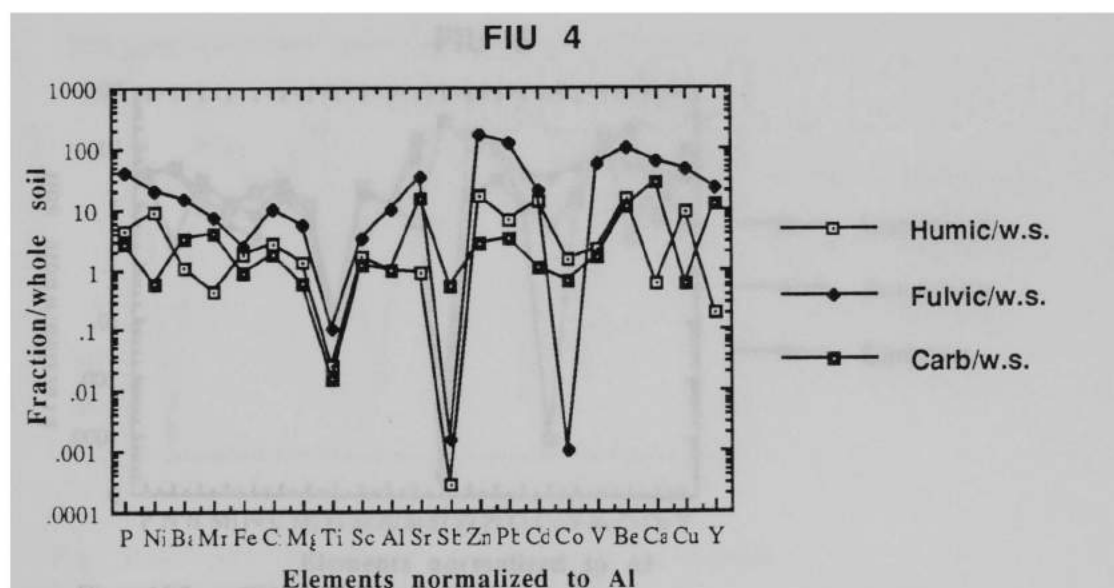


Fig. 100: FIU 4: Enrichment/depletion of organic and carbonate fractions relative to Al.

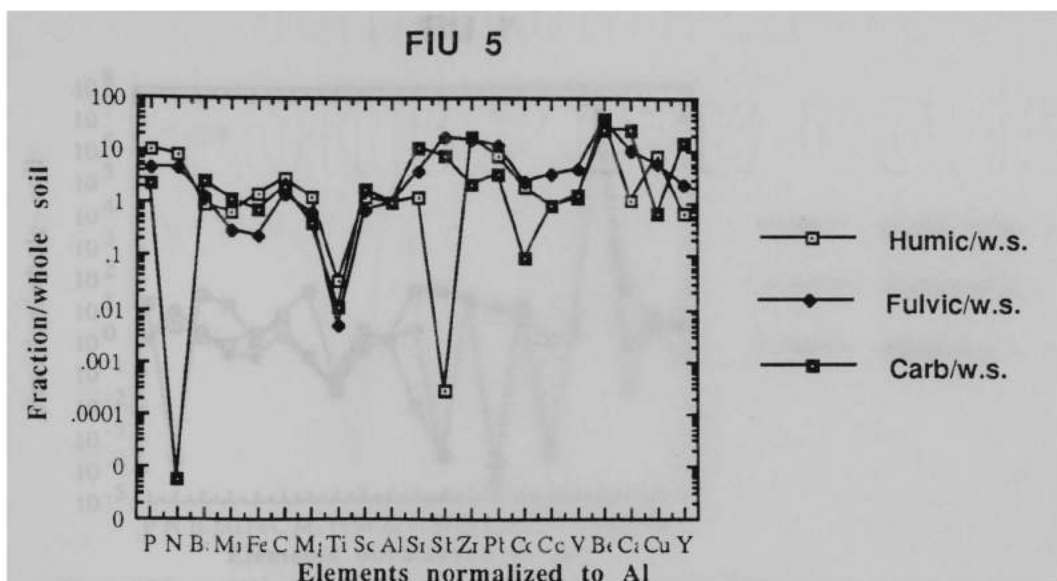


Fig. 101 FIU 5: Enrichment/depletion of organic and carbonate fractions relative to Al.

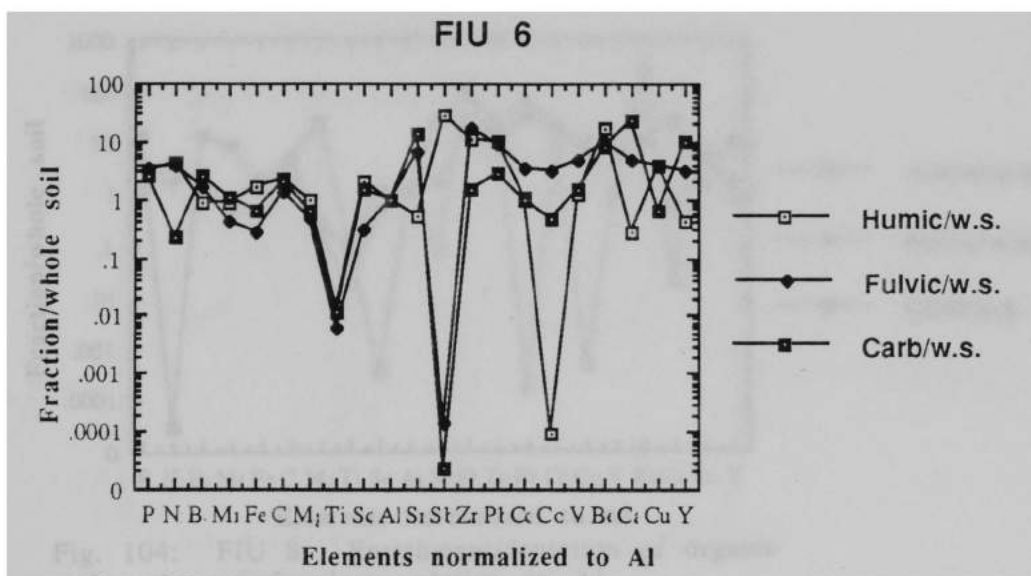


Fig. 102: FIU 6: Enrichment/depletion of organic and carbonate fractions relative to Al.

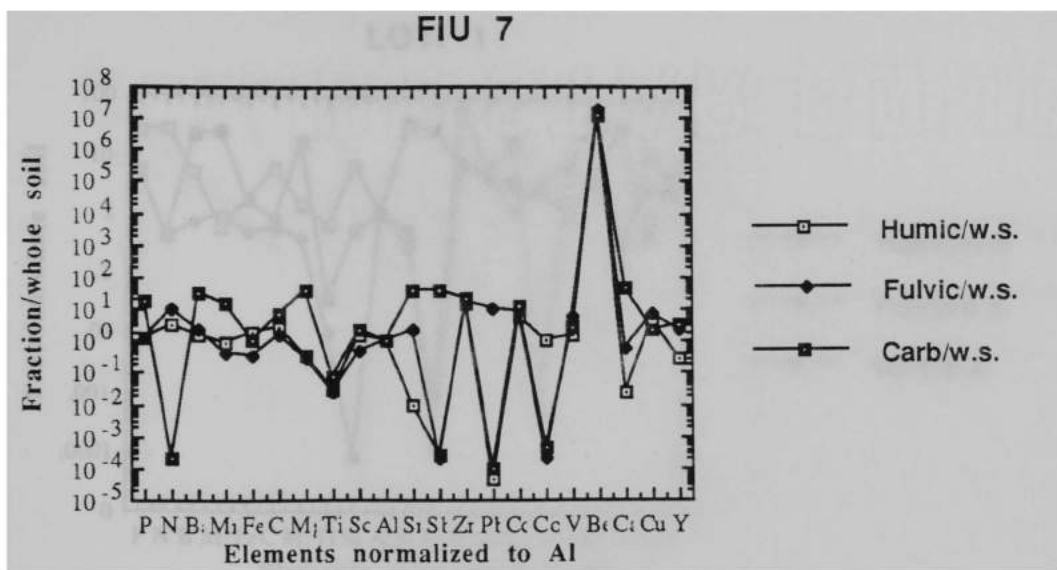


Fig. 103: FIU 7: Enrichment/depletion of organic and carbonate fractions relative to Al.

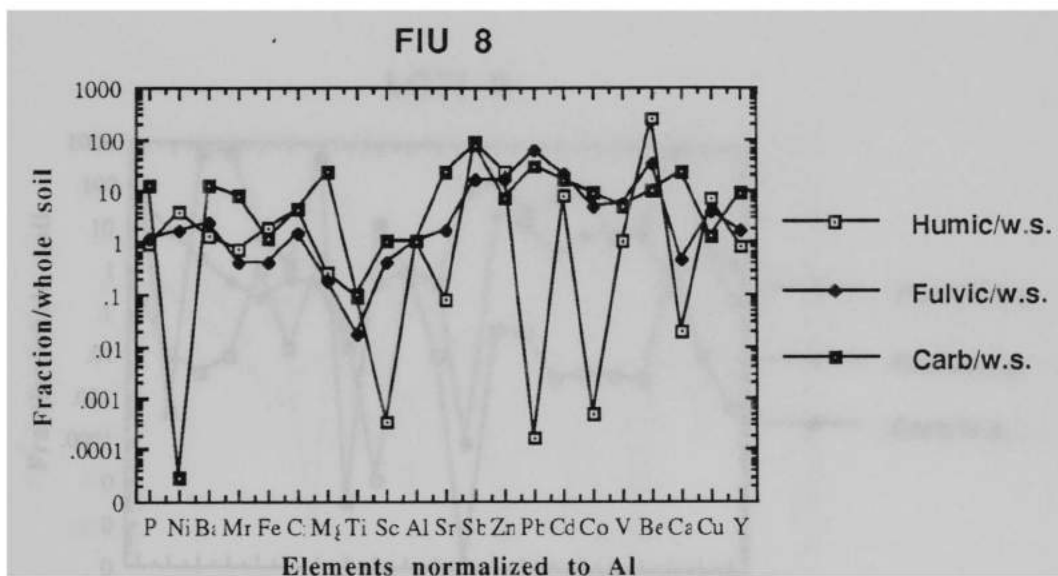


Fig. 104: FIU 8: Enrichment/depletion of organic and carbonate fractions relative to Al.

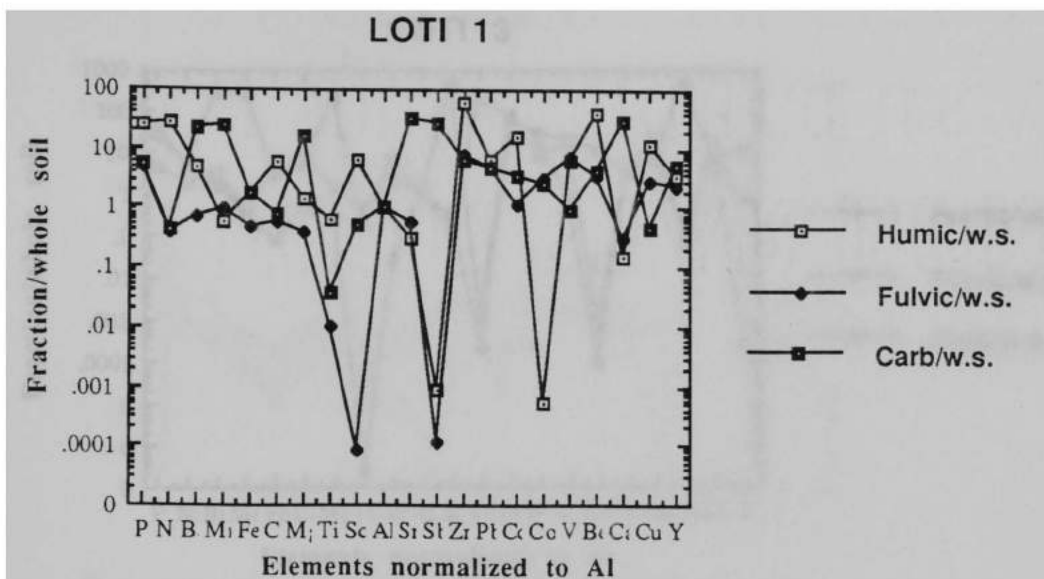


Fig. 105: LOTI 1: Enrichment/depletion of organic and carbonate fractions relative to Al.

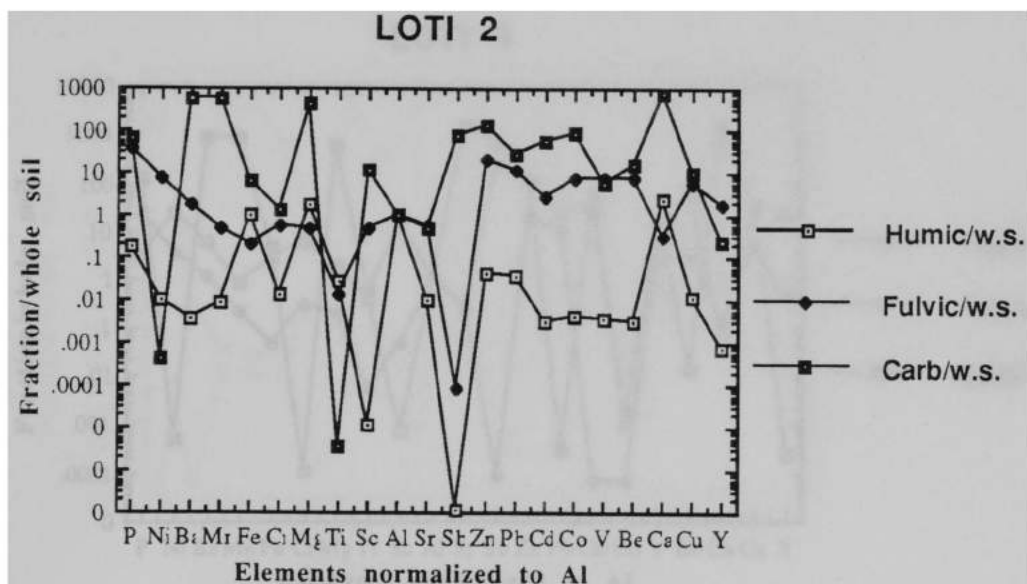


Fig. 106: LOTI 2: Enrichment/depletion of organic and carbonate fractions relative to Al.

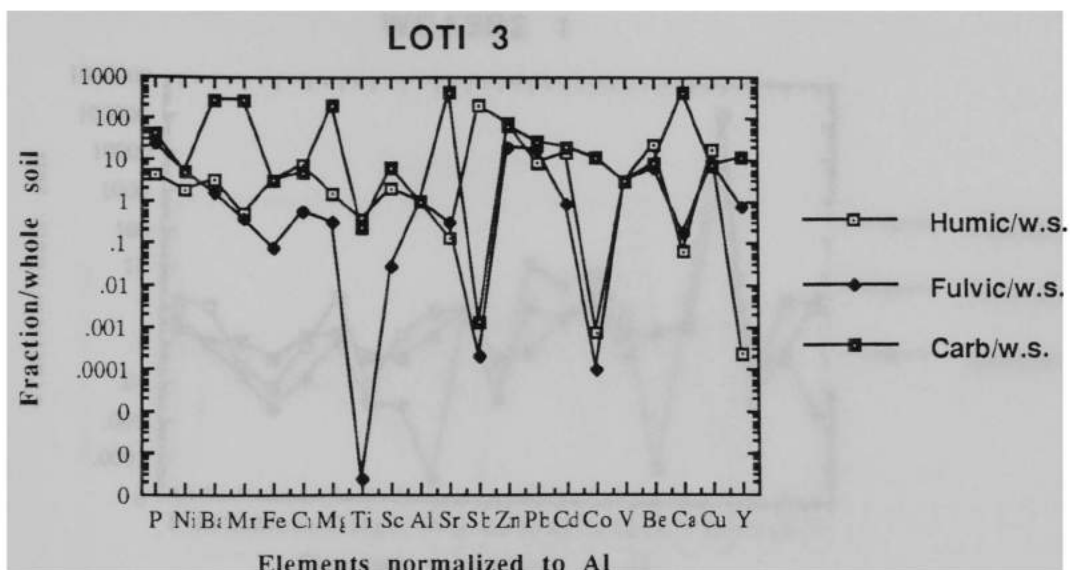


Fig. 107: LOTI 3: Enrichment/depletion of organic and carbonate fractions relative to Al.

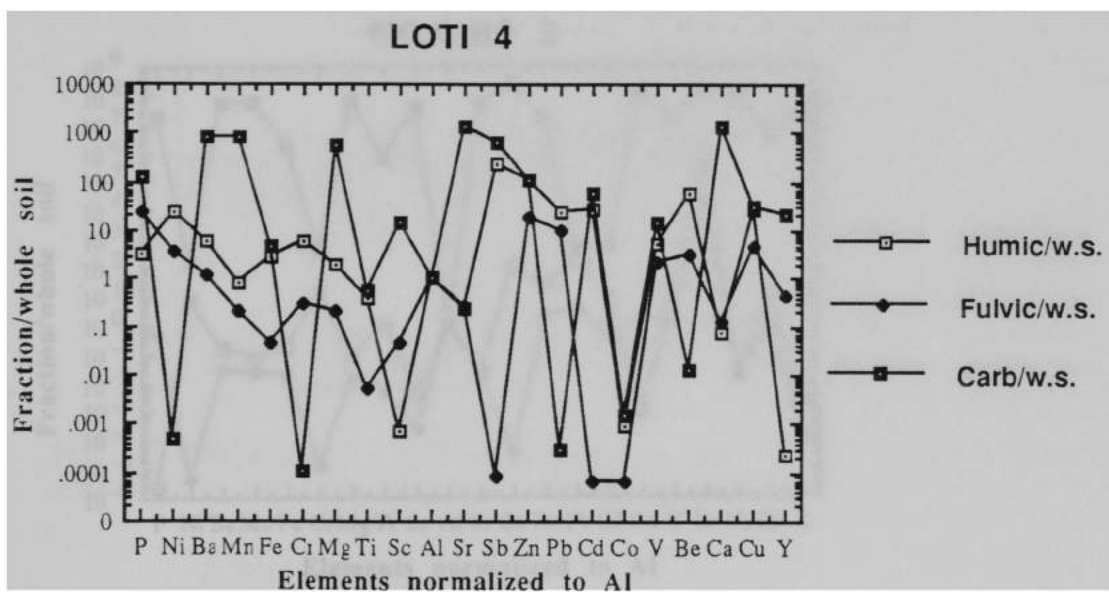


Fig. 108: LOTI 4: Enrichment/depletion of organic and carbonate fractions relative to Al.

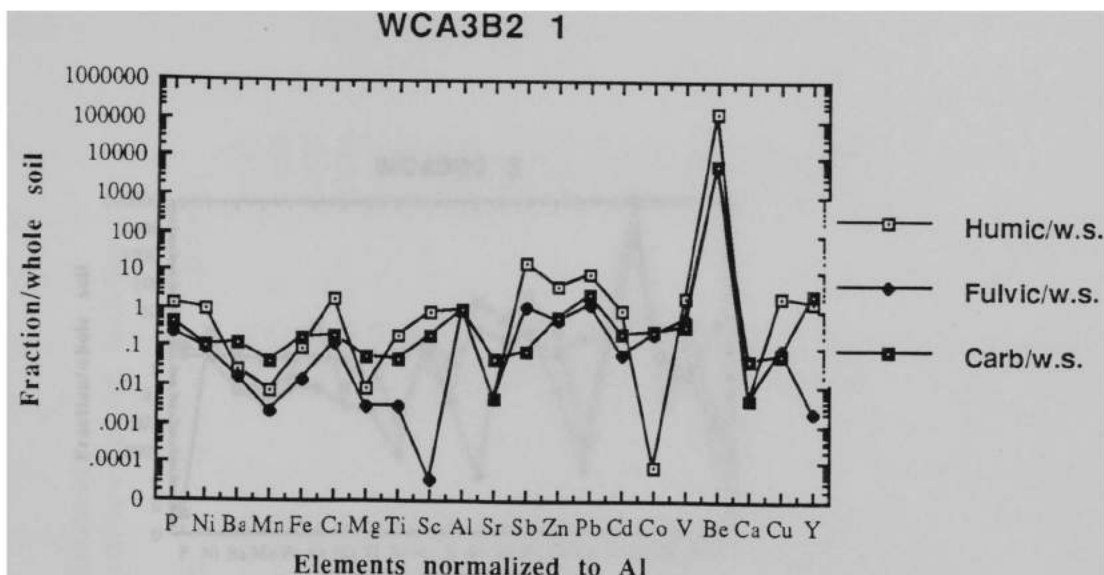


Fig. 109: WCA3B2 1: Enrichment/depletion of organic and carbonate fractions relative to Al.

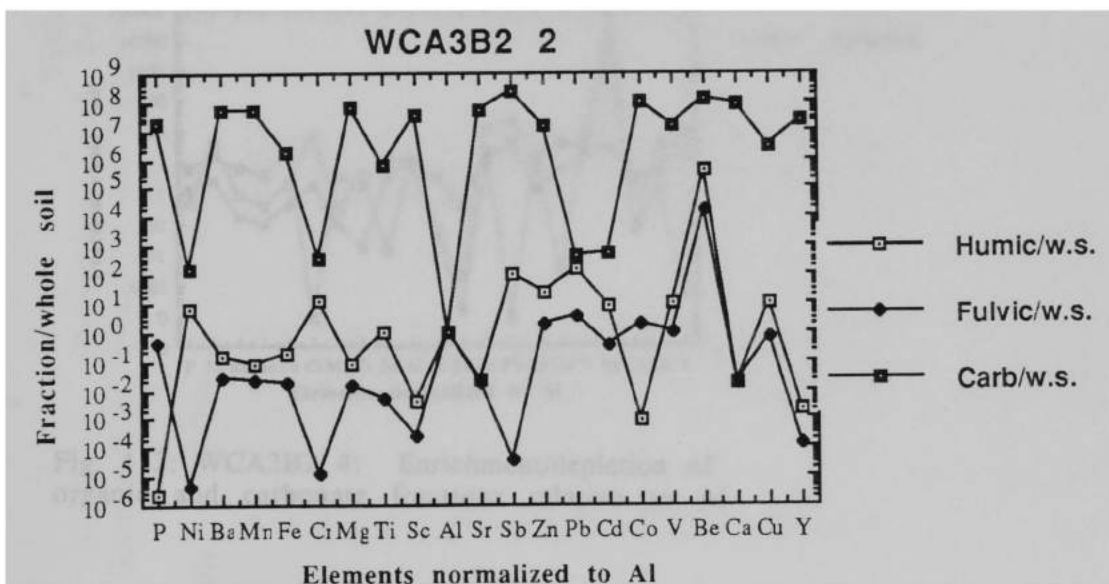


Fig. 110: WCA3B2 2: Enrichment/depletion of organic and carbonate fractions relative to Al.

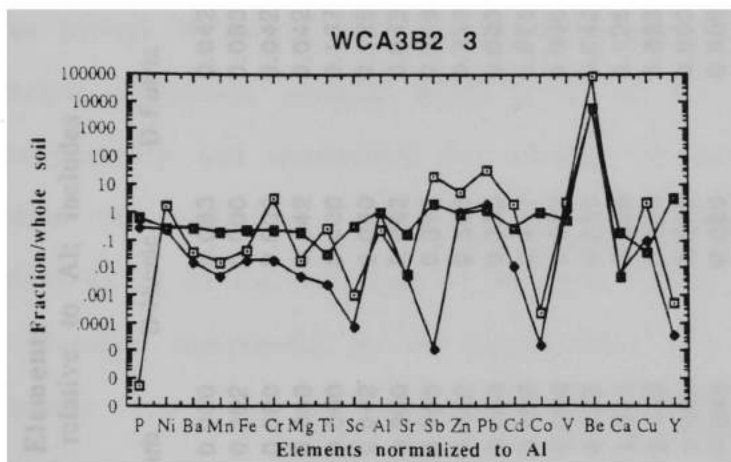


Fig. 111 WCA3B2 3: Enrichment/depletion of organic and carbonate fractions relative to Al.

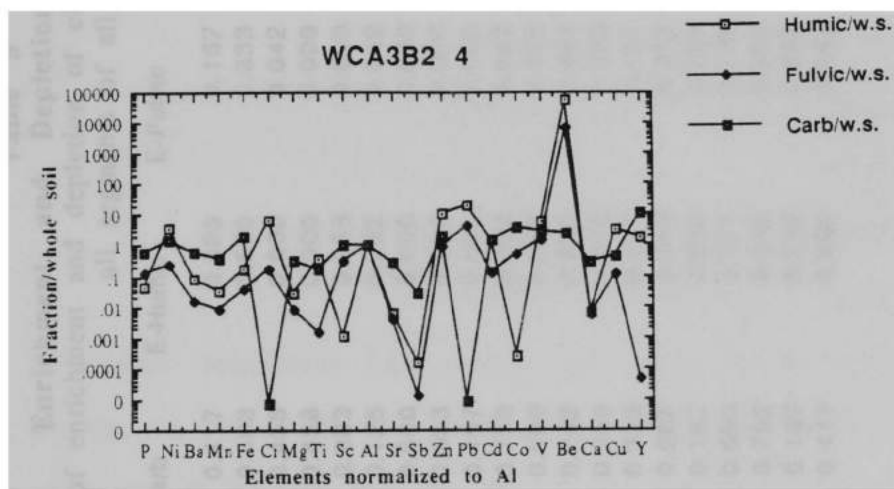


Fig. 112: WCA3B2 4: Enrichment/depletion of organic and carbonate fractions relative to Al.

Table 5
Enrichment and Depletion of Elements
 Occurrence of enrichment and depletion of elements relative to Al; includes
 all segments of all cores

Elements	E-Carb	E-Humic	E-Fulvic	D-Carb	D-Humic	D-Fulvic
P	0.417	0.083	0.167	0.000	0.083	0.042
Ni	0.083	0.500	0.333	0.292	0.000	0.083
Ba	0.458	0.000	0.042	0.000	0.000	0.042
Mn	0.458	0.000	0.000	0.000	0.042	0.042
Fe	0.083	0.083	0.000	0.000	0.000	0.167
Cr	0.125	0.292	0.042	0.042	0.000	0.125
Mg	0.500	0.000	0.000	0.000	0.042	0.042
Ti	0.083	0.000	0.000	0.750	0.375	0.958
Sc	0.167	0.000	0.000	0.042	0.500	0.333
Sr	0.750	0.000	0.042	0.000	0.250	0.083
Sb	0.500	0.542	0.125	0.083	0.417	0.875
Zn	0.292	0.833	0.583	0.000	0.000	0.000
Pb	0.250	0.375	0.333	0.125	0.250	0.042
Cd	0.333	0.417	0.167	0.042	0.000	0.125
Co	0.208	0.042	0.042	0.083	0.750	0.333
V	0.167	0.083	0.208	0.000	0.042	0.000
Be	0.500	0.917	0.708	0.042	0.000	0.000
Ca	0.792	0.000	0.083	0.000	0.333	0.083
Cu	0.167	0.292	0.042	0.083	0.000	0.000
Y	0.417	0.000	0.042	0.000	0.417	0.208

Fifth Methodological Approach:

Principal Component Analysis

A correlation matrix is constructed for all the elements in all the cores (except WCA3B2), and a principal component analysis is done. The principal component analysis looks at all of the variations in the data simultaneously and determines the number of endmembers necessary to explain the variations. Five principal components are found which explain 92.2% of the variations in the data. It is possible to characterize the principal components by the Eigenvectors, that is to determine which elements are strongly associated with the individual principal components.

Principal component	Eigenvector	Total
1	.517368	.517368
2	.258928	.776296
3	.066811	.843108
4	.053429	.896536
5	.032599	.929135

Principal component one reflects the variations in the behavior of Al, Be, Co, Cr, Ni, Pb, Sb, Sc, Ti, V and Y. Principal component two reflects the variations of Ba, Ca, Cd, Fe, Mg, P, Sr and Zn. Principal component three reflects Mn and the variations of Ca and Mg not previously accounted for in principal component two. Principal component four; Cu and the variations of Mg and Sr not previously accounted for in principal component two.

Table 6
Correlation Matrix for Whole Soil
Correlation matrix for all elements: element vs element

	Sb	Zn	Pb	Cd	V	Be	Cu	Y
Sb	1.0000	0.1099	0.7973	0.2756	0.7769	0.8667	0.5303	0.7639
Zn	0.1099	1.0000	0.3077	0.6528	-0.1377	-0.1504	0.3864	-0.2333
Pb	0.7973	0.3077	1.0000	0.3706	0.7902	0.7469	0.7212	0.7157
Cd	0.2756	0.6528	0.3706	1.0000	0.0025	-0.0575	0.2156	-0.1640
Co	0.8991	0.0153	0.8981	0.1781	0.9293	0.9354	0.5990	0.8921
V	0.7769	-0.1377	0.7902	0.0025	1.0000	0.9264	0.5727	0.8959
Be	0.8667	0.1504	0.7469	-0.0575	0.9264	1.0000	0.5335	0.9421
Cu	0.5303	0.3864	0.7212	0.2156	0.5727	0.5335	1.0000	0.5665
Y	0.7639	-0.2333	0.7157	-0.1640	0.0959	0.9421	0.5665	1.0000
P	0.0202	0.9072	0.1434	0.7512	-0.2555	-0.2552	0.1849	-0.3610
Ni	0.8588	-0.2080	0.7703	-0.0677	0.9343	0.9623	0.4786	0.9149
Ba	0.4142	0.4918	0.4020	0.6411	0.2669	0.2486	0.4905	0.1546
Mn	0.5876	0.2154	0.3445	0.3555	0.0720	-0.0468	0.0121	0.0277
Fe	0.2973	0.6744	0.3883	0.9921	0.0263	-0.0312	0.2324	-0.1444
Cr	0.8626	-0.1983	0.7349	-0.1182	0.8964	0.9770	0.5195	0.9492
Mg	0.3607	0.4207	0.3762	0.3376	0.3982	0.2862	0.5004	0.2226
Ca	-0.1993	0.4325	-0.0549	0.4412	-0.2299	-0.3189	0.0045	-0.3311
Ti	0.8597	-0.1937	0.7632	-0.0850	0.9264	0.9736	0.4759	0.9358
Sc	0.8721	-0.1482	0.7645	-0.0444	0.9356	0.9846	0.5167	0.9435
Al	0.8646	-0.1671	0.7762	-0.0570	0.9403	0.9825	0.5087	0.9496
Sr	-0.1539	0.5528	-0.1351	0.4241	-0.2565	-0.3041	0.0413	-0.4078

	P	Ni	Ba	Mn	Fe	Cr	Mg	Ca
Sb	0.0202	0.8588	0.4142	0.0576	0.2973	0.8626	0.3607	-0.1993
Zn	0.9072	0.2080	0.4918	0.2154	0.6744	-0.1983	0.4207	0.4325
Pb	0.1434	0.7703	0.4010	0.3445	0.3883	0.7349	0.3762	-0.0549
Cd	0.7512	-0.0677	0.6411	0.3555	0.9921	-0.1182	0.3376	0.4412
Co	-0.0983	0.9541	0.3250	0.1714	0.2009	0.9341	0.3200	-0.2176
V	-0.2555	0.9343	0.2669	0.0720	0.0263	0.8964	0.3982	-0.2299
Be	-0.2552	0.9623	0.2486	-0.0468	-0.0312	0.9770	0.2882	-0.3189
Cu	0.1849	0.4786	0.4905	0.0121	0.2324	0.5195	0.5004	0.0045
Y	-0.3610	0.9149	0.1546	-0.0277	-0.1444	0.9492	0.2226	-0.3311
P	1.0000	-0.3203	0.5967	0.2162	0.7793	-0.3190	0.3235	0.4978
Ni	-0.3203	1.0000	0.1888	0.0449	0.0455	0.9774	0.2555	-0.3688
Ba	0.5967	0.1888	1.0000	0.0154	0.6256	0.1687	0.5205	0.2051
Mn	0.2162	0.0449	0.0154	1.0000	0.3461	-0.0736	0.2395	0.5261
Fe	0.7793	-0.0455	0.6256	0.3461	1.0000	-0.0919	0.3596	0.4322
Cr	-0.3190	0.9774	0.1687	-0.0736	0.0919	1.0000	0.2001	-0.4145
Mg	0.3235	0.2555	0.5205	0.2395	0.3596	0.2001	1.0000	0.4435
Ca	0.4978	-0.3688	0.2051	0.6261	0.4322	-0.4145	0.4435	1.0000
Ti	-0.3088	0.9871	0.1640	-0.0197	-0.0590	-0.9884	0.1875	-0.4118
Sc	-0.2535	0.9798	0.2393	-0.0556	-0.0180	0.9880	0.2438	-0.3699
Al	-0.2792	0.9848	0.2014	0.0000	-0.0316	0.9881	0.2299	-0.3558
Sr	0.6211	-0.3896	0.3317	0.2233	0.4286	-0.4013	0.4500	0.8509

	Ti	Sc	Al	Sr
Sb	0.8597	0.8721	0.8646	-0.1539
Zn	-0.1937	-0.1482	-0.1671	0.5528
Pb	0.7632	0.7645	0.7762	-0.1351
Cd	-0.0850	-0.0444	-0.0570	0.4241
Co	0.9531	0.9545	0.9617	-0.2713
V	0.9264	0.9356	0.9403	-0.2565
Be	0.9736	0.9846	0.9825	-0.3041
Cu	0.4759	0.5167	0.5087	0.0413
Y	0.9358	0.9435	0.9496	-0.4078
P	-0.3088	0.2535	-0.2792	0.6211
Ni	0.9871	0.9798	0.9848	-0.3896
Ba	0.1640	0.2393	0.2014	0.3317
Mn	-0.0197	-0.0556	0.0000	0.2233
Fe	-0.0590	-0.0180	-0.0316	0.4286
Cr	0.9884	0.9880	0.9881	-0.4013
Mg	0.1675	0.2438	0.2299	0.4500
Ca	-0.4113	-0.3699	-0.3558	0.8509
Ti	1.0000	0.9928	0.9965	-0.4146
Sc	0.9928	1.0000	0.9970	-0.3436
Al	0.9965	0.9970	1.0000	-0.3642
Sr	-0.4146	-0.3436	-0.3642	1.0000

Table 7
Correlation Coefficients for Elements vs Volatile Loss
Correlation coefficients of each element vs volatile loss

	LOTI <550	LOTI >550	FIU <550	FIU >550	FCEG <550	FCEG >550	CSRA <550	CSRA >550
P	0.961	-0.964	0.478	0.009	0.639	0.129	0.254	-0.122
Ni	0.660	0.341	0.661	-0.738	-0.477	0.051	0.308	-0.927
Ba	0.734	-0.971	0.848	-0.735	0.903	-0.471	0.365	-0.967
Mn	0.842	-0.502	0.933	-0.392	0.868	-0.359	0.586	0.411
Fe	0.001	-0.111	0.961	-0.482	0.699	0.462	0.375	-0.952
Cr	0.123	0.000	0.583	-0.801	-0.007	-0.111	0.320	-0.935
Mg	-0.052	-0.019	0.136	-0.216	0.000	-0.112	0.413	0.772
Ti	0.138	0.000	0.757	-0.836	0.806	-0.971	0.301	-0.923
Sc	0.142	0.000	0.712	-0.796	0.587	-0.135	0.300	-0.930
Al	0.148	0.000	0.716	-0.780	0.996	0.767	0.311	-0.930
Sr	0.290	-0.576	-0.386	0.995	-0.821	0.415	0.383	0.153
Sb	0.660	0.042	0.597	0.232	0.920	-0.586	0.136	-0.783
Zn	0.940	-0.983	0.937	-0.496	-0.116	0.001	0.419	-0.170
Pb	0.886	-0.999	0.932	-0.516	0.510	-0.564	0.783	-0.971
Cd	0.006	-0.188	0.949	-0.505	0.840	-0.350	0.377	-0.955
Co	0.009	0.205	0.831	-0.733	0.969	-0.562	0.374	-0.947
V	0.030	-0.272	0.942	0.470	0.978	-0.601	0.378	-0.951
Be	0.106	0.002	0.661	-0.561	0.000	0.000	0.288	-0.923
Ca	0.018	-0.167	-0.378	0.998	-0.668	0.689	0.122	0.785
Cu	0.998	-0.874	0.880	-0.308	0.030	-0.235	0.608	-0.484
Y	-0.151	0.001	0.706	-0.751	0.779	-0.475	0.271	-0.933

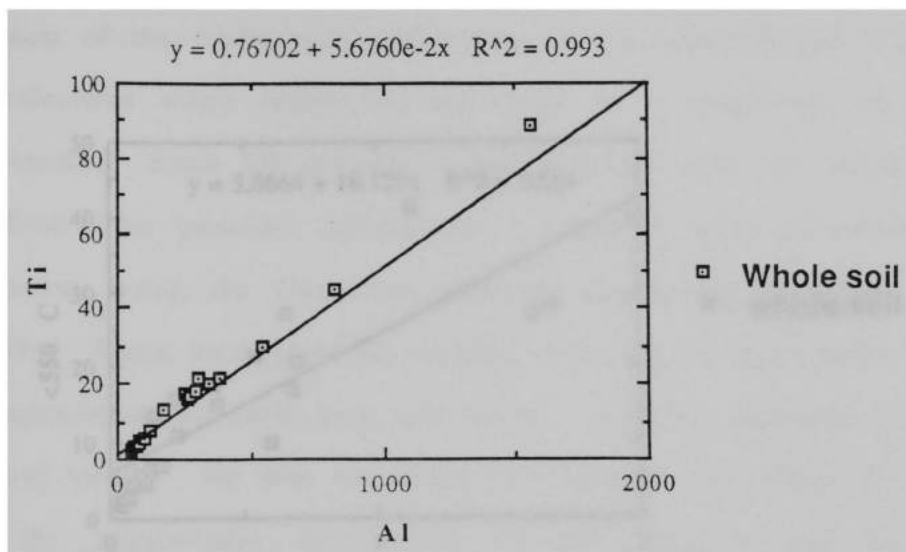


Fig. 113: Al vs Ti from all core segments whole soil.

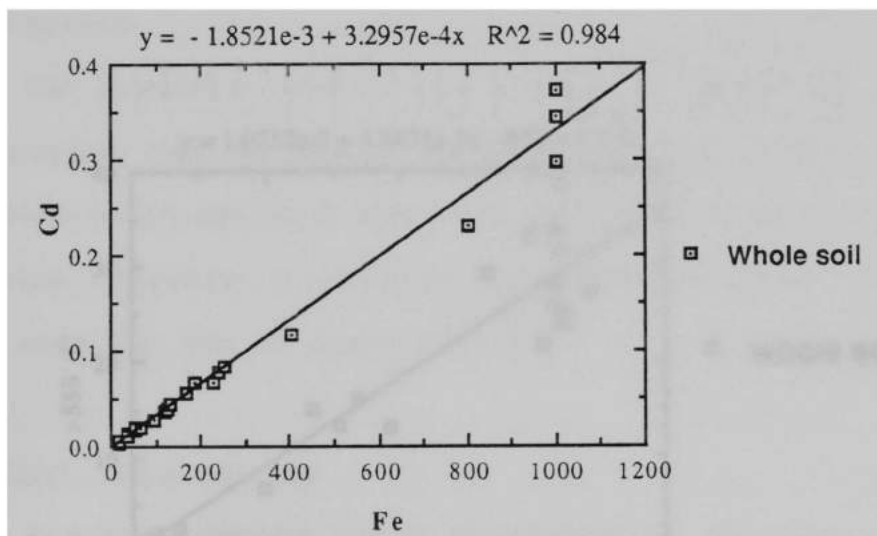


Fig. 114: Fe vs Cd from all core segments whole soil.

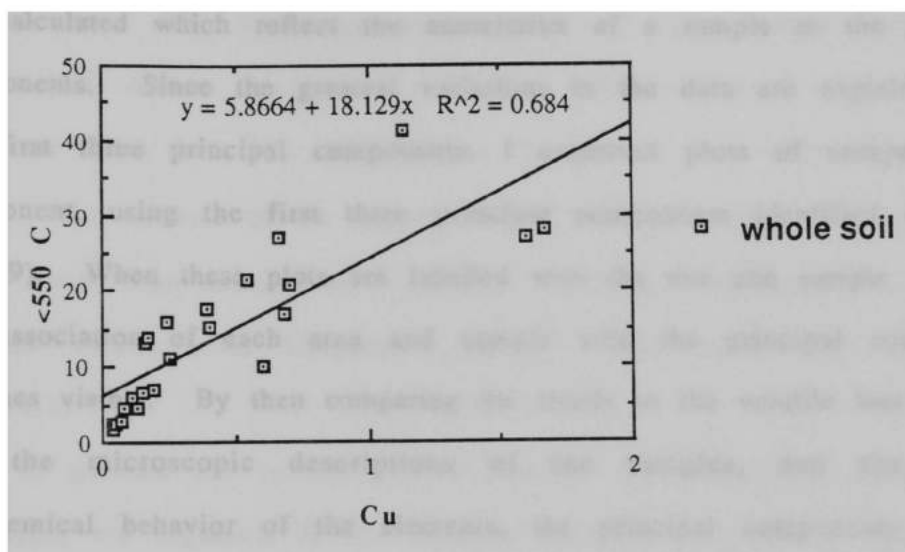


Fig. 115: Cu vs <550° C volatile loss from all core segments whole soil.

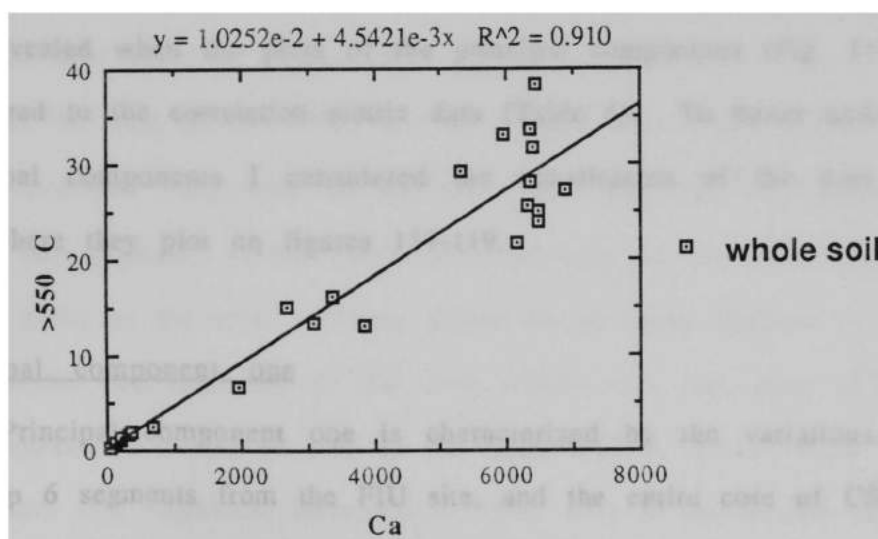


Fig. 116: Ca vs >550° C volatile loss from all core segments whole soil.

The variations are then applied specifically to the samples (the depth segments of the whole soil) rather than to the elements and Eigenvectors are calculated which reflect the association of a sample to the principal components. Since the greatest variations in the data are explained with the first three principal components, I construct plots of component vs component, using the first three principal components identified (fig 117 to 119). When these plots are labelled with the site and sample numbers, the association of each area and sample with the principal components becomes visible. By then comparing the trends to the volatile loss patterns and the microscopic descriptions of the samples, and the known geochemical behavior of the elements, the principal components can be described and identified with actual constituents of the soils.

Discussion

The association between each principal component and the samples are revealed when the plots of the principal components (Fig. 117-119) are compared to the correlation matrix data (Table 6). To better understand the principal components I considered the constituents of the core segments and where they plot on figures 117-119.

Principal component one

Principal component one is characterized by the variations found in the top 6 segments from the FIU site, and the entire core of CSRA. One endmember is composed of the variations of FIU 1 to 6 and CSRA 1 to 4, and the other endmember is composed of CSRA 5 and 6 (Fig. 117 and 119).

The FIU core shows distinct differences between the lithologic data from the upper six segments and those from the two lower most segments in the core. The upper segments consist of quartz mixed with organic matter and minute spicules, and contain relatively small proportions of carbonate (less than 2%) according to the greater than 550° C volatile loss study. The estimate of the organic content (less than 550° C) shows values which range from about 2 to 7 percent. In contrast, the lower two sections include unweathered limestone bedrock, and have high carbonate contents.

As pointed out in the site description the stratigraphy displayed in the upper six segments of this core is probably not natural, because the area sampled is located in the nature preserve of university grounds which was previously the site of an airport. It is likely that as such the site could have been subjected to windblown grains from construction, as well as from the liftoffs and landings of aircraft. The weathered material sampled also could be wholly or in part quarried fill.

In the case of the CSRA site the volatile loss studies show a relatively high estimated proportion of organic (less than 550° C) material in the upper two segments (28%, 17%), and especially in the lower two segments (41%, 27%) of the core. These values are in sharp contrast to those from the middle two segments of the core which have less than 11% organic. The estimate of carbonate loss by the same method shows values of 13% in the upper two segments, increased to 15%, 17% in the middle segments, to lowest percentages (7%, 3%) in the bottom two segments. These volatile loss

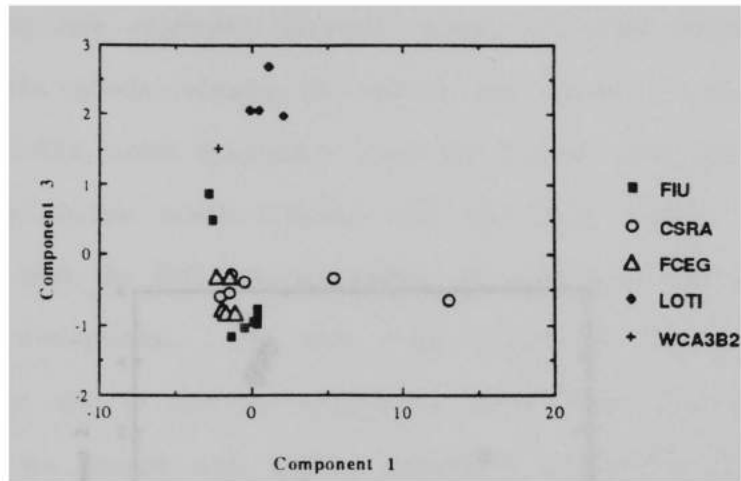


Fig. 117: Principal components 1 vs 3.

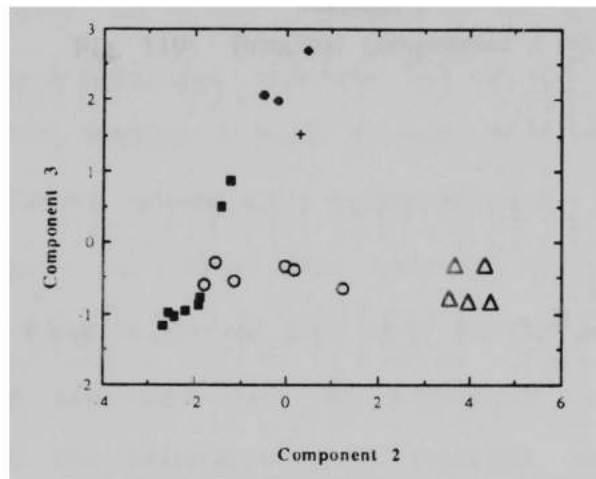


Fig. 118: Principal components 2 vs 3.

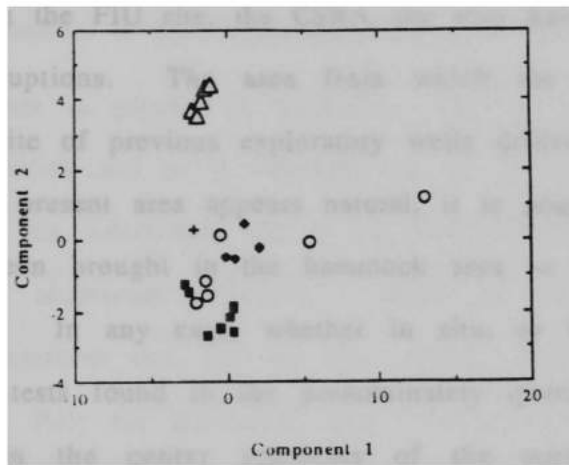


Fig. 119: Principal components 1 vs 2.

estimates are consistent with the physical description of the core, where the upper two segments consists mostly of plant residues mixed with micrite and quartz, whereas the middle two segments contain mostly quartz and reworked shell fragments, and the bottom two layers include only quartz and humic matter coupled with very little micrite.

As with the FIU site, the CSRA site may have been affected by man-induced disruptions. The area from which the core was recovered is nearby the site of previous exploratory wells drilled for oil (1947). Thus, although the present area appears natural, it is possible that some sand fill may have been brought in the hammock area to install pathways for the nature trails. In any case, whether in situ, or brought in the site, the foraminifera tests found in the predominately quartz content of the coarse fraction from the center segments of the core can be assigned to Elphidium or Cibicides, indicating that the material had a shallow marine origin. It is difficult to make an exact determination of the origin of the material without conducting a systematic survey of the surrounding area.

Because the cores were collected from an area underlain by limestone, which is also the most likely fill material, it is necessary to look at factors associated with the weathering of carbonate in order to understand the characteristics of principal component one. Calcium carbonate in limestone does not exist in a pure form, but carries trace elements within the rock. The weathering of CaCO_3 usually produces soils or insoluble residues of clay minerals with quartz and iron oxides that were incorporated in the rock matrix. The insoluble residues become concentrated as soil because the calcite is highly soluble and is effectively

removed from the weathering site through dissolution. Weathering progresses at a faster pace in soils where organic decay produces abundant carbon dioxide which becomes dissolved in water and leads to carbonate dissolution by these reactions:



Aluminum is present in carbonate rock as aluminum hydroxides and silicate impurities and as it weathers out of the carbonate, has a tendency to remain at the weathering site in the form of clay minerals, all of which are hydrous aluminum silicates. Many of the elements reflected in principal component one are the less soluble trace elements of carbonates (Ni, Co, Pb, Be); are associated with aluminum and could be incorporated into clay minerals or oxides (Be, V, Y, Sc, Cr, Pb, Sb, Co, Ti); or are known to have an affinity for organic materials (Be, Sb, Pb).

Therefore, in considering the geochemical behavior of the above elements and the volatile loss study coupled with the core descriptions, I conclude that principal component one is best described as being a mixture of residues from the weathering of carbonate bedrock and organic matter, with CSRA 5 and 6 being an organic rich endmember. Quartz sand observed in the cores, either of natural or human sources, probably is also a participant in this component, but contains small quantities of trace elements.

The concentrations of phosphorus in the CSRA core exceed the worldwide range, 100 to 1000 ppm, (Table 2) for the length of the core, and Sb exceeds the reported worldwide range, .05 to 4 ppm, (Table 2) in the

bottom segment (CSRA 6). The other elemental abundances fall within the worldwide ranges. The core has a small association with principal component two (Fig 118) but it is not an endmember of principal component two.

Principal component two

A comparison of the correlation matrix with the plots of the three dominant principal components (Fig 118 and 119) show that principal component two is associated with the trend that is dominated by variations of Fe, Zn, Cd, P, Ba and Mg, Ca and Sr variations not otherwise accounted for in principal components three or four. The samples which most strongly characterize principal component two are clearly associated with the five FCEG samples as one endmember. The lower segments of the CSRA core (5 and 6) are intermediate between these samples and those dominated by principal component one (Fig 117 and 118).

The stratigraphy of the FCEG core consists of thin laminae (less than 1 mm) throughout the length of the core. Although the area was a campground (ref. p. 33) the presence of the laminae may indicate that the natural sedimentation pattern is undisturbed. The laminae may have been induced by short term periodic environmental changes. One known instance in which similar periodic environmental changes are recorded in is varves, which result from the rhythmic changes in patterns of sediment distribution due to annual or seasonal variations. A similar process may have occurred here. Since the area is subject to a seasonal dry period, and historic water levels were higher before drainage systems were built, the rhythmic change in wet to dry environmental conditions

could account for the presence of lamination. The Everglades is a unique system characterized by the slow movement of water which would allow slow settling out of particulates from the water as it flowed southward.

The volatile loss estimate for organic material in the FCEG core (less than 550° C) shows a steady decrease in organic material through the core (21% to 10%) as the carbonate estimate (greater than 550° C) shows increasing proportions (22% to 27%).

Groupings based on geochemical behavior as previously discussed can be useful in identifying principal component two. Iron, zinc and cadmium may be grouped together based on their behavior and characteristics as ferroalloy metals. Calcium is grouped with Mg, Fe, Ba, Cd, Sr and Zn as trace elements in carbonates. Barium is known to concentrate in phosphorus concretions, and phosphorus in the form of phosphates forms complex mixtures of iron and calcium phosphates. Cadmium and zinc are associated with phosphates, both naturally occurring and as fertilizers. The bulk composition of FCEG samples are not unusual compared with other areas. Organic contents are comparable with CSRA samples associated with principal component one (weathered bedrock and organic matter) and carbonate contents are comparable with FIU segments 7 and 8 and LOTI which are dominated by unweathered CaCO_3 (principal component three, see below). Therefore, although the present physical conditions of site FCEG shows limited evidence of prior human activities at the hammock, (ref. p. 33) it is possible that principal component two is a foreign material introduced by anthropogenic activities, and not related to changing proportions of the soil constituents or lithology. Possible sources are: atmospheric input (particulate matter, airborne dusts) and

land based input (refuse dumping, leaching, other solid wastes, fertilizer application).

1) Aerial fallout of trace metals from sources such as coal combustion and metal smelting industries is reported (Adriano, 1986; Kabata-Pendias and Pendias, 1984) as being widely dispersed over considerable distances, and impacts on natural areas. In the present case it is less likely that the deposition of general atmospheric fallout would impact so strongly on this one site, well within the Everglades, while the other sites analyzed were not. This mode cannot be ruled out entirely, because air currents forming narrow plumes could accomplish this. However, it is also possible that a more localized event (a fire at an illegal dumpsite) could have strongly impacted this site, but not necessarily the other sites. In addition to the direct effects of anthropogenic activities at this site, other effects related to agricultural activities may be involved as well.

2) Land based sources of trace elements are subject to movement through ground water (as leachates), and in the case of the Everglades through surface water movements south from Lake Okeechobee. It is possible that some of the variations in principal component two are due to impact from application of phosphatic fertilizers. Some phosphatic fertilizers contain significant amounts of cadmium, zinc and/or barium depending upon their source rock, conversely other phosphatic fertilizers are lacking in these trace elements because they are retrieved from different source rocks. Phosphate ores from the western United States contain higher concentrations of these elements than ores recovered from the southeastern states (Adriano, 1986).

3) Sewage sludge or raw sewage disposal is another possible source of trace metals which could account for some of the element variations at this site. Cadmium and zinc generally are enriched in sewage sludge and raw sewage, and variations in Cd and Zn in part characterize principal component two. However, sludge and raw sewage also usually contain concentrations of Ni, Pb and Cu; and these element variations are not found to characterize principal component two. Sewage may not have been used in agriculture practices here, but its presence cannot be entirely ruled out (unsanitary refuse disposal).

4) Animal wastes may also be involved in increased trace element concentrations. However, there is great variability in the elements excreted and the amounts excreted, depending upon factors such as the type and age of the animal(s), as well as the type of foodstuff and dietary supplements the animals might receive. Element enrichment in animal wastes is generally associated with livestock, and are rarely enriched in potentially toxic trace elements (Adriano, 1986). Although the possibility of impact from this source is not strong, (lack of livestock herds) it cannot be ruled out altogether (unpenned animal inhabitants).

5) Irrigation water runoff from distant sources is another possible source of elements at this site, but is unlikely to have strongly impacted only this site.

Samples from the lower portion of CSRA (5 and 6) and LOTI show a slight association with principal component two. These samples have a wide range of carbonate contents (2% to 33%), including some very low values, so it is unlikely that this component is related to CaCO_3 . Like FCEG, all these samples have relatively high organic contents (13% to 26%), and

CSRA 5 and 6 form the organic rich endmember of component one. Therefore, it is likely that there is a relationship between principal component two and organic matter, although one that is distinct from the variation described by principal component one. The association of component two and organic matter suggests that it originates from phosphate fertilizers or refuse (human or animal) of fertilized plants.

Overall, it is difficult to clearly describe the nature of the material represented by principal component two based on the available information. It does show some variations associated with carbonates; Ca, Sr, Mg, and to a lesser extent Fe, Ba, Cd, Zn and P. However, the variations in Cd and P are likely to be associated with an anthropogenic source, most probably phosphatic material such as fertilizer.

Principal component three

Principal component three reflects the behavior of three elements, Mn, and the variations of Ca and Mg not accounted for in principal components two or four.

The plots of the principal components (Fig 117 and 118) show that principal component three is described by the variations in the LOTI core, the WCA3B2 sample and FIU segments 7 and 8.

The volatile loss study for estimated proportion of carbonate (greater than 550° C) show the samples to contain a high proportion of carbonate (LOTI 28-34%; WCA3B2 39%; FIU 7 and 8 30%, 38%). The organic estimate (less than 550° C) is more variable, from 2 to 28 percent (Appendix D).

The LOTI core is composed of mostly pure micrite with rare quartz, ostracod, mollusk and gastropod fragments. It is thinly laminated

throughout which may be natural structures indicating rhythmic environmental changes. As discussed for the FCEG site, the lamination here could have also been the result of subtle seasonal changes like differences in rainfall or temperature which affect sediment distribution, or biogenic or chemical precipitation within the lake.

The two lower segments of the FIU core which are included in principal component three are almost pure micrite, mixed with little decayed organic matter and quartz. These two segments are most likely upper bedrock.

The WCA3B2 core lacked identifiable sedimentary structures and only one segment was available for whole soil analysis and inclusion in the principal component analysis (the other segments were consumed during the volatile loss study).

The most notable characteristic of principal component three are that only the variations of three elements (Ca, Mg, Mn) are described. The variations in the principal component are also described by samples which show high estimated proportions of carbonate. In contrast to the trace elements associated with principal component one, these are the most soluble elements in carbonates. The common link between the samples is the high estimated proportion of carbonate, and the key to the principal component is the direct observation of relatively unweathered carbonate of the FIU samples. I conclude, therefore, that principal component three reflects the presence of relatively unweathered carbonate.

Summary and Conclusions

FIU

In the FIU core the upper six segments contain mostly quartz cemented with some organic material, sponge spicules and very little carbonate (.3 to 1.9%) while the two lower segments, the bedrock, are composed of mostly pure micrite (29 and 33% carbonate).

None of the whole soil element concentrations are found to exceed the reported bulk worldwide ranges (Appendix F). The site shows a pattern of general decreasing whole soil elemental abundances with depth, with the exceptions of Ca, Sr, Mg, and P. The concentrations of calcium and strontium increase in the lower segments reflecting the change in bulk composition of the core.

The correlation matrix and principal component analysis indicates that the variations encountered in the soils and sediments at this site are associated with two principal components. The segments which are above the bedrock are included in principal component one, which describes mixing of organic matter, weathered carbonate and quartz sand. The two bedrock segments are included in principal component three which describes the large fresh carbonate component.

CSRA

The upper two segments of the CSRA core contain mostly organic matter (28 and 17%) in the form of plant residue mixed with micrite (13% carbonate each), quartz and some mollusk tests. The middle segments are predominately quartz with a few reworked shell fragments and foraminifera with little organic matter (4 and 11%). The two lower

segments are mostly quartz and organic material (41 and 27% respectively).

The majority of the element abundances fall within the worldwide ranges with the exception of antimony which exceeds its range in CSRA 6, and phosphorus which shows excessive concentrations throughout the length of the core.

Chemical variations in the CSRA core are best described by principal component one: the elemental variations resulting from the mixing of residual material from carbonate weathering, organic matter and quartz. The core is also associated with principal component two, in that some samples are unusually enriched in phosphorus.

FCEG

The FCEG core displays lamination consisting of micrite and organic matter mixed with some quartz and shell fragments. Most of the elemental abundances for this core fall within the worldwide ranges with the exception of Cd and P concentrations which exceed the ranges throughout the length of the core. When the element concentrations are compared to changes in the soil constituents in the core as determined by the volatile loss study, no clear pattern emerges.

The principal component analysis indicates that the FCEG samples are most strongly associated with principal component two, which is possibly a foreign material introduced by anthropogenic activities. This is consistent with enrichment of Cd and P, and is apparently not related to changing proportions of the soil constituents or lithology of the core.

LOTI

The core from Lake Okeechobee is composed of mostly micrite, some organic matter, quartz and very rare freshwater molluscan fragments. The volatile loss study for estimated proportion of carbonate (greater than 550° C) shows the samples in this core to contain a high proportion of carbonate (28-34%).

This core contains whole soil trace element concentrations consistent with worldwide ranges and show little variation in abundances with depth with the exception of Al, Ca, Fe, Mg and Ti, and to a lesser extent P and Sr. It is primarily associated with principal component three, characteristic of the large unweathered carbonate content, but also shows a slight association with principal component two. This association is probably related to organic matter, yet in a different relationship than described by principal component one.

WCA3B2

This core consists of mostly decayed to partly decayed organic material cemented with micrite, with some spicules and carbonized plant remains. Only one segment is available for whole soil analysis, and the element abundances determined for this core segment are not elevated above the worldwide ranges. The greater than 550° C volatile loss procedure determined a high carbonate content for this core sample (38%). When plotted (Fig 118 and 119) it lies between the LOTI samples and the lower two samples from the FIU core, and as such is associated with principal component three, characteristic of its large unweathered carbonate content.

In conclusion, analysis of principal components of South Florida soils and sediments revealed that 84% of the element variations in the samples are described by three principal components.

Principal component one is characterized by the variations of Al, Be, Co, Cr, Ni, Pb, Sb, Sc, Ti, V, and Y and is best described as being a mixture of residues from the weathering of carbonate bedrock or fill and organic matter with CSRA 5 and 6 comprising an organic rich endmember.

The CSRA core and the upper 6 segments of the FIU core are associated with principal component one, with CSRA 5 and 6 comprising an organic rich endmember of that component.

Principal component two is characterized by the variations in Ba, Ca, Cd, Fe, Mg, P, Sr, and Zn. It is not associated with any one bulk constituent of the soils. Based on its composition it is probably the residue of phosphatic fertilizer or fertilized plant material. The CSRA core shows elemental abundances of P and Sb elevated above ranges which are generally accepted as normal and presumably safe worldwide. These elevated concentrations are related to principal component two, and may result from the application of phosphatic fertilizer (P) and/or pesticides (Sb) in the past.

The FCEG core shows the strongest association with principal component two, and clearly comprises an endmember of this component. This core has elevated levels of phosphorus and cadmium which is probably related to the application of phosphatic fertilizer.

Principal component three represents the variations of Mn, and the variations of Ca and Mg not accounted for in principal components two or four and reflects the presence of relatively unweathered carbonate.

The Lake Okeechobee core (LOT1), the WCA3B2 sample, and the FIU 7 and 8 segments show element concentrations within the generally accepted ranges of background levels worldwide. These samples are associated strongly with principal component three, relatively unweathered carbonate.

Most vertical changes in soil major and trace element contents are related to variations in the proportions of bulk soil constituents: unweathered carbonate, the residue of carbonate weathering, organic matter and quartz sand. These changes are comparable to those seen between different sites. Unusual abundances of P, Cd and Sb are found at some sites and levels, but are not related to changing proportions of bulk constituents. It is probable that this chemical signature indicates input from anthropogenic sources. The trace element contents of the bulk soil constituents can be used as a baseline against which to identify anthropogenic influence.

Areas for Future Research:

Further research on trace metal abundances and their variations with depth is warranted in South Florida. The results presented in this thesis can be tested and built upon in several ways.

One way to extend this study and to test the methodological approaches to data analysis is to sample a larger number of different environments where soils will have different proportions of bulk constituents and possibly new bulk constituents not encountered here. This could be accomplished by selecting areas based on their characteristics, as done here, or by working on a grid and using random sampling. Such

research will help to determine if the three principal components identified in this thesis are widely applicable to South Florida.

A second way to extend this research would be to choose areas that show fine-scale sedimentological features, for example, the laminated LOTI cores, and perform trace element analyses on the small layers. In order to do this properly, a better sampling technique must be used so that the layers are not disrupted and so they are large enough to analyze. A box corer may be more appropriate, because of the increased area sampled and the lesser disruption of layering near the center of the box. Since the laminae are formed by varying proportions of bulk constituents, this approach could help to test whether the trace element concentrations in the bulk constituents are consistent in a single area, or whether they change with time and/or depth.

A third area for future research is to continue sampling the same areas sampled in this study. All these samples were taken at the end of a severe drought, and many areas, such as WCA3B, LOTI and FCEG are normally under water at least part of the year. Therefore, it would be interesting to see whether the increased water flow changes the elemental abundances in the whole soils and bulk constituents over the next few years and over longer periods of time. This is especially important since restoring water flow through the Everglades has recently been mandated by law.

REFERENCES CITED

- Adriano, D.C. 1986. Trace elements in the terrestrial environment. Springer-Verlag, New York. 533 pp.
- Bohn, H. L., McNeal, B. L. and G. A. O'Connor. 1985. Soil chemistry. J. Wiley and Sons, New York, Second Edition. 341 pp.
- Brownlow, A. 1979. Geochemistry. Prentice-Hall Inc. Englewood Cliffs, New Jersey. 498 pp.
- Deluxe Map of Florida. Rand McNally Corp., Chicago, Illinois, 1991.
- Evans, L. J. 1989. Environ. Sci. Technol. 23: 9; pp. 1046-1056. Chemistry of Metal Retention by Soils.
- FitzPatrick, E. A. 1980. Soils: their formation, classification, and distribution. Longman, London. 353 pp.
- Hoffmeister, J. E. 1974. Land from the Sea; the Geologic History of South Florida. University of Miami Press, Coral Gables, Florida. 143 pp.
- Kabata-Pendias A. K. and H. Pendias. 1984. Trace elements in soils and plants. CRC Press, Boca Raton, Florida. 315 pp.
- Sposito, G. 1989. The chemistry of soils. Oxford University Press, New York. 277 pp.

APPENDIX A

SITES SAMPLED BUT NOT ANALYZED

A. Cores were obtained from these sites, however, they were not used in the present study.

WCA3B1 core was collected from the Francis B. Taylor Preserve. The approximate latitude was 25°45'45" N and the longitude was 80°30' W and is found on the Coopertown, Florida quadrangle. The core was recovered from the shallow muddy flats next to the boat ramp for canal C-4, using the rigid plastic tube method.

WCA3B3 core was collected from the Francis B. Taylor preserve at approximately latitude 25°47'30" N and longitude 80°30' W and is on the Coopertown, Florida quadrangle. The sample was collected approximately 2 km north of canal C-4, using the rigid plastic tube.

CAL67A core (Conservation Levy 67A). The site is located at approximately latitude 25°45'30" N and longitude 80°40' W and is on the Long Island, Florida quadrangle map. The site is north of the Tamiami Trail 19.2 km west of US 27, approximately 3 meters north of the parking area between levy 67A and 67C, and 5 meters east of levy 67A and was collected using the hand held piston corer.

TP-1 core (Turkey Point). The site is located at approximately latitude 25°27' N and longitude 80°21' W and is on the Arsenicker Keys, Florida quadrangle map. The site is in a hammock 10 meters south of SW 344th St and 1.8 km east from 117th St. The core was recovered with the rigid plastic tube.

BFP-1 core (Homestead Bayfront Park). The site is located at approximately latitude 25°28' N and longitude 80°21'15" W and is on the

Arsenicker Keys, Florida quadrangle. The site is in a hammock 5 meters south of SW 328th St, approximately .66 km west of the entrance to Homestead Bayfront Park. The rigid plastic tube was used.

CSR-1 core (Card Sound Road). The site is located at approximately latitude 25°24' N and longitude 80°27' W and is on the Homestead, Florida quadrangle map. The site is 15 meters west of Card Sound Road and 2 meters south of the westbound unimproved road south of the Naval Reservation and north of the quarry and radio towers. The core was collected with the rigid plastic tube.

EGNP-3 core (Everglades National Park). The site is located at approximately latitude 25°25'30" N and longitude 80°40'45" and is on the Long Pine Key, Florida quadrangle map. The sample was collected east of the Pinelands Trail and approximately 20 meters north of old US 27 using the rigid tube.

B. Surface samples were collected from these sites because the sites were not suitable for coring. These samples were retained for future study.

S-333 surface sample (South Florida Water Management District spillway S-333). The site is located at approximately latitude 25°45'30" N and longitude 80°40'30" W and is on the Long Island, Florida quadrangle. The sample consisted of bottom sediments from canal C-11 and was collected upstream from gate S-333 and canal C-4. Upstream as defined by SFWMD is from the same side of the cement barrier where the metal gate rests in the water.

50MB surface sample (Fifty Mile Bend Primitive Campground). The site is located approximately latitude 25°51' N and longitude 80°55'30" W and

is on the Fifty Mile Bend, Florida quadrangle. The sample was taken from the bottom sediments of a small canal which is not recorded on either the topographical map or the South Florida Water Management District map, 15 meters west of the northwest corner of the rock lake.

MSLR surface sample (Monroe Station Logging Road). The site is located at approximately latitude $25^{\circ}47'30''$ N and longitude $81^{\circ}06'$ W and is on the Monroe Station, Florida quadrangle. The site is 3 miles south of US 41 in Monroe Station and 2 meters east of the old logging road.

FCEG-2 surface sample (Frog City Everglades). The site is located at latitude $25^{\circ}43'$ N and longitude $80^{\circ}36'30''$ W and is on the South of Coopertown, Florida quadrangle. The sample is from the mud at the edge of a cut into the hammock 10 meters east of the FCEG-1 sample site.

HDWD surface sample (Howard Drive West Dade). The site is located at approximately latitude $25^{\circ}38'$ N and longitude $80^{\circ}31'$ W and is on the South of Coopertown, Florida quadrangle. This sample was taken in Dade county 10 meters south of Howard Drive (SW 136th Ave) approximately half way between SW 217th and 212th Avenues.

NWPP surface sample (Navy Well Pineland Preserve). The site is located approximately at latitude $25^{\circ}26'$ N and longitude $80^{\circ}30'30''$ W and is on the Royal Palm Ranger Station, Florida quadrangle. It is 30 meters south of the parking area in the Navy Wells Pineland Preserve, approximately .2 km west of state road Florida 9336, south of Florida City and north of the Dade County Correctional Institution.

TP-2 surface sample (Turkey Point). The site is approximately 15 meters from the north side of SW 344th St and the Florida City canal at

latitude 25°27' N and longitude 80°20'45" W and can be found on the Arsenicker Keys, Florida quadrangle.

S-178 surface sample (South Florida Water Management District spillway S-178). The site is located at approximately latitude 25°24'30" N and longitude 80°33'30" W and is found on the Royal Palm Ranger Station, Florida quadrangle. The sample is from the canal bottom in approximately .8 meters of water, downstream from gate S-178 on the C-111E canal just off Florida 9336 route which leads to Flamingo, Florida. Downstream in the context of the South Florida Water Management District is the opposite side of the cement barrier from where the metal gate rests in the water.

EGNP-1 surface sample (Everglades National Park). The site is located at approximately latitude 25°24'30" N and longitude 80°37'30" W and is on the Long Pine Key, Florida quadrangle. The site is off the hiking/biking trail which wends east from the road leading from Florida 9336 to the Long Pine Key campground. The site is approximately .3 km east of the road near a very sharp bend toward the south and approximately 5 meters north of the bend in the trail.

APPENDIX B

SAMPLE COLLECTION

Samples were collected by the use of some type of coring apparatus, the selection of which was dependent upon the conditions encountered at any particular sampling site. The three types of coring apparatus which were selected and transported to the field were 1) the Wildco Hand Corer 2420, 2) a hand built, hand held piston coring device constructed from plastic tubing and silicon caulk, and 3) a rigid plastic tube of acrylic or cellulose acetate butyrate (CAB).

The Wildco Hand Corer is a device intended for shallow water coring in fresh, salt or brackish water. It consists of a brass core tube into which is inserted a 50.8 cm long liner tube of a chemically clean plastic such as CAB, polycarbonate (Lexan) or acrylic (Plexiglass). The top of the unit contains a flutter valve which seals creating a partial vacuum to prevent loss of the sediment upon retrieval. The bottom of the unit has an optional eggshell core catcher and nosepiece which are used to prevent washout of the sample. The unit has attachable handles whereby the end of the corer can be placed at the sampling site, pushed into the soil or sediment and then using the handles may be pulled free (Wildco Hand Corer Descriptive Pamphlet, Wildlife Supply Company).

The second coring apparatus is a piston coring device constructed from two lengths of acrylic and CAB tubing of slightly different interior diameters. The smaller bored tube is seated in the larger bored tube and the space between is sealed by a snug fitting layer of silicon caulk which has been applied to the smaller tube, allowed to dry and then trimmed to fit with a razor blade. This caulked surface is then lightly lubricated with an

inert vacuum grease allowing the two tubes to fit together, yet be adjustable and have a waterproof seal. The two tubes are placed on the sampling site surface and the outer tube is advanced downward into the sediments while the inner tube is gently pulled upward as the sediments enter the outer sampling tube.

The third sampling apparatus is to use a rigid plastic tube such as CAB. In this method the tube is placed at the sampling site, covered with a heavy board which is then struck with a hammer until the desired depth is reached. The tube is then removed with the sediments inside.

Once a sample is obtained it is capped on both ends with plastic caps to prevent leakage or loss and the tube and caps are labelled with the site name. The site name and location are recorded in the field notebook. The samples are then transported upright, to avoid disturbing any sedimentary structures which might be present, to an upright freezer where they are placed until frozen. Once frozen the cores are transferred in a recreational cooler (ice chest) to a freezer on campus where they are stored until prepared for analysis.

APPENDIX C

SAMPLE PREPARATION AND CHEMICAL ANALYSIS

Examination and Division

The frozen cores were transported to the FIU physics department in a cooler where each frozen core was cut in half lengthwise with a band saw. Each half-core was wrapped securely in plastic wrap, labelled, returned to the cooler, and transported back to the geology department. Since the cut surface was now contaminated by the metal of the band saw the surfaces were then cleaned using a teflon spatula. One pass was made across the width of the half-core with the teflon spatula removing the cut surface which had contacted the band saw. The spatula was then rinsed with tap water, then again with deionized, distilled water, and dried with a Chem wipe before again coming in contact with the core. Rock fragments that were exposed to the band saw were removed, washed with distilled, deionized water and replaced. Leaf litter, identifiable plant material located at the top of the core was removed.

Once the cut surfaces were removed the cores were photographed, and one half-core from each core set aside for archival purposes. The remaining half core was then observed and described.

Once fully described, the half-core was then divided into segments using a teflon spatula and taking care to avoid contamination between segments by rinsing as described above. Each segment was placed into a clean 4 ounce glass jar and labelled with its site location and numerically with #1 denoting the top segment. The division into cores had to be done in such a way as to try to allow adequate sample to be available for analysis in each segment. Sample size was not a fixed constraint, but varied from

segment to segment depending upon the stratigraphy of the material being segmented.

Each uncapped segment was dried in a 110° C oven. During drying the samples were frequently stirred with a teflon spatula kept clean as detailed previously. This served to homogenize the samples and prevent clumping during drying. Once dry, the samples were removed and placed in the desiccator until cooled, then closed with labelled caps.

The cooled, dried samples were then sieved through an 18 mesh sieve (1 mm sieve opening). The coarse fraction of each segment was placed into a clean plastic bag or glass jar, labelled and saved for future reference. The fine fraction of each segment was returned to the 4 ounce glass jar and recapped.

Chemical Preparation

Extraction of Fulvic and Humic Acids

1. A 4 gram \pm .0040 aliquot was removed from each fine fraction with the exception of these three samples, the weight of which comprised the entire fine fraction of each sample:

WCA3B2-1 2.4949 g

WCA3B2-3 3.0527 g

WCA3B2-4 3.0238 g

2. Each 4 g aliquot was placed into a labelled centrifuge tube and added to each was 40 ml of 0.1 N sodium hydroxide (NaOH). The centrifuge tubes were capped and shaken for one hour on the wrist action shaker.

3. After shaking was completed the supernatant fluid from each tube was filtered through a 40 Whatman filter paper in a plastic funnel into a clean, labelled glass beaker. They were allowed to rest for one hour to ensure all supernatant fluid had passed through the filter papers. The centrifuge tubes with the drained residue were capped and saved for the carbonate dissolution.
4. The supernatant was acidified to pH 1 by the addition of 4 ml of 1.5 N nitric acid (HNO_3) to the beaker. The resulting precipitate was the humic acid; the fulvic acid remained in solution.
5. The solution from each beaker was filtered through 40 Whatman filter paper into clean, labelled centrifuge tubes to separate the humic acid from the fulvic acid.
6. The fulvic acid fraction was then diluted to a volume of 35 ml by the addition of 0.1 N HNO_3 and capped.

Dissolution of Humic Acid

1. The precipitates from the above separation (humic acid) were each washed from the filter paper into a clean, labelled glass beaker using 1.5 N HNO_3 . (CSRA 1 was left overnight to drain and the humic acid was unsalvagable as it would not rinse from the filter paper. This was discarded and repeated for this sample.)
2. The beakers were placed on a hot plate and the solutions allowed to evaporate to dryness.
3. To each beaker of dry residue 2 ml of HNO_3 was added. The solutions were again allowed to evaporate to dryness on the hot plate.

4. Step three was repeated.
5. To each beaker of dry residue was added 4 ml Aqua Regia (3ml 12 N HCl and 1 ml 15.7 N HNO₃).
6. The solutions in the beakers were again brought to dryness on the hot plate.
7. The dried residue in each beaker was brought to a volume of 35 ml by the addition of 1 N HCl. The solutions of dissolved humic acid were then transferred to clean, labelled centrifuge tubes and capped.

Carbonate Dissolution

1. The residue from step 3 of the extraction of fulvic and humic acid had been saved for each aliquot weighed out. Each centrifuge tube of residue was washed into a clean, labelled dry glass beaker using HCl. Care was taken to keep the volume less than 30 mls. (FCEG1-3 was diluted to 40 ml).
2. The contents of the beakers was allowed to effervesce for approximately 10 minutes, the beakers were swirled occasionally.
3. The contents of the beakers were then filtered through 40 Whatman filter paper in a funnel into clean, labelled centrifuge tubes and capped. (One drop of FCEG1-3 was spilled).
4. The residue from each beaker was rinsed through the filter paper with HCl and allowed to filter through.
5. This solution was discarded.
6. The residue in the filter papers were allowed to air dry. Each filter paper was wrapped in plastic, labelled and saved for possible future analysis.

7. The solutions in the labelled centrifuge tubes from step 3 were then diluted to a volume of 30 ml with 1 N HCl.

Whole soil analysis

1. The samples (previously dried to 110° C) were heated to 550° C to decompose the organic compounds which are resistant to dissolution. (A portion of the more volatile elements may have been lost during this procedure).
2. A 0.5 gram aliquot from each sample was weighed out and placed into a 30 ml teflon beaker.
3. 4 ml of concentrated HCl was then added to each aliquot in the beakers and allowed to effervesce.
4. Once the effervescence ceased, 1 ml of concentrated HNO₃ was added to the solutions to oxidize any remaining organic compounds.
The samples were then treated as silicate/oxide mixtures.
5. To the solutions in the beakers was added 3 ml HF and one drop of perchloric acid.
6. The beakers were covered and the samples allowed to digest overnight.
7. The following day the samples were brought to dryness on the hot plate which drove off the HF plus the Si as SiF₄ and left the remaining cations as perchlorates.
8. The samples were picked up in 6 N HCl and then brought to dryness.
9. The previous step was repeated.

10. The dried residue in each beaker was finally dissolved in 25 ml 1 N HCl.

Trace metal grade reagents were used for this procedure and a blank (including all of them) was also analyzed. The whole soil analysis gives the composition of the whole sample.

APPENDIX D

VOLATILE LOSS PROCEDURE

1. The samples were allowed to dry for 24 hours at 110° C.
2. Approximately one gram of each sample was weighed into a previously weighed quartz crucible.
3. The samples were heated to 550° C for one hour.
4. The were allowed to dry in a desiccator cabinet and reweighed.

The weight lost between 110° C and 550° C is the result mainly of the decomposition of organic material and the dehydration of clay and oxides if present.

5. The samples were heated to 1000° C for one hour.
6. Step 4 was repeated.

The weight lost between 550° C and 1000° C is produced by the decarbonation of carbonate.

Each weight lost is a rough estimate of the proportion of each sample that is organic matter and calcium carbonate.

Table 8
Volatile Loss Study
Percent weight lost as a result of heating to 550° C and 1000° C

SITES	SAMPLE WT	< 550° C	> 550° C	% wt. loss
LOTI-1	1.003	27.069%	28.076	
LOTI-2	1.001	15.974	33.147	
LOTI-3	1.003	13.335	33.483	
LOTI-4	1.002	13.795	31.783	
FIU-1	1.000	6.870	1.900	
FIU-2	1.000	0.644	1.640	
FIU-3	1.002	5.998	1.268	
FIU-4	1.002	4.450	0.718	
FIU-5	1.000	2.309	0.300	
FIU-6	1.003	2.932	1.057	
FIU-7	0.999	2.322	29.176	
FIU-8	1.000	1.579	38.331	
WCA3B2-2	1.003	11.168	38.508	
FCEG1-1	1.004	20.990	21.588	
FCEG1-2	1.007	21.560	23.953	
FCEG1-3	1.007	17.562	25.608	
FCEG1-4	1.005	15.342	24.923	
FCEG1-5	1.001	10.120	27.173	
CSRA-1	1.002	28.020	13.037	
CSRA-2	1.002	17.136	13.373	
CSRA-3	1.001	4.505	15.023	
CSRA-4	1.002	11.251	16.172	
CSRA-5	1.002	41.354	6.530	
CSRA-6	1.004	26.958	2.500	

APPENDIX E

RAW DATA AND DATA QUALITY

The following tables contain raw data obtained from the chemical analyses in the study. The element concentrations are recorded as parts per million in the sample solutions. For whole soil analyses the ppm in the soil sample is also indicated for comparison with published values.

In order to ensure accurate results and optimize reproducibility, the ICP was calibrated to standards used for the elements analyzed in the study. The standards used for the high calibration were obtained from the US Bureau of Standards and diluted to the necessary strength. The low standard consisted of an acid solution which was essentially blank for the elements in question. The ICP instrument was recalibrated to these standards after the analysis of every 10th sample to ensure longterm precision.

Each value is the average of measurements taken over a one minute interval. Typical standard deviations for these values (in %) are also listed on the table.

	CSRA 1 Bulk	CSRA 1 Humic	CSRA 1 Fulvic	CSRA 1 Carb	CSRA 2 Bulk	CSRA 2 Humic	CSRA 2 Fulvic	CSRA 2 Carb
P	66.297	0.222	1.549	67.520	52.824	0.371	1.308	100.700
Ni	0.076	0.029	0.022	0.022	0.027	0.022	0.016	0.019
Ba	1.247	0.007	0.011	0.613	1.059	0.005	0.008	0.442
Mn	0.796	0.005	0.022	1.258	0.422	0.003	0.011	0.649
Fe	53.861	0.236	0.749	30.820	33.892	0.188	0.624	26.940
Cr	0.450	0.013	0.008	0.120	0.288	0.004	0.007	0.163
Mg	432.990	0.931	3.288	7773.700	272.670	0.936	2.971	629.100
Ti	5.789	0.040	0.002	0.021	4.505	0.018	0.001	0.035
Sc	0.013	0.000	0.001	0.002	0.014	0.000	0.000	0.002
Al	105.290	0.206	1.016	25.920	84.163	0.276	1.904	26.620
Sr	13.241	0.012	0.140	24.470	9.770	0.009	0.130	31.170
Sb	0.015	0.024	0.000	0.049	0.007	0.031	0.000	0.012
Zn	0.693	0.099	0.077	0.851	0.260	0.054	0.067	0.501
Pb	0.332	0.027	0.026	0.116	0.244	0.000	0.052	0.364
Cd	0.020	0.003	0.000	0.013	0.013	0.001	0.003	0.015
Co	0.032	0.000	0.000	0.014	0.014	0.000	0.000	0.006
V	0.221	0.008	0.123	0.025	0.137	0.012	0.098	0.083
Be	0.001	0.001	0.001	0.000	0.000	0.001	0.001	0.002
Ca	3859.700	2.394	30.520	7286.000	3077.700	1.507	28.010	9726.000
Cu	1.670	0.028	0.053	0.030	0.684	0.021	0.040	0.072
Y	0.142	0.000	0.001	0.051	0.144	0.000	0.001	0.248
Si		0.040	0.547	2.064		0.050	0.292	2.073

	CSRA 3 Bulk	CSRA 3 Humic	CSRA 3 Fulvic	CSRA 3 Carb	CSRA 4 Bulk	CSRA 4 Humic	CSRA 4 Fulvic	CSRA 4 Carb
P	51.200	0.143	0.418	158.400	31.072	0.264	0.832	65.240
Ni	0.029	0.011	0.009	0.007	0.047	0.018	0.013	0.008
Ba	1.056	0.004	0.011	0.319	0.847	0.005	0.013	0.540
Mn	0.298	0.003	0.005	0.651	0.406	0.005	0.005	0.598
Fe	13.927	0.231	0.360	11.760	37.661	0.369	0.954	18.700
Cr	0.178	0.011	0.005	0.279	0.296	0.011	0.010	0.186
Mg	225.020	1.217	2.950	907.600	244.720	1.240	2.566	659.800
Ti	3.240	0.017	0.001	0.053	7.458	0.022	0.003	0.053
Sc	0.010	0.000	0.000	0.008	0.017	0.000	0.000	0.003
Al	62.781	0.443	2.431	11.300	122.330	1.109	11.520	6.174
Sr	77.255	0.008	0.104	36.530	9.943	0.008	0.140	33.140
Sb	0.006	0.000	0.000	0.011	0.015	0.011	0.000	0.064
Zn	0.104	0.029	0.055	0.150	0.123	0.036	0.057	0.156
Pb	0.087	0.002	0.053	0.089	0.153	0.001	0.053	0.206
Cd	0.006	0.001	0.003	0.008	0.012	0.004	0.000	0.009
Co	0.009	0.000	0.006	0.010	0.017	0.000	0.000	0.008
V	0.091	0.003	0.056	0.157	0.180	0.016	0.027	0.130
Be	0.000	0.002	0.001	0.002	0.001	0.001	0.001	0.003
Ca	2709.300	1.414	26.120	11960.000	3359.000	1.734	30.660	10840.000
Cu	0.126	0.010	0.020	0.039	0.249	0.016	0.028	0.035
Y	0.147	0.000	0.000	0.511	0.110	0.000	0.002	0.275
Si		0.037	0.324	2.164		0.046	0.694	3.285

	CSRA 5 Bulk	CSRA 5 Humic	CSRA 5 Fulvic	CSRA 5 Carb	CSRA 6 Bulk	CSRA 6 Humic	CSRA 6 Fulvic	CSRA 6 Carb
P	54.753	0.705	1.876	83.080	53.773	0.886	1.686	42.601
Ni	0.339	0.017	0.029	0.102	0.691	0.042	0.036	0.615
Ba	1.925	0.009	0.034	2.548	2.837	0.017	0.048	2.830
Mn	0.612	0.005	0.011	0.674	0.742	0.007	0.006	0.202
Fe	230.420	1.946	2.393	81.370	402.000	3.351	1.406	52.880
Cr	1.673	0.025	0.020	0.390	3.303	0.052	0.024	0.292
Mg	392.500	2.773	3.575	350.600	618.840	3.602	2.521	70.320
Ti	45.269	0.038	0.008	0.037	88.768	0.008	0.007	0.221
Sc	0.144	0.002	0.001	0.011	0.281	0.002	0.002	0.017
Al	815.130	5.742	25.470	420.100	1555.700	10.320	29.610	254.400
Sr	10.541	0.017	0.245	12.970	7.416	0.022	0.246	14.830
Sb	0.065	0.000	0.000	0.037	0.275	0.017	0.000	0.093
Zn	0.341	0.034	0.058	0.132	0.448	0.066	0.061	0.141
Pb	0.647	0.027	0.043	0.214	1.018	0.045	0.058	0.458
Cd	0.067	0.001	0.001	0.011	0.118	0.004	0.002	0.016
Co	0.097	0.001	0.002	0.010	0.175	0.000	0.000	0.008
V	0.999	0.060	0.079	0.263	1.666	0.072	0.885	0.846
Be	0.016	0.001	0.001	0.013	0.035	0.001	0.001	0.032
Ca	1979.200	2.889	50.980	3188.000	701.620	3.180	43.330	2149.000
Cu	1.139	0.026	0.039	0.017	1.600	0.047	0.054	0.119
Y	0.338	0.001	0.009	0.174	0.598	0.004	0.023	0.801
Si		1.105	1.762	17.170		0.231	2.934	14.540

CSRA	Bulk sigma %	Carb sigma %	H.A. sigma %	F.A. sigma %
P	1.44	1.84	23.18	8.55
Ni	18.56	35.80	30.43	70.67
Ba	1.40	1.80	23.18	11.67
Mn	1.59	1.41	9.18	10.72
Fe	1.60	1.51	1.85	1.13
Cr	2.93	2.82	25.40	62.67
Mg	1.57	1.43	1.22	1.16
Ti	2.21	1.69	8.82	30.33
Sc	2.65	6.87	17.70	58.67
Al	1.90	1.89	1.76	0.87
Sr	2.45	1.35	1.04	1.11
Sb	64.17	114.67	81.33	-
Zn	1.82	2.04	5.08	4.33
Pb	4.17	24.80	24.60	60.00
Cd	5.33	20.83	167.50	100.50
Co	4.80	32.33	210.00	370.25
V	2.06	80.17	22.10	2.48
Be	3.28	248.83	190.00	513.33
Ca	1.13	2.47	1.49	1.02
Cu	1.35	7.40	8.77	4.02
Y	1.20	3.09	201.33	72.42
Si		2.01	10.33	3.60

	FCEG 1 Bulk	FCEG 1 Humic	FCEG 1 Fulvic	FCEG 1 Carb	FCEG 2 Bulk	FCEG 2 Humic	FCEG 2 Fulvic	FCEG 2 Carb
P	625.050	0.552	2.400	249.600	399.580	0.777	2.365	525.400
Ni	0.034	0.014	0.013	0.000	0.063	0.015	0.010	0.030
Ba	2.938	0.006	0.047	1.733	3.084	0.008	0.066	4.412
Mn	3.147	0.007	0.056	3.313	3.414	0.011	0.075	5.917
Fe	1000.000	7.172	4.155	49.390	1000.000	15.810	5.840	190.400
Cr	0.119	0.011	0.001	0.009	0.058	0.010	0.003	0.039
Mg	503.700	1.286	8.479	768.900	397.550	0.534	8.141	687.800
Ti	4.856	0.029	0.002	0.013	3.933	0.027	0.002	0.029
Sc	0.010	0.000	0.000	0.000	0.012	0.000	0.000	0.000
Al	78.808	0.235	0.863	2.121	78.514	0.290	1.093	40.770
Sr	26.101	0.015	0.322	33.570	24.013	0.017	0.431	52.810
Sb	0.060	0.010	0.000	0.068	0.073	0.049	0.000	0.033
Zn	1.789	0.036	0.075	0.324	1.114	0.036	0.056	1.204
Pb	0.513	0.018	0.041	0.005	0.475	0.051	0.023	0.114
Cd	0.298	0.004	0.003	0.012	0.371	0.002	0.003	0.051
Co	0.040	0.000	0.001	0.015	0.043	0.000	0.004	0.027
V	0.193	0.002	0.005	0.005	0.205	0.001	0.007	0.027
Be	0.000	0.003	0.001	0.000	0.000	0.003	0.001	0.000
Ca	6155.300	3.461	85.640	7578.000	6475.600	4.475	126.800	12390.000
Cu	0.707	0.017	0.031	0.008	0.546	0.019	0.026	0.032
Y	0.022	0.000	0.000	0.001	0.023	0.000	0.000	0.013
Si		0.037	1.312	11.280		0.066	1.179	16.390

	FCEG 3 Bulk	FCEG 3 Humic	FCEG 3 Fulvic	FCEG 3 Carb	FCEG 4 Bulk	FCEG 4 Humic	FCEG 4 Fulvic	FCEG 4 Carb
P	526.230	0.350	2.127	842.100	683.720	0.280	2.662	314.000
Ni	0.056	0.017	0.012	0.013	0.043	0.024	0.017	0.000
Ba	2.961	0.005	0.033	4.528	2.739	0.006	0.032	1.797
Mn	3.209	0.006	0.024	4.592	2.820	0.007	0.023	2.892
Fe	1000.000	6.839	2.497	214.500	800.000	3.687	2.416	79.560
Cr	0.091	0.006	0.000	0.053	0.122	0.012	0.000	0.008
Mg	354.090	1.041	3.147	484.600	332.590	1.108	2.618	373.400
Ti	3.268	0.020	0.002	0.159	3.159	0.022	0.003	0.019
Sc	0.011	0.000	0.000	0.003	0.011	0.000	0.001	0.000
Al	67.384	0.116	0.886	44.490	62.382	0.199	1.713	3.783
Sr	24.941	0.009	0.222	61.360	27.475	0.015	0.252	45.040
Sb	0.044	0.040	0.000	0.027	0.037	0.015	0.000	0.026
Zn	0.753	0.041	0.046	1.103	0.898	0.064	0.087	0.268
Pb	0.318	0.000	0.004	0.129	0.253	0.065	0.069	0.000
Co	0.345	0.002	0.003	0.099	0.230	0.005	0.002	0.021
Co	0.037	0.000	0.002	0.027	0.030	0.000	0.004	0.016
V	0.174	0.001	0.001	0.057	0.131	0.003	0.001	0.007
Be	0.000	0.001	0.001	0.002	0.000	0.001	0.001	0.000
Ca	6320.800	1.807	47.900	13160.000	6461.400	2.718	46.710	10110.000
Qu	0.392	0.011	0.018	0.048	0.398	0.033	0.066	0.010
Y	0.022	0.000	0.001	0.038	0.022	0.000	0.000	0.001
Si		0.117	0.578	11.880		0.032	0.404	5.110

	FCEG 5 Bulk	FCEG 5 Humic	FCEG 5 Fulvic	FCEG 5 Carb	Bulk sigma %	Carb sigma %	H.A. sigma %	F.A. sigma %
P	759.820	184.600	1.870	134.100	1.50	1.89	25.78	37.40
Ni	0.021	16.320	0.000	0.000	45.60	35.50	40.20	88.25
Ba	2.253	4.390	0.022	0.585	2.26	3.28	22.32	4.62
Mn	2.576	3.160	0.023	1.429	1.80	1.56	4.26	1.59
Fe	255.960	760.800	1.282	12.400	0.34	2.34	1.52	0.99
Cr	0.083	7.320	0.000	0.000	18.00	46.13	49.00	100.00
Mg	469.230	1077.000	3.558	306.800	1.27	1.54	1.36	0.69
Ti	2.358	16.860	0.000	0.010	1.51	5.19	4.12	55.75
Sc	0.009	0.000	0.000	0.000	4.92	76.95	.	245.00
Al	47.651	290.300	2.588	0.000	1.38	4.80	2.68	1.52
Sr	36.210	14.330	0.312	29.180	1.48	1.27	1.61	0.79
Sb	0.023	0.000	0.000	0.044	39.40	93.60	78.60	.
Zn	2.032	37.610	0.081	0.084	1.81	1.97	4.70	3.86
Pb	0.331	78.790	0.057	0.000	3.54	115.48	84.00	157.44
Cd	0.083	1.730	0.003	0.006	1.70	13.82	90.20	63.20
Cu	0.020	0.000	0.004	0.008	5.84	30.26	520.00	101.00
V	0.070	0.000	0.002	0.004	1.10	21.32	210.00	182.00
Be	0.000	0.580	0.001	0.001	.	87.95	320.40	572.00
Ca	6863.700	2140.000	44.180	5191.000	1.37	2.50	2.67	1.53
Cu	0.600	19.440	0.029	0.003	1.36	23.90	7.24	10.22
Y	0.016	0.000	0.000	0.001	1.78	122.04	1000.00	332.00
Si		38.310	0.722	2.621		1.67	15.90	1.30

	FIU 1 Bulk	FIU 1 Humic	FIU 1 Fulvic	FIU 1 Carb	FIU 2 Bulk	FIU 2 Humic	FIU 2 Fulvic	FIU 2 Carb
P	3.328	0.113	0.327	2.906	2.905	0.1	0.323	2.232
Ni	0.169	0.002	0.012	0.056	0.174	0.015	0.011	0.041
Ba	0.573	0.005	0.013	0.546	0.595	0.007	0.014	0.505
Mn	1.093	0.006	0.019	2.293	0.980	0.007	0.017	1.799
Fe	127.450	1.653	0.511	26.610	118.200	1.989	0.513	27.870
Cr	0.647	0.013	0.008	0.231	0.626	0.022	0.013	0.245
Mg	159.750	1.781	1.866	57.870	157.690	2.103	1.697	45.190
Ti	21.543	0.007	0.002	0.094	21.401	0.008	0.002	0.093
Sc	0.048	0.000	0.000	0.007	0.050	0.001	0.000	0.008
Al	299.340	1.825	4.078	88.060	303.430	3.137	5.121	88.890
Sr	1.947	0.006	0.068	7.020	1.800	0.006	0.073	6.263
Sb	0.029	0.017	0.000	0.004	0.072	0.000	0.000	0.027
Zn	0.206	0.022	0.064	0.231	0.177	0.033	0.069	0.099
Pb	0.394	0.011	0.000	0.616	0.336	0.000	0.045	0.452
Cd	0.038	0.004	0.001	0.012	0.035	0.002	0.000	0.009
Co	0.046	0.000	0.000	0.014	0.044	0.000	0.004	0.012
V	0.298	0.006	0.033	0.123	0.292	0.006	0.036	0.125
Be	0.004	0.004	0.001	0.008	0.004	0.000	0.001	0.009
Ca	372.860	1.014	19.340	1999.000	333.690	0.944	20.920	1672.000
Cu	0.187	0.009	0.018	0.048	0.153	0.009	0.015	0.029
Y	0.108	0.000	0.003	0.306	0.108	0.000	0.004	0.313
Si		0.096	2.821	9.800		0.125	2.733	9.222

	FIU 3 Bulk	FIU 3 Humic	FIU 3 Fulvic	FIU 3 Carb	FIU 4 Bulk	FIU 4 Humic	FIU 4 Fulvic	FIU 4 Carb
P	3.144	0.107	0.233	1.752	1.661	0.107	0.184	1.006
Ni	0.161	0.015	0.014	0.043	0.146	0.019	0.008	0.020
Ba	0.498	0.011	0.022	0.556	0.436	0.007	0.018	0.343
Mn	0.739	0.013	0.022	1.087	0.447	0.003	0.009	0.391
Fe	93.567	3.466	0.708	26.660	67.686	1.769	0.462	13.050
Cr	0.657	0.034	0.016	0.154	0.598	0.023	0.018	0.237
Mg	146.590	4.195	2.092	39.190	122.850	2.442	1.969	16.060
Ti	18.188	0.004	0.002	0.094	17.142	0.007	0.005	0.061
Sc	0.047	0.002	0.000	0.010	0.042	0.001	0.000	0.011
Al	291.340	7.547	7.165	99.240	252.920	3.887	7.209	59.040
Sr	1.208	0.015	0.102	5.090	0.663	0.008	0.063	2.228
Sb	0.060	0.044	0.022	0.048	0.023	0.000	0.000	0.003
Zn	0.144	0.035	0.047	0.067	0.121	0.029	0.058	0.071
Pb	0.256	0.012	0.040	0.348	0.206	0.020	0.069	0.158
Cd	0.027	0.003	0.003	0.007	0.020	0.004	0.001	0.005
Co	0.037	0.000	0.000	0.009	0.035	0.001	0.000	0.005
V	0.260	0.007	0.030	0.111	0.211	0.007	0.034	0.076
Be	0.004	0.002	0.004	0.010	0.003	0.001	0.001	0.007
Ca	209.070	1.571	25.150	1472.000	108.590	0.999	19.210	673.400
Cu	0.106	0.010	0.013	0.023	0.084	0.012	0.011	0.012
Y	0.107	0.001	0.006	0.362	0.094	0.000	0.006	0.273
Si		0.162	2.635	4.258		0.145	2.425	6.076

	FIU 5 Bulk	FIU 5 Humic	FIU 5 Fulvic	FIU 5 Carb	FIU 6 Bulk	FIU 6 Humic	FIU 6 Fulvic	FIU 6 Carb
P	1.024	0.189	0.146	0.433	1.576	0.177	0.188	0.907
Ni	0.097	0.014	0.013	0.000	0.157	0.022	0.022	0.008
Ba	0.341	0.006	0.013	0.165	0.383	0.012	0.022	0.211
Mn	0.333	0.004	0.003	0.071	0.310	0.009	0.005	0.077
Fe	37.855	1.032	0.273	5.337	51.925	2.898	0.500	7.566
Cr	0.410	0.021	0.019	0.149	0.682	0.054	0.034	0.300
Mg	77.885	1.949	1.632	5.582	117.600	3.917	2.055	16.320
Ti	13.302	0.008	0.002	0.027	16.271	0.008	0.004	0.042
Sc	0.028	0.001	0.001	0.009	0.044	0.003	0.000	0.014
Al	166.670	3.066	5.301	30.610	257.950	9.058	9.366	56.620
Sr	0.315	0.007	0.042	0.679	1.697	0.03	0.391	5.064
Sb	0.019	0.0	0.011	0.027	0.019	0.000	0.000	0.000
Zn	0.085	0.027	0.044	0.037	0.098	0.057	0.058	0.032
Pb	0.126	0.018	0.054	0.088	0.158	0.057	0.048	0.092
Cd	0.013	0.000	0.001	0.000	0.016	0.001	0.002	0.004
Co	0.024	0.000	0.003	0.004	0.032	0.000	0.003	0.003
V	0.130	0.003	0.019	0.035	0.204	0.009	0.035	0.065
Be	0.001	0.001	0.001	0.003	0.004	0.002	0.001	0.006
Ca	44.278	0.994	14.290	207.200	202.130	1.856	34.660	1029.000
Cu	0.055	0.008	0.010	0.007	0.073	0.010	0.010	0.010
Y	0.062	0.001	0.004	0.155	0.103	0.001	0.011	0.233
Si		0.129	1.662	3.576		0.295	2.839	5.214

	FIU 7 Bulk	FIU 7 Humic	FIU 7 Fulvic	FIU 7 Carb	FIU 8 Bulk	FIU 8 Humic	FIU 8 Fulvic	FIU 8 Carb
P	2.170	0.116	0.134	0.801	2.170	0.070	0.182	2.118
Ni	0.027	0.003	0.014	0.000	0.027	0.006	0.005	0.000
Ba	0.168	0.010	0.017	0.103	0.168	0.004	0.016	0.090
Mn	0.115	0.004	0.002	0.036	0.115	0.002	0.003	0.059
Fe	16.930	1.268	0.288	0.360	16.930	0.604	0.298	0.888
Cr	0.259	0.028	0.020	0.035	0.259	0.021	0.017	0.050
Mg	145.500	2.031	2.056	113.700	145.500	1.273	1.979	243.400
Ti	5.643	0.007	0.007	0.008	5.643	0.007	0.003	0.019
Sc	0.013	0.001	0.000	0.001	0.013	0.000	0.000	0.001
Al	95.583	3.873	4.696	1.900	95.583	1.434	3.203	3.358
Sr	29.990	0.011	3.411	23.720	29.990	0.074	3.698	49.490
Sb	0.011	0.000	0.000	0.008	0.011	0.031	0.014	0.067
Zn	0.054	0.034	0.051	0.024	0.054	0.026	0.041	0.020
Pb	0.054	0.000	0.029	0.000	0.054	0.000	0.083	0.040
Cd	0.007	0.002	0.003	0.002	0.007	0.001	0.004	0.003
Co	0.011	0.000	0.000	0.000	0.011	0.000	0.002	0.004
V	0.124	0.008	0.032	0.007	0.124	0.003	0.035	0.035
Be	0.000	0.001	0.001	0.000	0.000	0.004	0.001	0.000
Ca	5309.600	4.958	165.400	4921.000	5309.600	3.498	179.600	9126.000
Cu	0.045	0.009	0.014	0.002	0.045	0.008	0.010	0.004
Y	0.043	0.000	0.005	0.003	0.043	0.001	0.003	0.017
Si		0.160	1.435	1.478		0.098	1.182	0.746

FIU	Bulk sigma %	Carb sigma %	H.A. sigma %	F.A. sigma %
P	7.72	8.19	50.63	33.41
Ni	13.32	39.80	95.50	46.83
Ba	2.67	1.72	25.90	8.31
Mn	2.18	1.27	4.20	4.50
Fe	1.70	2.46	1.07	1.87
Cr	3.41	6.98	15.63	28.11
Mg	1.61	1.29	1.12	1.21
Ti	1.96	2.48	13.33	54.25
Sc	2.20	15.71	22.96	139.13
Al	1.52	3.32	0.91	1.08
Sr	2.15	1.28	1.29	1.24
Sb	56.27	235.76	94.00	195.00
Zn	1.65	3.48	5.88	5.79
Pb	8.80	15.69	123.40	55.86
Cd	4.45	81.99	79.38	130.75
Co	6.46	59.14	250.00	167.50
V	1.46	45.96	32.10	9.55
Be	4.10	157.40	313.19	363.25
Ca	1.50	2.26	0.97	1.08
Cu	2.77	12.49	16.28	24.85
Y	1.57	1.78	131.82	8.74
Si		1.18	7.44	1.43

	LOT11 Bulk	LOT11 Humic	LOT11 Fulvic	LOT11 Carb	LOT12 Bulk	LOT12 Humic	LOT12 Fulvic	LOT12 Carb
P	15.659	1.162	1.903	5.619	9.893	0.156	6.011	1.081
Ni	0.222	0.020	0.002	0.006	0.139	0.008	0.020	0.000
Ba	0.489	0.007	0.009	0.682	0.290	0.003	0.009	0.272
Mn	7.840	0.014	0.179	13.230	6.231	0.007	0.055	5.531
Fe	189.780	1.008	2.200	21.300	130.510	0.920	0.501	1.380
Cr	0.642	0.012	0.009	0.034	0.494	0.011	0.005	0.001
Mg	310.290	1.407	3.027	344.100	249.340	1.468	2.178	163.300
Ti	19.810	0.039	0.005	0.050	16.611	0.023	0.004	0.000
Sc	0.047	0.001	0.000	0.002	0.033	0.000	0.000	0.001
Al	338.570	1.090	8.447	22.650	272.290	0.864	4.791	0.454
Sr	14.141	0.014	0.192	32.150	12.006	0.009	0.119	0.010
Sb	0.035	0.000	0.000	0.065	0.066	0.000	0.000	0.008
Zn	0.269	0.052	0.052	0.112	0.162	0.039	0.060	0.036
Pb	0.679	0.015	0.081	0.213	0.316	0.030	0.065	0.015
Cd	0.065	0.003	0.002	0.016	0.044	0.003	0.002	0.004
Co	0.062	0.000	0.005	0.011	0.044	0.004	0.006	0.006
V	0.436	0.009	0.077	0.029	0.303	0.003	0.040	0.003
Be	0.005	0.001	0.000	0.002	0.004	0.003	0.001	0.000
Ca	6348.300	3.259	50.220	12540.000	5933.200	1.918	34.110	6992.000
Cu	0.667	0.027	0.047	0.020	0.238	0.011	0.024	0.004
Y	0.155	0.002	0.009	0.057	0.122	0.001	0.004	0.000
Si		0.070	0.655	2.185		0.047	0.638	0.945

	LOT13 Bulk	LOT13 Humic	LOT13 Fulvic	LOT13 Carb	LOT14 Bulk	LOT14 Humic	LOT14 Fulvic	LOT14 Carb
P	9.453	0.088	4.37	1.196	10.316	0.051	4.951	1.051
Ni	0.185	0.001	0.016	0.003	0.279	0.009	0.017	0.000
Ba	0.300	0.002	0.009	0.267	0.378	0.004	0.008	0.275
Mn	5.181	0.006	0.035	4.416	4.323	0.005	0.017	3.214
Fe	171.470	1.219	0.247	1.720	243.460	1.050	0.223	1.008
Cr	0.714	0.012	0.008	0.010	1.045	0.010	0.006	0.000
Mg	319.040	1.164	1.896	189.600	397.590	1.151	1.723	201.500
Ti	21.692	0.018	0.000	0.015	30.049	0.018	0.003	0.015
Sc	0.057	0.000	0.000	0.001	0.088	0.000	0.000	0.001
Al	385.430	0.882	7.513	1.182	539.500	0.834	10.850	0.473
Sr	13.205	0.004	0.085	16.150	13.573	0.005	0.068	16.380
Sb	0.024	0.011	0.000	0.000	0.062	0.022	0.000	0.034
Zn	0.152	0.026	0.001	0.031	0.176	0.029	0.063	0.017
Pb	0.292	0.006	0.096	0.025	0.402	0.016	0.083	0.000
Cd	0.056	0.002	0.001	0.003	0.079	0.003	0.000	0.004
Co	0.054	0.000	0.000	0.002	0.072	0.000	0.000	0.000
V	0.352	0.003	0.022	0.003	0.505	0.004	0.021	0.006
Be	0.006	0.000	0.001	0.000	0.009	0.001	0.001	0.000
Ca	6338.100	0.890	22.940	7661.000	6384.100	0.725	16.030	7734.000
Cu	0.162	0.007	0.028	0.004	0.169	0.007	0.017	0.005
Y	0.177	0.000	0.003	0.006	0.288	0.000	0.003	0.005
Si		0.055	0.849	1.073		0.050	1.185	1.402

LOTI	Bulk sigma %	Carb sigma %	H.A. sigma %	F.A. sigma %
P	2.45	9.68	39.95	5.45
Ni	5.65	170.00	52.25	207.50
Ba	2.48	1.32	46.75	27.50
Mn	1.71	1.05	7.92	2.20
Fe	1.43	1.78	2.06	2.48
Cr	3.98	191.30	28.00	71.00
Mg	1.33	1.02	2.25	1.56
Ti	1.67	3.23	4.35	50.33
Sc	1.88	34.75	179.33	220.00
Al	1.45	15.45	2.15	1.25
Sr	1.96	5.15	2.46	1.48
Sb	29.55	127.33	77.00	-
Zn	1.76	2.70	6.88	4.25
Pb	3.51	98.00	202.50	31.50
Cd	2.02	35.25	68.00	85.33
Co	2.87	47.33	66.00	69.00
V	1.81	23.00	43.75	10.53
Be	2.89	87.50	263.70	585.00
Ca	1.27	1.98	2.67	1.53
Cu	1.81	28.40	15.43	7.82
Y	2.13	9.17	172.50	11.73
Si		2.17	23.07	2.78

	CA3B 1 Humic	CA3B 1 Fulvic	CA3B 1 Carb	CA3B 2 Bulk	CA3B 2 Humic	CA3B 2 Fulvic	CA3B 2 Carb
P	0.618	1.068	9.978	0.003	0.000	0.264	0.393
Ni	0.015	0.014	0.072	0.000	0.009	0.000	0.000
Ba	0.006	0.035	1.490	0.001	0.003	0.010	0.585
Mn	0.002	0.006	0.562	0.002	0.002	0.009	0.809
Fe	1.191	1.958	101.200	0.083	0.204	0.314	1.137
Cr	0.009	0.006	0.052	0.000	0.006	0.000	0.000
Mg	1.253	4.065	356.000	0.845	0.895	3.119	395.800
Ti	0.042	0.006	0.472	0.001	0.017	0.002	0.005
Sc	0.000	0.000	0.003	0.000	0.000	0.000	0.000
Al	2.057	20.060	95.750	0.013	0.178	3.088	0.000
Sr	0.021	0.191	10.080	0.027	0.008	0.116	11.880
Sb	0.034	0.022	0.007	0.000	0.016	0.000	0.021
Zn	0.067	0.079	0.480	0.000	0.032	0.046	0.012
Pb	0.038	0.060	0.567	0.000	0.057	0.024	0.000
Cd	0.004	0.002	0.037	0.000	0.003	0.002	0.000
Co	0.000	0.003	0.016	0.000	0.000	0.003	0.006
V	0.010	0.030	0.096	0.000	0.004	0.007	0.003
Be	0.003	0.001	0.005	0.000	0.001	0.000	0.000
Ca	4.479	42.140	2172.000	5.954	1.552	25.680	3398.000
Cu	0.033	0.013	0.048	0.000	0.013	0.014	0.002
Y	0.001	0.000	0.062	0.000	0.000	0.000	0.001
Si	0.074	0.379	3.167		0.025	0.138	0.247

	CA3B 3 Humic	CA3B 3 Fulvic	CA3B 3 Carb	CA3B 4 Humic	CA3B 4 Fulvic	CA3B 4 Carb
P	0.256	0.592	3.398	0.006	0.242	0.682
Ni	0.008	0.017	0.045	0.018	0.012	0.052
Ba	0.005	0.016	0.796	0.006	0.014	0.368
Mn	0.003	0.007	0.696	0.003	0.009	0.285
Fe	0.428	1.226	38.830	0.735	1.998	63.140
Cr	0.009	0.000	0.014	0.011	0.004	0.000
Mg	1.034	2.932	295.200	1.221	4.141	116.400
Ti	0.030	0.002	0.063	0.023	0.001	0.085
Sc	0.000	0.000	0.001	0.000	0.000	0.001
Al	0.786	10.400	25.640	0.655	8.058	5.188
Si	0.010	0.106	8.850	0.008	0.068	2.748
Sb	0.041	0.000	0.049	0.000	0.000	0.000
Zn	0.129	0.072	176.000	0.052	0.060	0.075
Pb	0.050	0.042	0.066	0.029	0.071	0.000
Cd	0.000	0.000	0.011	0.002	0.002	0.013
Co	0.000	0.000	0.014	0.000	0.003	0.012
V	0.007	0.027	0.033	0.010	0.031	0.033
Be	0.001	0.000	0.001	0.000	0.000	0.000
Ca	2.514	27.800	2260.000	1.920	18.510	698.500
Qu	0.026	0.007	0.006	0.016	0.006	0.017
Y	0.000	0.000	0.019	0.000	0.000	0.014
Si	0.072	0.231	0.836	0.074	0.198	0.220

WCA3B	Bulk sigma %	Carb sigma %	H.A. sigma %	F.A. sigma %
P	12.00	7.820	181.60	41.25
Ni	22.00	15.700	73.25	57.67
Ba	0.65	1.140	46.50	23.75
Mn	1.40	0.610	23.15	9.19
Fe	1.60	0.890	1.61	2.83
Cr	32.00	18.450	45.50	114.00
Mg	1.60	0.560	1.79	2.03
Ti	1.90	2.790	3.12	216.75
Sc	17.00	35.500	92.00	100.00
Al	2.30	0.660	2.84	1.38
Sr	1.70	1.310	1.79	1.60
Sb	67.00	212.670	77.00	-
Zn	0.44	3.940	4.58	2.55
Pb	22.00	27.200	93.50	51.25
Cd	5.70	13.530	117.50	237.50
Co	10.00	30.000	-	76.00
V	3.90	22.050	42.50	11.98
Be	-	90.500	390.28	715.00
Ca	0.87	2.900	1.53	2.95
Cu	1.50	14.700	10.00	9.65
Y	2.50	78.750	500.00	-
Si		2.290	29.20	11.93

APPENDIX F

WHOLE SOIL CONCENTRATIONS CORRECTED FOR DILUTION

The following table gives the concentration of elements in the whole soil samples, corrected for dilution, compared with the ranges of concentrations reported for soils worldwide.

Sources for the world ranges are:

- + Bohn et al. (1985) Table 11-3, p. 304
- * Bohn et al. (1985) Table 11-4, p. 311
- # Browlow (1979) Table 7-3, p. 294-295
- ∞ Kabata-Pendias and Pendias (1984), Tables 50 and 51, p. 94-95
- ° Kabata-Pendias and Pendias (1984), Table 53 and 54, p. 97
- § Kabata-Pendias and Pendias (1984), Tables 83 and 84, p. 140
- Kabata-Pendias and Pendias (1984), Table 112, p. 178

Sample	Al *	Ba °	Be *	Ca #	Cd *	Co *	Cr *	Cu *
	10,000-200,000	84-838	1-40	.07-1.7%	.01-7	1-50	5-3000	2-100
range								
CSRA-1	5264	62	0.04	192985	1.00	1.61	22.5	83.5
CSRA-2	4208	53	0.00	153885	0.65	0.70	14.4	34.2
CSRA-3	3139	53	0.00	135465	0.30	0.43	8.9	6.3
CSRA-4	6116	42	0.32	167950	0.60	0.87	14.8	12.5
CSRA-5	40756	96	0.81	98960	3.30	4.83	83.6	57.0
CSRA-6	77785	142	1.73	35081	5.90	8.77	165.2	80.0
FCEG-1	3904	147	0.00	307765	14.88	1.98	6.0	35.3
FCEG-2	3926	154	0.00	323780	18.57	2.13	2.9	27.3
FCEG-3	3369	148	0.00	316040	17.25	1.87	4.5	19.6
FCEG-4	3119	137	0.00	323070	11.49	1.50	6.1	19.9
FCEG-5	2383	113	0.00	343187	4.15	1.02	4.2	30.0
LOTI-1	16928	24	0.27	317415	3.27	3.11	32.1	33.4
LOTI-2	13614	15	0.21	296660	2.21	2.21	24.7	11.9
LOTI-3	19272	15	0.29	316905	2.27	2.27	35.7	8.1
LOTI-4	26975	19	0.44	319205	3.94	3.62	52.3	8.5
WCA3B2-2	632	74	0.00	297725	1.11	0.39	1.6	4.7
FIU1	14967	29	0.18	18643	1.90	2.29	32.4	9.4
FIU2	15172	30	0.17	16684	1.77	2.22	31.3	7.6
FIU3	14567	25	0.19	10454	1.36	1.86	32.9	5.3
FIU4	12626	22	0.15	5430	1.01	1.74	29.9	4.2
FIU5	8334	17	0.04	2214	0.62	1.19	20.5	2.7
FIU6	12897	19	0.18	10106	0.82	1.58	34.1	3.7
FIU7	4779	8	0.00	265480	0.33	0.53	13.0	2.2
FIU8	2571	5	0.03	321570	0.14	0.38	9.0	2.0

Fe*	Mg %	Mn*	Ni*	P +	Pb *	Sb *	Sc %	Sr ∞
10,000-30	0 .03-.84%	200-3000	10-1000	100-1000	2-200	.05-4	.5-45	18-3500
2693	21600	40	3.8	3315	36.4	0.74	0.65	662
1695	13634	21	1.3	2640	13.0	0.34	0.71	489
691	11251	15	1.5	2560	5.2	0.29	0.51	386
1883	12236	20	2.4	1555	6.2	0.73	0.86	497
11521	19622	31	17.0	2740	17.1	3.23	7.18	527
20100	30942	37	34.6	2690	22.4	13.73	14.03	371
10000	25185	157	1.7	31250	89.5	3.00	0.50	1305
50000	19878	171	3.2	19980	55.7	3.65	0.60	1201
50000	17704	160	2.8	26310	37.7	2.20	0.54	1247
40000	16630	141	2.2	34185	44.9	1.87	0.53	1374
12798	23462	129	1.0	37990	101.6	1.16	0.43	1811
9489	15514	392	11.0	785	13.5	1.74	2.36	707
6525	12467	312	6.9	495	8.1	3.32	1.63	600
6573	15952	259	9.3	472	7.6	1.18	2.86	660
12173	19880	210	12.0	515	8.8	3.09	4.42	679
4168	42270	90	4.5	143	4.9	0.59	0.09	1331
6372	7988	55	8.4	167	10.3	1.45	2.40	97
5910	7884	49	8.7	145	8.9	3.61	2.50	90
4678	7730	37	8.0	107	7.2	3.00	2.36	60
3384	6142	22	7.3	83	6.0	1.14	2.10	33
1893	3894	17	4.9	51	4.2	0.97	1.42	16
2596	5880	16	7.8	79	4.9	0.95	2.20	85
847	7275	6	1.3	108	2.7	0.53	0.66	1500
567	8390	6	2.6	127	2.1	0.67	0.53	1746

Ti *	V *	Y *	Zn *
1000-10,000	20-500	20-200	10-300
289	11.0	7.1	16.6
225	6.9	7.2	12.2
162	4.5	7.4	4.4
373	9.0	5.5	7.6
2263	49.9	16.9	32.4
4438	58.3	29.9	50.9
243	9.7	1.1	25.7
197	10.3	1.2	23.7
163	8.7	1.1	15.9
158	6.6	1.1	12.6
118	3.5	0.8	16.6
990	21.8	7.7	34.0
831	15.2	6.1	15.8
1085	17.6	8.9	14.6
1502	25.2	14.4	20.1
59	15.9	0.2	1.3
1077	14.9	5.4	19.7
1070	14.6	5.4	16.8
909	13.0	5.3	12.8
857	10.5	4.7	10.3
665	6.5	3.1	6.3
814	10.2	5.2	7.9
282	6.2	2.1	2.7
146	5.4	1.5	1.1

APPENDIX G TERMS AND DEFINITIONS

adsorption: the process of sorption of chemical elements from solutions by soil particles (Kabata-Pendias and Pendias, 1984).

co-precipitation: the simultaneous precipitation of a chemical element with other elements by any mechanism and at any rate. Co-precipitation includes adsorption, inclusion and solid solution formation (Sposito, 1989).

inclusion: occurrence together as morphologically distinct solids (Sposito, 1989).

fulvic acid: the mixture of organic substances remaining in solution upon acidification of a dilute alkali extract of soil (FitzPatrick, 1980).

humic acid: the dark organic substances precipitated upon acidification of a dilute alkali extract of soils (FitzPatrick, 1980).

sorption: 1) the ability to fix many species of trace ions; 2) all phenomena at the solid solution boundary (Kabata-Pendias and Pendias, 1984).

humic substances: the dark microbially transformed organic materials that persist in soil throughout profile development. The two most investigated humic substances are humic and fulvic acid. (Sposito, 1989)

translocation: the movement of material in solution, suspension, or by organisms from one horizon to another (FitzPatrick, 1980).

trace element: any chemical element whose mass concentration in a solid phase is less than or equal to 100mg kg⁻¹ (Sposito, 1989).