

THE INFLUENCE OF ELEVATION ON THE  
HUMIC-FULVIC ACID RATIO IN SOILS OF THE  
SANTA CATALINA MOUNTAINS, PIMA COUNTY, ARIZONA

by

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TO MY FATHER  
JOHN JOSEPH GALIOTO  
AND MY MOTHER  
OLIVIA RIVAS GALIOTO  
WITH LOVE

## PREFACE

In soil formation, the biotic factor pertains to the genetic constitution of an organism. Humans as biological soil formers, cannot be so simply described, as our outlook on nature is also guided by the views and economics of the society in which we grow up. Our activities have affected soils by agricultural and silvicultural erosion, the decline of humus and soil nitrogen during cultivation, the alkalization of arid lands and acidification by fertilization (Jenny, 1980).

Soil fertility is being depleted by shipping mineral-rich grains to cities and dumping sewage into the seas. The latest threat was triggered by the energy crisis and proposes plant biomass conversion to fuel. Unless a substantial portion of organic matter is returned to the soil, the soil will deteriorate and wind and water erosion will soar (Jenny, 1980).

In spite of creeping soil deterioration industrialized society has succeeded in greatly improving plant and animal productions. The outputs keep it well-fed. Nevertheless, injecting crop-stimulating fertilizers into

soil does not recreate soil mass lost or restore natural soil structures and soil life (Jenny, 1980).

My formal education during the 1960's and 1970's formed my life's goals and lead to the choosing of soil as their foundation, to be studied and worked with symbiotically. During those years my parents studied organic gardening and health foods. In our backyard, I witnessed the decomposition of tons of leaves and grass clippings and the production of overwhelming crops.

Today I garden with truckloads of shreaded palm fronds from the University of Arizona. I hand water daily and observe the breakdown of the organic matter, formation of fertile soil and growth of many plant species without the use of chemicals.

From my education and empirical observation over six years I conclude that humic acids are: Planets within solar systems; galaxies and a universe. Each a paradise of life with flowing water and fresh foods; teaming populations rebuilding and conserving their world, providing for others when they die of old age. A cosmic planet of earthworms and beetles, ants and even man; a peaceful, sleepy store of energy.

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## ABSTRACT

An elevational study of organic matter components was made of shallow soils of the Santa Catalina Mountains, Pima county, Arizona. At nineteen elevations (900 to 2700 m), total carbon, extractable organic carbon, humin carbon (tightly bound organic carbon), humic acid carbon, fulvic acid carbon, humic-fulvic acid ratios and E4/E6 ratios were determined. Parameters except the humic-fulvic acid ratios showed high correlations,  $R^2$  at least .78, with elevation. Of these only the E4/E6 ratio was negatively correlated with elevation. Uncorrelated humic-fulvic acid ratios indicate no proportional trend of the relative proportions of humic and fulvic acids. The E4/E6 ratio decrease with elevation agreed with all parameters. Humic acids are older, larger and contain higher concentrations of aromatics with increasing elevation. The humic-fulvic acid ratio, based on classical organic matter separation, does not produce a descriptively useful means for a range of climatically different soils. The E4/E6 ratio is more useful in evaluating soil genesis via composition.

## CHAPTER 1

### INTRODUCTION

Organic matter is the most biochemically active part of soil. The nature of the transformation of plant residues is focused in it. The types of bond between organic matter and minerals, its stability and mobility, can be judged from the fractional composition of humus. The content and composition of humus are important diagnostic features that reflect the relation between soils and the environment and, especially, its bioclimatic constituents (Kuz'min and Chernegova, 1981). Therefore, a study of the composition of organic matter in the soils of the Santa Catalina Mountains that form under specific conditions may shed some light on their ecological and genetic characteristics.

Humus, a product of organic matter, microbes and soil, has been studied since the earliest civilizations in Africa. The word we use comes from the Roman term for soil. Historically to the present, it was and is, thought to be food for plants and more recently highly regarded in the humus theory of plant nutrition. Today we also recognize its importance in soil genesis. Indeed, some have described soil as the result of the organic matter cycle found on/in a particular soil.

Study of the composition and properties of humus is an essential part of soil research. It is particularly important in the case of mountain soils, which are distinguished by what S. A. Zakharov (cited by Vladychenskiy and Borovkova, 1982) descriptively called "lithomorphism", meaning that their mineral part has many properties directly inherited from the parent material. The humus characterizes to a large degree the soil features produced by the soil-forming process itself (Vladychenskiy and Borovkova, 1982).

By examining the humus of the soil, scientists can gain knowledge about the genesis of the soil. The objective of this study is to determine the influence of elevation as it affects climate and vegetation on the amount and nature of the soil organic matter in the Santa Catalina Mountains, Pima County, Arizona. Figure 1 is a topographic map of the mountains showing the access road along which soil samples were obtained and (inset) location in Arizona.

To do this, several widely recognized soil parameters are sought. Particular emphasis is placed on the humic-fulvic acid ratio and related properties. They are the total carbon, extractable organic carbon, humin carbon, humic acid carbon, fulvic acid carbon (as percentage of the air dry weight of the soil), humic-fulvic acid ratio and E4/E6 ratio.

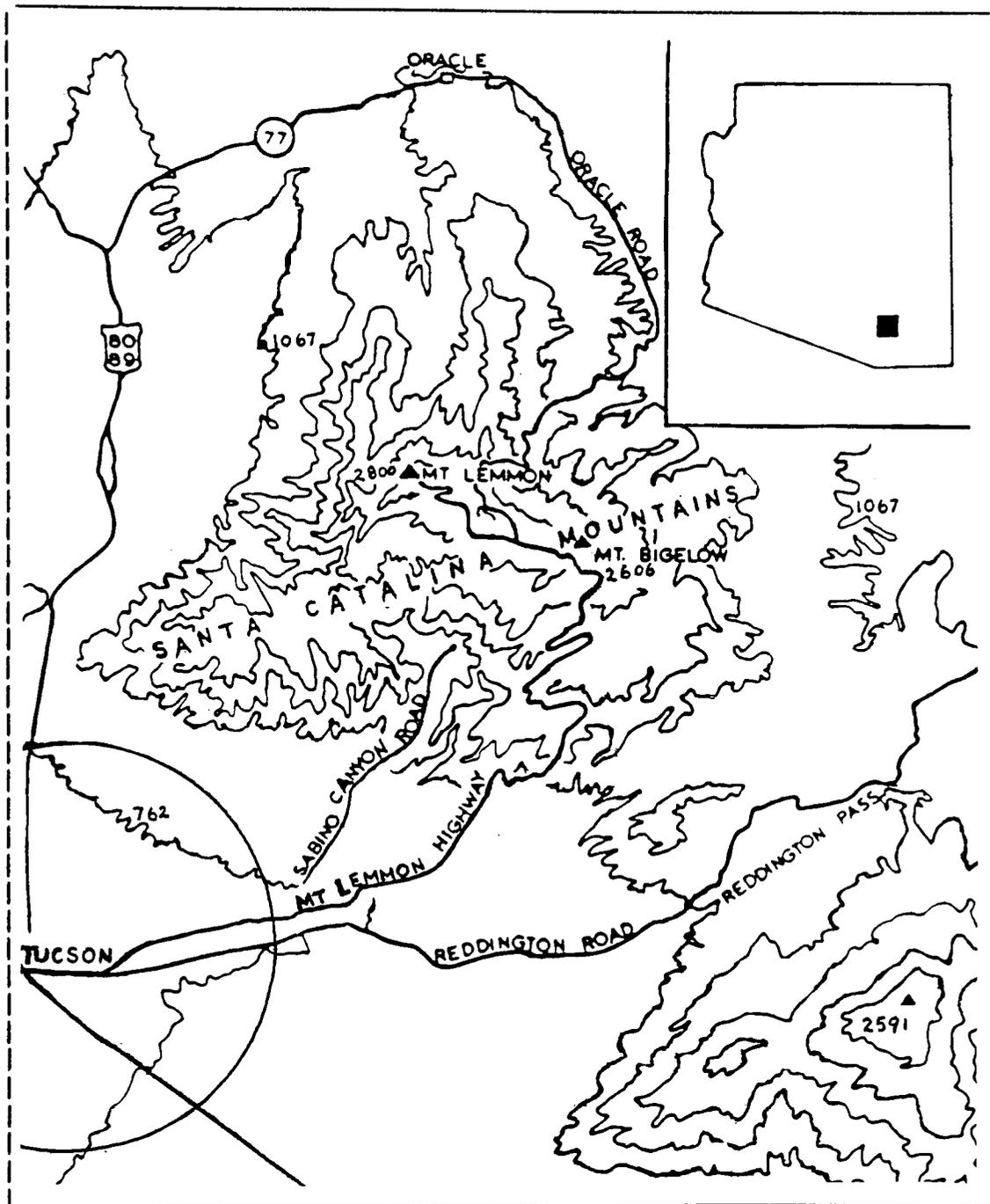


Figure 1. The Santa Catalina Mountains showing access road along which soil samples were obtained and (inset) location in Arizona (Whittaker, 1965)

Total carbon represents the total of the organic compounds in the soil exclusive of undecayed plant and animal tissues, their partial decomposition products and soil organisms. The extractable organic carbon is the amount of humic and fulvic acids lightly adsorbed onto clay micelles and/or occurs as discrete organic particles and was determined from an alkali extract (sodium pyrophosphate and sodium hydroxide) of the soil.

The humin carbon is the amount of organic carbon adsorbed onto clay micelles that cannot be removed by the extraction solution. Humin carbon was determined by subtracting the extractable organic carbon from the total organic carbon. The humic acid carbon was determined by an acid fractionation of another aliquot of organic carbon extract and was later subtracted from the first to measure the acid soluble fulvic acids. As a result, the humic-fulvic acid ratio could be made.

The E4/E6 ratio is a spectrophotometric ratio of two spectral absorbances, at 465 and 665 nm, of dilute humic or fulvic acids. It is a common means of describing the concentration of aromatic rings in these substances. This study examined only humic acids. For low ratios to occur certain processes must be present. This parameter gives important information expressing the nature of the soil phenomena in the Santa Catalina Mountains.

The soils collected range from those formed with humus existing under sparse bush litter in primarily the 0 horizons in the desert to those with a more developed humus profile, albeit shallow, that contain a more even distribution of organic matter.

Although this study is for a specific mountain range, it can provide a means of comparing soils of latitudes of more northern, or southern exposure from the same latitude on either side of the equator. Moreover the mountain provides vertical zonation whereby moisture is added and temperature is subtracted so that soil properties can be observed within a few kilometers which correspond to changes across thousands of kilometers of horizontal latitudinal zones.

Only a few researchers have looked at the humus of mountains with respect to elevation (Kuz'min and Chernegova, 1981; Luo and Li, 1979; Mikhaylova 1970; Mukatanov, 1978; Rubilin and Dzhumagulov, 1977; Dorvfeera and Kaurichev 1974; Assing, 1960). This study is unique in that the organic matter is the focus of attention.

The available location of the Santa Catalina Mountains at the edge of the Rocky Mountains in the Sonoran Desert with affiliations with Mexican mountains provides an interesting combination of geography, climate, flora and fauna.

At the beginning of the century the distribution of vegetation with elevation was studied over about 20 years. The findings are interesting because they show the complex relationships between climate, topography, organisms, parent material and time in the formation of soils and plant communities that grade into one another in remarkable ways depending on aspect and elevation (Shreve, 1915).

In an earlier study of the San Francisco Mountains, 3899 m, near Flagstaff, Merriam, (1890) divided the region into seven zones, each of which was characterized by the possession of forms of life not found in the others. Local topography and aspect resulted in a normal average difference in altitude of the same zone on the southwest and northwest sides of 275 m.

Mount Graham, 3005 m, has also been studied (Martin and Fletcher, 1943). The investigation of representative soil profiles showed that the successive soil types representing climatic variation between that of the cold, highly humid forest and that of the hot, dry desert are in conformity with the system of the great soil groups.

The Santa Catalina Mountains rise from about 850 to 2790 m and are located within a few kilometers of Tucson for easy access. The vegetation of the mountains, particularly with regard to its ecology and distribution has been extensively studied (Niering and Whittaker, 1963; Whittaker

and Niering, 1964, 1965; Whittaker et al, 1968). The vegetation pattern of the south slope is represented in figure 2 (Whittaker, 1968).

The higher mountain ranges exhibit a graduated sequence of vegetation from that of the desert valleys through a scrub of evergreen oaks to forests of pine, spruce and fir. The bodies of mesophilous vegetation which occupy this isolated mountain summit and the stages which connect them with the vegetation of the desert, present innumerable phenomena of the greatest interest to both physiological and floristic plant geography.

Whittaker et al (1968) emphasized soil formation in the Santa Catalina Mountains in which they observed that certain soil properties changed with elevation in response to changing moisture and temperature regimes. The soil properties stressed in their work included pH, organic matter, nitrogen, C/N ratio, CEC, the calcium, magnesium, potassium and sodium percentage of the CEC and the percent base saturation. However, the humus of these soils, its composition and properties, and their relation to plant associations under which these soils form have not been adequately investigated. In this thesis the soils are being reinvestigated by characterizing the soil organic matter in greater detail.

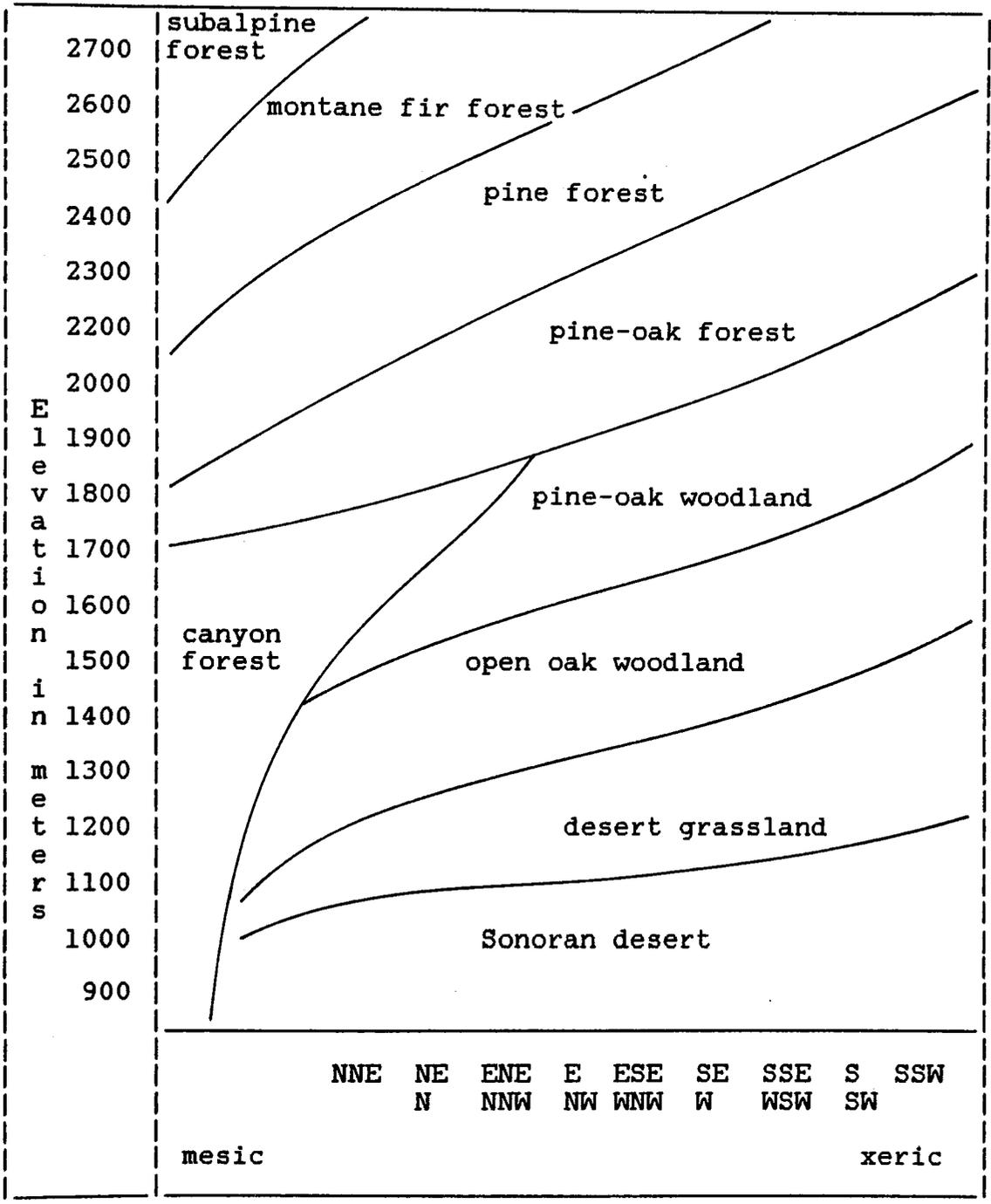


Figure 2. Vegetation of the Santa Catalina Mountains, (Whittaker, 1965)

## CHAPTER 2

### LITERATURE REVIEW

#### A Geobiocenotic System

Soil humus is one of the components of geobiocenotic systems, a terrestrial ecology of animals and plants. It performs important biospheric functions by directly transforming carbon, indirectly accumulating solar energy and preventing the geochemical removal of the most important nutrients into the ocean (Utenkova and Nichiporovich, 1979).

In recent years the humosphere has come to be regarded as an enormous geochemical accumulation of solar energy in the crust of the earth (Ponomareva, 1974). A large part of the radiant energy of the sun is accumulated in the humus as carbon-carbon bonds (Volobuyev, 1958). The amount of organic carbon in world soils is now estimated at  $30 \times 10^{14}$  kg, an amount which is an order of magnitude greater than any other surface carbon reservoir (Bohn, 1976).

Soil humus is the total diverse mixture of organic compounds in the soil exclusive of (1) undecayed plant and animal tissues, (2) their partial decomposition products and (3) soil organisms. These compounds are intimately

associated with the sesquioxide and clay fractions. Although the recognizable plant and microbial components constitute 15 to 25 % of all carbon forms present in the soil (Paul, 1969), the recognizable plant components were not determined in this study.

This mixture of compounds, a class of organic molecules, is high in molecular weight, dark in color, amorphous and resistant to decomposition by microbes. It is similar in elemental composition and functional groups even though isolated from different areas of the world (Paul, 1969; Schnitzer, 1977).

Soil humus can hold up to 20 times its weight in water to prevent drying and shrinking and may significantly improve the moisture-retaining properties of sandy soils. Soil humus cements soil particles into structural units and aggregates which permits the exchange of gases, stabilization of structure and an increase in permeability (Stevenson, 1982).

It is generally realized that the soil system is only a part of a much larger system that is composed of the upper part of the lithosphere, the lower part of the atmosphere and a considerable part of the biosphere. This larger system has been designated as a climate soil type by some and as a natural landscape by others (Jenny, 1941).

According to Jacks (1963) as quoted by Stevenson (1982), "the union of mineral and organic matter to form the organo-mineral complex is a synthesis as vital to the continuance of life as, and less understood than, photosynthesis."

### History

Experience in science and practice over many centuries has shown the great importance of humus in soil formation and in the production of optimum conditions in the soil for the supply of water, air, carbon, mineral nutrients and also biotic substances to plants (Kononova, 1961). Humic acids, in soils rich in bases, combine immediately with the latter and enhance fertility.

Humus has been studied for a very long time due to its wide importance in soil forming processes and soil fertility and partly by its complexity. This last aspect has resulted in the need for different approaches to the problem (Kononova, 1961).

Research on humus was like the familiar soil fertility barrel which could not hold its full capacity due to a missing amount of some special element. Prior to the development of soil microbiology, studies of the origin of humus were scientifically misplaced (Kononova, 1961). Early studies of humus applied the known concepts of chemistry in

which humus was thought of as oxidation products of certain plant materials. This idea led to other errors.

### Second Half of the 18th Century

A history of humus gives an indication of the correct approach to its study. Initially humus was thought to originate from the rotting of animals and plants and was plant or animal food (Kononova, 1961). In 1786, humus was extracted with alkali (Kononova, 1961). In 1809, it was concluded that soil fertility was largely dependent on the accumulation of humus in the soil, the sole and direct source of plant nutrients (Kononova, 1961). Then in 1840-41, the theory of the mineral nutrition of plants was founded (Kononova, 1961).

Due to lack of knowledge about the intimate role of soil microbes in soil production via humus manufacture, humus formation was thought of as simple chemistry involving discrete chemical compounds derived from plant and animal tissues by spontaneous oxidation reactions (Kononova, 1961).

### First half of the 19th Century

The faulty methods and misunderstood origin gave rise to erroneous ideas on the mechanism of the process. Sprengle in the 1820's and 1830's gave a detailed analysis of humic acid as well as describing the important properties of it, its salts, and their solubility, especially in hot

water (Kononova, 1961). He combined solubility with the humus theory of plant nutrition to connect high fertility to the presence of humic acids in soluble form. He also established the acid nature of humic acids (Kononova, 1961).

Berzelius (1806) found lighter colored humic substances and named them apocrenic and crenic acids. After several salt studies he established their great mobility compared to the humic acids previously known. He believed in the humus nutrition theory, advised applying organic manures to soils and wrote the Textbook of Chemistry (Kononova, 1961).

Artificial humic substances were produced in the early 19th century and came to be regarded as identical with natural humic acids. Sucrose was thought to become humic acid through dehydration (Kononova, 1961).

A student of Berzelius, Mulder, investigated the chemical properties of humic substances as individual compounds. He tried to free them from nitrogen which he and many others believed was a contaminant (Kononova, 1961). Another contemporary, German, who also believed that humus was a direct source of plant nutrients, believed that nitrogen was a constituent of humus (Kononova, 1961). This correct idea led to the microbial origin of humus. German also believed in discrete chemical compounds and the numbers

of isolated and named compounds gradually grew (Kononova, 1961).

### Second Half of the 19th Century

The presense of an increasing number of humic substances whose independent existence was not confirmed by corresponding investigations, and the resulting confusion in terminology, produced doubts as to the existence in the soil of humic substance as a separate group of organic compounds of a specific nature (Kononova, 1961).

From the investigations of Tarkhov (1881) and Van Bemmelen (1888), it was plain that even if humic acid formed mineral salts this reaction was more complex than would be expected from stoichiometric laws and that it was marked by the formation of absorption compounds (Kononova, 1961). Van Bemmelen concluded that these substances were in fact amorphous and colloidal.

Baumann and Gully (1910) concluded that the acid properties of humus were not due to the presence of compounds with functional groups but to its colloidal properties and humus became thought of as absorption compounds (Kononova, 1961).

Ideas on the nature of humus from chemical and physico-chemical studies became increasingly complex and continued to obscure the role of humus. Opposition to the idea that humus was a direct source of plant nutrients came

from Liebig in 1840 (Kononova, 1961). He felt that humus was primarily a source of carbon dioxide, which was formed during its decomposition, and which promoted the solubility of inorganic soil compounds essential for plant nutrition (Kononova, 1961).

Into this atmosphere of contradictory and obscure views came an influx of new ideas on the nature and origin of humic substances and their role in the soil. The brilliant investigations of Pasteur established the science of the biochemistry of microbes. Following his discoveries, Von Post (1862) and Darwin (1882) as well as several others established the important fact that humus formation is not a chemical or physical process but a biological one, resulting from the soil ecology (Kononova, 1961).

The emergence of this new biological trend in soil-humus study was all the more important because during this period Dokuchaev (1883) and Kostychev (1886) laid the foundations of soil science in which soil was recognized as a natural body formed through the combined action of natural factors, particularly biological factors of soil formation such as the vegetative cover and the activity of living organisms (Kononova, 1961).

The new trend in soil-humus study, which was the result of the development of two disciplines, microbiology and pedology, occupied a prominent place towards the end of

the last century. With the development of soil science the study of humus became wider, more profound and more definite. With the development of microbiology studies on the complex problems of humus formation were put on a correct basis (Kononova, 1961).

### The First Two Decades of the 20th Century

The main divergences in views on the nature of soil humus arose during this period. Some felt humic substances were a group of compounds of specific nature and others felt they were a complex mixture of organic substances resulting from biological decomposition. Schreiner and Shorey et al, from 1908 to 1930 very carefully extracted over 40 chemically different compounds belonging to various groups of organic chemistry such as hydrocarbons, sterols, fats, organic acids, aldehydes, carbohydrates, organic phosphorus compounds and nitrogen-containing substances (Kononova, 1961).

As a result of the detailed work of many others, Oden (1912, 1914, 1919), Maillard (1912 to 1917), Beijerinck (1900), Bertrand (1898), Trusov (1914 to 1916), Shmuk (1914, 1924, 1930), Williams (1897, 1902, 1914, 1939), the existence of humic substances in the soil as natural products was convincingly demonstrated (cited by Kononova, 1961).

It was established that various plant materials can serve as sources of humic substances as well as products of bacterial synthesis. Humic acids were shown to result from two stages, decomposition and synthesis, both involving microbial enzymes. Further, the view that they were the products of a condensation of aromatic compounds with nitrogen containing organic compounds was expressed (Kononova, 1961).

#### Further Investigations in the 20th Century

During this period, investigations on the chemistry of the humus of coal, brown coal and peat, largely developed in Germany, had a fundamental influence on the study of soil humus. During the 1920's and 1930's Waksman's view that lignin was the origin of humus became popular. Finally he came under criticism, especially by Tyurin in 1937 (Kononova, 1961).

Extensive studies were made by Jenny and his co-workers on the effect of climate on organic matter and N levels in soil. For soils along a north to south transect of the semi-humid region of the central United States, the nitrogen content of the soil decreased 2 to 3 times for each rise of  $10^{\circ}$  C in mean annual temperature (Stevenson, 1982).

Enders (1943) presented a unique concept concerning the synthesis of genuine stable humus. He concluded that the best soil conditions for the synthesis and preservation

of humic substances having high nitrogen contents were frequent and abrupt changes in the environment (eg. humidity and temperature) and consequently, soils formed in harsh continental climates should have high organic matter and nitrogen contents (Stevenson, 1982).

Harmsen, (1951) used this same theory to explain the greater synthesis of humic substances in grassland soils, as compared to arable land, claiming that in the former the combination of organic substrates in the surface soils and frequent and sharp fluctuations in temperature, moisture and irradiation leads to greater synthesis of humic substances (Stevenson, 1982).

After WWII, soil humus continued to attract much attention. Today, the developed nations use spectroscopic techniques which are applicable in characterizing these materials. These include nuclear magnetic resonance, electron spin resonance, X-ray analysis, ultraviolet, visible and infra-red light absorption.

Color, which is an indication of light absorption over the visible spectrum, is used in soil classification and can be applied to determine the qualitative and quantitative difference in the soil humic constituents. Relative light absorption at 465 and 665 nm and the Munsell notation values are proving particularly useful (Paul, 1969).

The origin and mechanism of formation using biochemical studies have helped to show that the formation of humic substances is due to complex transformations of the original organic residues. Enzymatic activity of both macro and micro soil organisms brings about the transformations (Kononova, 1961).

Agricultural studies have revealed the important fact the soil organic matter participates in the physiological processes of the plant and also in the biochemistry of its nutrition (Kononova, 1961).

#### Nomenclature

Besides humus formation, which is an inseparable part of soil formation, other processes that transform plant residues, such as peat formation, sapropel formation and organic compost formation, develop in the biosphere. Humification is also typical of each of these processes not only for transforming plant residues but for the formation of different materials such as peat, sapropel, etc.

The term humus should be applied only to the part of the organic matter which forms and accumulates directly in the soil. It participates in the formation of the humus accumulative, humus-eluvial, and humus-illuvial horizons. Humification is a general term where by humic compounds are

formed. Humus formation refers to the accumulation of humic compounds in the soil.

Humic substances are a special class of organic, multifunctional nitrogen-containing acids characterized by high but variable molecular weights, and heterogeneous in chemical composition, which may be divided into two groups: humic acids and fulvic acids (Aleksandrova, 1975). Humic substances which are not extracted from decalcified soil during treatment with alkali solutions are placed in the humin group. They are tightly associated with clay micelles. According to Sprengel (Kononova, 1961), they occupy a position intermediate between humic acid and coal.

### Humus Formation

#### Continuity of Movement

Humus formation is a system of interrelated biological phenomena governed by the law of continuity of movement. Humus is the result of an equilibrium between reciprocally related processes: life goes to death; symbiosis goes to antibiosis; the synthesis of organic substances in the living plant goes to their decomposition by microbes, which after death, goes to the synthesis of humic substances (Kononova, 1961).

Any study relating to soil genesis should be based on the concept of the unity of the soil-forming processes

and of the leading role of organisms in this process. Higher plants are especially of significance, since they concentrate organogenic elements and are the source of the most active soil constituent, organic matter. Higher plants remove from the soil, nutrients in mineral form and return them in the newly synthesized form of organic carbon compounds. This determines the considerable role of organic carbon in the formation of soil, considered as a unique organomineral natural body (Ponomareva, 1969).

Plants do not simply grow in an environment to which they must adapt or die, but they in fact do change their environment, frequently in a radical fashion (Kovda and Yakushevskaya, 1971).

#### Biogeochemical Conclusion

Many aspects of soil formation consists of different types of transformations and interactions of organic carbon compounds in the upper lithosphere, with the active participation of microbes and atmospheric factors (Ponomareva, 1969). The important energetic role of organic carbon in the formation of soil types is still not fully understood, nor is it sufficiently well defined (Ponomareva, 1969).

## Role of Carbon

Transformation of the organic carbon of plants on the surface of the Earth produces acids ranging from simple carbonic acid to complex humus acids. The lithosphere on the other hand, consists chiefly of bases except for silicic acid. This general, acid type of transformation of organic residues is probably one of the major reasons why plants are able to make use of nutrients originally bound in crystal lattices of minerals, and still bound in the soil to a certain extent (Ponomareva, 1969).

As soil formation proceeds, the products formed from the transformation of organic carbon from plants provide a means for obtaining and mobilizing, as well as for accumulating reserves of mineral nutrients and nitrogen in a more accessible form (Ponomareva, 1969). One important aspect of soil formation, regardless of local conditions, is a process of interaction between acids of organic origin and bases of the lithosphere. The most important product of this interaction are the humic acids (Ponomareva, 1969).

The processes of transformation of organic plant-residues, disregarding preservation, follow three main courses: (1) processes of humification i.e., the accumulation in soils of complex polymolecular organic substances of the type of humic acids, (2) processes of formation of simpler, water-soluble organic products of the

type of fulvic acids and (3) processes of complete mineralization down to  $\text{CO}_2$  (Ponomareva, 1969). A correct understanding of the role played by organic carbon in soil forming processes must take into account not only processes of humus accumulation, but also the entire cycle of the processes of transformation of organic carbon in soils. This cycle includes humification, mineralization and eluviation, which do not merely accompany each other but are functionally interrelated (Ponomareva, 1969).

In desert soils, the mere fraction of a percent or less humus cannot account for the properties of the soil even under a detailed examination. This does not mean that the soil develops almost without the intervention of carbon, rather that mineral, not humic, forms of carbon (carbonates and bicarbonates) often play an important role in the formation of the profile of such soils.

#### Voluminous Literature

Tate and Theng, (1980) note that the chemistry of soil organic matter, and more particularly, of humic substances has been the topic of a voluminous literature which has periodically been reviewed (e.g. Dubach and Mehta, 1963; Felbeck, 1965; Kononova, 1966; Stevenson and Butler, 1969; Paul, 1970; Schnitzer and Khan, 1972; Flaig et al, 1975; Hayes and Swift, 1978; Stevenson, 1982; Hayes 1984). Similarly a great deal of information has accumulated on the

interactions of humic substances with inorganic soil constituents as attested by the reviews by Greenland (1971), Schnitzer and Kodama (1977), Schnitzer (1978a) and Theng (1979) according to Tate and Theng (1980). It is not desirable to give a comprehensive account of these topics. The nature of soil organic matter is not the main thrust of this thesis. What follows is a brief discussion presenting some of the highlights of the subject.

### Chemical Synthesis

Most workers favor a mechanism based on condensation of phenolic poly compounds and quinones derived exclusively from microbial transformation of plant litter input. The number of precursor molecules is large and the number of combinations in which they react is astronomical. The possibility that a given suite of compounds will combine in exactly the same way to form two identical molecules is so remote that it's probably safe to say that few, if any, humic molecules will be precisely the same.

Polyphenols, derived from lignin or synthesized by microbes, are enzymatically converted to quinones, which undergo self condensation or combine with amino compounds to form nitrogen containing polymers. Humic substance reactivity is largely caused by their high content of oxygen containing functional groups: carboxyl, phenolic, and/or enolic, hydroxy, alcoholic, ketonic of quinones and hydroxy-

quinones, as well as alpha and beta unsaturated ketones (Pauli, 1967).

### Age

The term mean residence time, MRT, has been used to express the results of carbon 14 measurements for the average age of modern humus. Typical MRTs obtained for carbon in the surface layer of soil are recorded. Whereas considerable variations in mean ages have been reported, usually 250 to 1900 years, the findings attest to the high resistance of humus to microbial attack.

The dynamics of the various fractions of soil organic matter determine their rate of cyclization in nature. Normal tracers can be utilized to follow the materials with a high turnover rate, and carbon dating is applicable to the large concentration of resistant fractions. Carbon dates ranging from modern to 2400 years B.P. have been measured in the surface soils of western Canada (Paul, 1969).

Only a small fraction, which turns over relatively rapidly, can be considered to be the "active" fraction (Paul, 1969). In general the humus of Mollisols appears to be more stable than that for other mineral soils (Kononova, 1961). As one might expect, the MRT of organic matter increases with depth (Stevenson, 1982).

## Structure

### Heteropolycondensates

The humic acid molecule is a product of the condensation of aromatic compounds with products of protein decomposition, with the possible participation of substances of a carbohydrate nature. Since the formation is due to the condensation of various substances they have been named heteropolycondensates. The primary condensates formed from "structural units," or micelles, are monomers which combine to form polymers. Figure 3 shows a typical structure of a fulvic acid molecule (Schnitzer, 1977). The result is three dimensionally interlinked, amorphous, colloidal systems of predominantly aromatic nature with phenolic, quinoid and ketonic carbonyl character (Pauli, 1967).

The linkages between structural units, aromatic rings of the di or trihydroxyphenol type, and monomers are established by oxygen bridges and also by way of  $-\text{NH}_2-$ ,  $=\text{N}-$ ,  $-\text{S}-$ ,  $-\text{O}-$ ,  $-\text{CH}_2-$ ,  $\text{H}_2\text{O}$  and other groups. They contain both free OH groups and the double linkages of quinones.

The presence of these bridges gives the humic-acid molecule a loose structure and no single structural formula will suffice (Pauli, 1967). Fractions must be regarded as being made up of a series of molecules of different sizes, few having precisely the same structural configuration or array of reactive groups.

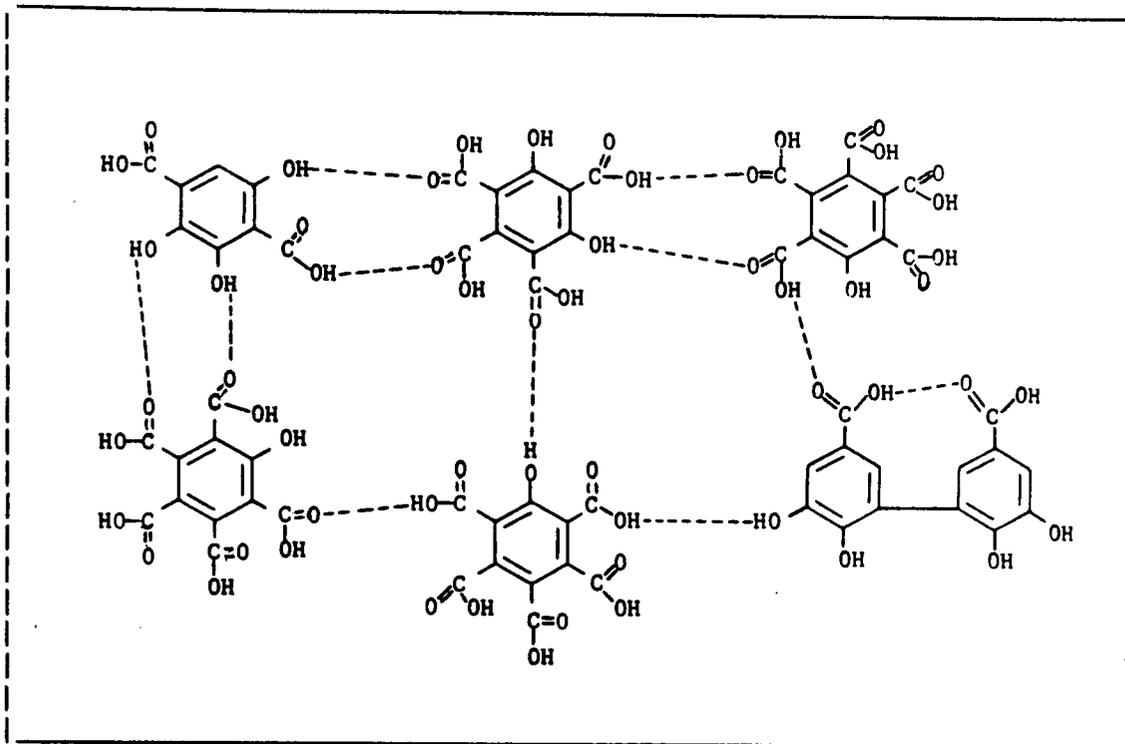


Figure 3. Typical structure of the fulvic acid molecule (Schnitzer, 1977)

## pH Effects

pH and the presence of neutral salts influence the size and shape of these long coiled or two or three dimensionally cross linked molecules. Under neutral or slightly alkaline conditions they are fully expanded due to mutual repulsion of charged acidic groups. At low pH and high salt concentration contraction occurs because of charge reduction and molecular aggregation (Stevenson, 1982).

## Molecular Weights and Size

Zolotarevskaya (1951), Flaig and Beutelspacher (1952, 1954), Beutelspacher (1952) and Kukharensko (1953 b, 1955) cited by Kononova (1961) conclude that humic acids consist of tiny spherical particles capable of uniting into chains and of forming racemose aggregates. Under certain conditions these particles may undergo coacervation. The aggregation of humic acids in an acid medium takes place through hydrogen bonding (Flaig, 1958). Humic compounds have diameters of 60 to 100 Angstroms, CEC of 3 to 8 meq/g of soil and specific surface areas of  $5.7 \times 10^4 \text{ m}^2/\text{g}$  (Pauli, 1967).

The question of the size and weight of humic acid molecules is not altogether clear. Some authors put the value at 1000 to 1200. However, Flaig and Beutelspacher using an ultracentrifuge, reported values from 30,000 to 50,000 (Flaig, 1958).

### Structural Significance

The shape of the molecule of organic substances is of great importance in the formation of soil structure: substances with molecules of linear form participate in this process more actively than humic acids of spherical form (Kononova, 1961).

As humic acids increase in maturity their aromatic nature becomes increasingly clear. Important properties of humic acids like the rate of their exchange reactions, the mobility of nitrogen and also their hydrophilic properties depend on the ratio between aromatic and aliphatic structures in the molecules.

The pronounced hydrophilic nature of humic acids from Spodosols (podzolic soils) is explained by the predominance of aliphatic structures possessing hydrophilic properties. Humic acids from Mollisols, which have clearly expressed aromatic ring structures possessing hydrophobic properties instead, are less hydrophilic. This explains the important fact that, compared with humic acids from Mollisols, humic acids from Spodosols possess a high capacity for peptization, are more stable towards electrolysis and are extremely mobile (Kononova, 1961).

### Effect on Soil Structure

A study of the structure of humic acid molecules is extremely important in understanding their role in soil

processes. The fact that humic-acid molecules are not compact but have a loose spongy structure with a large number of internal spaces is of great importance in soil processes. These characteristics of the structure determine the water-holding capacity and the sorptive properties of humic acids to a considerable degree.

Important properties of humic acids such as the rate of exchange reactions, the mobility of nitrogen and hydrophilic properties depend on the ratio between aromatic and aliphatic structures in the molecules. In regard to calcium within the soil environment, the behavior of fulvic acids is just the opposite of the behavior of humic acids. The latter can accumulate and become stable under natural conditions because of the presence of calcium. Fulvic acids are not fixed by calcium, and their accumulation depends mainly upon aluminium and to a lesser degree upon iron (Ponomareva, 1969).

Humus of forest soils is characterized by a high content of fulvic acids while that of peat and grasslands is high in humic acid. Humic acids of different soils cannot be regarded as entirely equal in their effects on soil properties and on soil forming processes.

## Properties

### Color

Color production is due to chromophores such as nitro, axo, azoxy, azines, quinone-like structures, ketonic, cyanide, alkenes and sulfides (Stevenson, 1982).

The typical dark color of many soils, caused by organic matter, modifies the soil temperature. Although black soils having high humus content absorb more heat than light-colored soils, they also frequently hold more water. The water requires relative larger amounts of heat than the soil minerals to raise its temperature and water also requires considerable heat to evaporate it. The net result is that many dark soils may be cooler than adjacent lighter colored soils (Donahue, Miller and Shickluna, 1983).

### Humic Acids vs Fulvic Acids

Humic substances have been separated into fulvic and humic acids representing extremes of a heteropolycondensate molecule of infinite variation. The operational separation, via acidification after alkali extraction, is only empirical as no division naturally occurs. Beginning at fulvic acid, previously named crenic acid, the range has been chemically separated into the following named compounds over the years: fulvic acid, apocrenic acid, brown humic and gray humic acid. They follow the color sequence of light yellow to

yellow brown to dark brown to gray-black (Stevenson, 1982). Table 1 gives the classification and chemical properties of humic substances according to Stevenson (1982) citing (Stevenson and Butler, 1969). Table 2 presents the analysis of 'ideal' humic and fulvic acids. With limited success, the carbon content of these two fractions can be used to differentiate between soil groups (Tate and Theng, 1980).

The humic fraction of the soil consists of a complex system of molecules which have a wide range of molecular weights. The acids, beginning with fulvic acid, increase in degree of polymerization and molecular weight, from 2000 to 300,000. The average range for humic acids is from 50,000 to 100,000 with a few at 250,000. Typical fulvic acids range from 500 to 2000 (Stevenson, 1982).

Across the spectrum, beginning with fulvic acids, carbon content rises from 40 % to 59 % while oxygen on the other hand decreases from 50 % to 33 %, tables 3 and 4, and there is a decrease in exchange acidity from 14.2 to 5.6 meq/g, tables 5 and 6 (Schnitzer, 1977). While the oxygen in fulvic acids can be accounted for largely in known functional groups, especially, COOH, OH, and C=O, a high proportion of the oxygen in humic acids seems to occur as a structural component of the nucleus as ether or ester linkages.

Table 1. Classification and chemical properties of humic substances (Stevenson, 1982)

fulvic		humic	
crenic	apocrenic	brown humic	gray humic
light yellow	yellow-brown	dark brown	gray-black
----- increase in degree of polymerization ----->			
2,000	----- increase in molecular weight ----->		300,000
45 %	----- increase in carbon content ----->		62 %
48 %	----- decrease in oxygen content ----->		30 %
14	----- decrease in exchange acidity ----->		5

Table 2. Analysis of 'ideal' humic and fulvic acids, the means of all data (Schnitzer, 1977)

Element	humic	fulvic
	percent	
C	56.2	45.7
H	4.7	5.4
N	3.2	2.1
S	0.8	1.9
O	35.5	44.8
Functional groups		
	meq/g	
total acidity	6.7	10.3
CO <sub>2</sub> H	3.6	8.2
phenolic OH	3.9	3.0
alcoholic OH	2.6	6.1
quinonoid C=O	2.9	2.7
ketonic C=O		
OCH <sub>3</sub>	0.6	0.8
E4/E6	4.8	9.6

Table 3. Elementary analysis of humic acids extracted from soils from widely differing climatic zones (Schnitzer, 1977)

element	climatic zone				
	arctic	cool/temperate		subtropical	tropical
		acid	neutral		
percent					
C	56.2	53.8-58.7	55.7-56.7	53.6-55.0	54.4-54.9
H	6.2	3.2-5.8	4.4-5.5	4.4-5.0	4.8-5.6
N	4.3	0.8-2.4	4.5-5.0	3.3-4.6	4.1-5.5
S	0.5	0.1-0.5	0.6-0.9	0.8-1.5	0.6-0.8
O	32.8	35.4-38.3	32.7-34.7	34.8-36.3	34.1-35.2

Table 4. Elementary analysis of fulvic acids extracted from soils from widely differing climatic zones (Schnitzer, 1977)

element	climatic zone				
	arctic	cool/temperate		subtropical	tropical
		acid	neutral		
percent					
C	47.7	47.6-49.9	40.7-42.5	42.2-44.3	42.8-50.6
H	5.4	4.1-4.7	5.9-6.3	5.9-7.0	3.8-5.3
N	1.1	0.9-1.3	2.3-2.8	3.1-3.2	2.0-3.3
S	1.6	0.1-0.5	0.8-1.7	2.5	1.3-3.6
O	44.2	43.6-47.0	47.1-49.8	43.1-46.2	39.7-47.8

Table 5. Functional group analysis and E4/E6 ratios of humic acids extracted from soils from widely differing climatic zones (Schnitzer, 1977)

functional group	climatic zone				
	arctic	cool/temperate ----- acid      neutral		subtropical	tropical
	meq/g				
total acidity	5.6	5.7-8.9	6.2-6.6	6.3-7.7	6.2-7.5
CO <sub>2</sub> H	3.2	1.5-5.7	3.9-4.5	4.2-5.2	3.8-4.5
phenolic OH	2.4	3.2-5.7	2.1-2.5	2.1-2.5	2.2-3.0
alcoholic OH	4.9	2.7-3.5	2.4-3.2	2.9	0.2-1.6
quinonoid C=O	2.3	0.1-1.8	4.5-5.6	0.8-1.5	1.4-2.6
ketonic C=O	1.7				0.3-1.4
OCH <sub>3</sub>	0.4	0.4	0.3	0.3-0.5	0.6-0.8
E4/E6	5.3	3.8-5.0	4.0-4.3	3.9-5.1	5.0-5.8

Table 6. Functional group analysis and E4/E6 ratios of fulvic acids extracted from widely differing climatic zones (Schnitzer, 1977)

functional group	climatic zone				
	arctic	cool/temperate		subtropical	tropical
		acid	neutral		
meq/g					
total acidity	11.0	8.9-14.2	ND	6.4-12.3	8.2-10.3
CO <sub>2</sub> H	8.8	6.1-8.5	ND	5.2-9.6	7.2-11.2
phenolic OH	2.2	2.8-5.7	ND	1.2-2.7	0.3-2.5
alcoholic OH	3.8	3.4-4.6	ND	6.9-9.5	2.6-5.2
quinonoid C=O	2.0	1.7-3.1	ND	1.2-2.6	0.3-1.5
ketonic C=O	2.0				1.6-2.7
OCH <sub>3</sub>	0.6	0.3-0.4	ND	0.8-0.9	0.9-1.2
E4/E6	11.5	9.0	ND	8.4-9.5	7.6-11.2

Table 7. Composition and some characteristics of humus in different soil groups of the U. S. S. R., Kononova (1966, 1975) (Tate and Theng, 1980)

soil group	humus content <sup>a</sup>	carbon content <sup>b</sup>		humic-fulvic acid ratio	E4/E6 <sup>c</sup>
		humic	fulvic		
Podzolic <sup>d</sup>	2.5-3.0	12-15	25-28	0.6	~5
Grey Forest	4.0-6.0	25-30	25-27	1.0	~3.5
Chernozems	5.5-10	28-40	16-20	1.5-2.5	3.0-3.5
Chestnut	2.0-4.0	29-35	20-25	1.2-1.7	3.8-4.0
Serozems	0.8-2.0	17-20	24-25	0.7-1.0	4.0-4.5
Krasnozems	4.0-6.0	15-20	22-28	0.6-0.8	~5

<sup>a</sup> average value, expressed as percent of whole soil

<sup>b</sup> percent of total soil carbon

<sup>c</sup> for humic acid

<sup>d</sup> These are the Russian great groups used by Kononova and are roughly equivalent to Spodosols, Alfisols, Mollisols, Mollisols, Aridisols and Ultisols, respectively.

The total acidities per gram of soil of fulvic acids are greater at 6.4 to 14 meq/g than the 5.6 to 7.7 meq/g of humic acids. The content of acidic oxygen-containing functional groups in fulvic acids appears to be substantially higher than for any other naturally occurring organic polymer (Stevenson, 1982).

The capacity of binding strong bases at pH 7 amounts on average to about 5 meq/g ash-free humus. Fulvic acids are strong organic acids (Stevenson, 1982). Fulvic acids are not merely more highly dispersed but also more dissociated than humic acids.

#### Optical Density, the E4/E6 Ratio

The E4/E6 ratio refers to the ratio of the spectrophometric absorbances of a dilute solution of humic acids at 465 and 665 nm, respectively (Kononova, 1961). Tables 5, 6 and 7 list some E4/E6 ratios of humic and fulvic acids extracted from soils from widely differing climatic zones. Humic acids predominate when the ratio is less than 5. When fulvic acids predominate the ratio is from 6 to 8.5. The ratio decreases with increasing molecular weight and concentration of aromatic rings.

The ratio is believed to serve as an index of aromatic constituents and of the degree of humification (Kononova, 1961). A high ratio reflects a low concentration of aromatic rings and infers the presence of relatively more

aliphatic structures. It is governed by (1) particle size and weight, (2) total acidity, (COOH content, C, O), and is inversely related to (3), mean residence time (MRT) (Pauli, 1967). Most mobile humic substances are optically dense and they arrive at the middle part of the Mollic epipedon (Kononova, 1961).

### Fertility

The soil, composed of intimately bonded organo-minerals, has fertility, a dynamic property for producing crops. The evolution of soil fertility depends on the organic residues reaching the soil as plant and animal remains. After microbial transformation of the residues, microbial polysaccharides stabilize the soil structure. This keeps the soil in an open, crumbly condition, which is essential for an optimum air-water relationship, influencing both the water retention and the heat exchange of the soil (Pauli, 1967).

Plants and edaphon, the soil flora and fauna, make their habitat into a fertile soil by emitting energy into it. The final result of the compression and distortion of the soil mass by countless organisms is a soil structure in which a selective pressure constantly changes the flora with time. Therefore soil fertility is a manifestation and

measure of the success of the population in reaching a high standard of living (Pauli, 1967).

All factors influencing the respiration of the plant will therefore play a role in nutrient uptake. Besides light, temperature, and oxygen supply, molecules of humic compounds, with their quinone like structure, are of great importance in these processes. Since the end-point in plant respiration is the combination of the activated hydrogen with the oxygen of the air, catalysis through dehydrogenases and oxidases, it is probable that humic substances act as additional oxidation-reduction systems. This becomes even more evident when we regard the humic compounds of the soil as having a single supra dimensional quinhydron molecule representing a 50 % oxidized and a 50 % reduced system (Pauli, 1967).

The gradual release of the nutrients combined in humus upon decomposition is a major factor in maintaining soil fertility. At the same time, humus has a favorable effect on the physical, physiochemical and biochemical characteristics of the soil by creating a more stable medium for the plants (Tyurin and Kononova, 1962). Its nutritional function is thus complimented by both its biological function which profoundly affects the activities of microflora and microfauna and its physical function which

promotes good soil structure, thereby improving tilth, aeration and retention of moisture (Stevenson, 1982).

The availability of humic acids to microbes and subsequently to plants, depends on the form of nitrogen linkage in the humic acids. This important fact should be taken into consideration when estimating the nitrogen reserves of soils (Kononova, 1961).

#### Cation Exchange Capacity (CEC)

As a consequence of their high negative charge density, humus contributes substantially to the CEC of many soils, depending on organic matter content, kind and amount of clay, pH, and colloids exhibiting buffering over a wide pH range. The charge characteristics of humic substances are at the source of the reactivity of humic substances toward the various inorganic soil constituents. In aqueous solution above pH 3, humic and fulvic acids exist and behave as negatively charged polyelectrolytes due to the dissociation of carboxyl ( $3 < \text{pH} < 9$ ) and phenolic hydroxyl ( $\text{pH} > 9$ ) groups in the molecule, Posner (1964), (cited by Tate and Theng, 1980). Below pH 3, the dissociation of these functional groups is suppressed and the molecule behaves more as an uncharged polymer than a poly anion. The dissociation functional groups in the molecule occur in such numbers as to give an average exchange capacity of 3 meq/g at pH 7 (Tate and Theng, 1980).

Fulvic acids and individual biochemical compounds are involved in the movement of micro-nutrients to plant roots with the fulvic acids being the most efficient in complexing metals. The growth promoting effects of humic substances may partly be caused by increased uptake of bound nutrients by plants (Kononova, 1961). The stability and water solubility of the resultant complexes depend on the nature of the metal ion, the size of the humic polymer, the metal/polymer ratio, pH and ionic strength. Thus, for fulvic acid at pH 3 and ionic strength 0.1, Schnitzer and Hansen (1970) (cited by Tate and Theng, 1980) found the following order of decreasing stability,  $Fe^{3+} > Al^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Pb^{2+} = Ca^{2+} > Mn^{2+} > Mg^{2+}$ . The position of iron and aluminum in the sequence is noteworthy since organic matter complexes of these cations play a part in the genesis of Spodosols (Tate and Theng, 1980).

### Nitrogen

Soil humic acids contain nitrogen, the amount being approximately 3.5 to 5 %. Investigators of the last century thought that humic acids were of carbohydrate origin and regarded the nitrogen in them as an accidental admixture. This view was later shared by investigators of the chemistry of humic substances of peat and coal for it accorded with

their theory on the lignin origin of humic acids (Kononova, 1961).

Organic residues entering the soil are decomposed by microbes, the decomposition of the original organic compounds being accompanied by the new formation or resynthesis, of microbial plasma, which consists of 80 to 90 % proteinaceous substances. Thus the nitrogen present in humic acids is of microbial origin and present in a much modified form.

During the hydrolysis of humic acids by means of 6 N HCl a large part of the nitrogen passes into solution, part of the nitrogen is represented not by typical proteins but by simpler forms, and the capacity of the nitrogen for hydrolysis with 6 N HCl differs with different humic acids. In humic acids from Mollisols only 44 % of the total amount of nitrogen passes into solution, while in humic acids from Spodosols, 73 % passes into solution (Kononova, 1961).

The residue after hydrolysis contains cyclic indolic forms of nitrogen. The hydrolysable part of the nitrogen of humic acids is represented, not by typical protein, but apparently by products of fairly advanced decomposition which are in the form of an unstable linkage with the humic acid ring (Kononova, 1961).

The unhydrolysable part of the nitrogen of humic acids which amounts to 40 to 50 % of the total amount is

generally thought to be represented by more oxidized nitrogenous forms occurring in a stable linkage with the remaining part of the humic acid molecule (Kononova, 1961).

### Solubility

Organic constituents that are both soluble and insoluble form complexes with metal ions. Low weight acids solublize metals while high weight ones act as sinks and move sesquioxides into the soil. Humus forms stable complexes with  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$  and other polyvalent cations, enhancing the availability of micro-nutrients to higher plants. Insolubility of organic matter is due to its association with clay. Also, humic salts of divalent and trivalent cations are insoluble. Because isolated humus is only partly soluble in water little is lost by leaching. Humus exhibits buffering in slightly acid, neutral and alkaline ranges to help maintain a uniform reaction in the soil (Stevenson, 1982).

Humic and fulvic acids have properties similar to weak-acid polyelectrolytes in that charges on the molecules are strongly influenced by pH and the presence of neutral salts. A variety of ionizable acidic groups are present, but they cannot easily be discerned by acid-base titrations because the titration of one type begins before that of the other is ionized. Protonated molecules are contracted. When completely disassociated the molecules assume a

stretched configuration because of mutual repulsion of charged groups.

Trivalent cations, and to some extent divalent ones too, are effective in precipitating humic substances from very dilute solutions; monovalent cations are relatively ineffective and then only at high particle concentrations.

### Soil Genesis

The natural fractionation or differentiation of humic substances in the soil profile is very widespread in nature and is one of the main factors accounting for the differentiation of soil profiles by horizons. Natural fractionations of fulvic acids are their accumulation in humus-illuvial horizons of Spodosols and their prevalence in lower or deeper horizons of nearly all types of soil, including Mollisols (Ponomareva 1969).

Since none of the fractions of humic substances is an individual chemical compound, the fractions must be considered as compounds of variable composition. Their properties in nature vary to the point where, for instance, these humic substances give rise under certain conditions to the specific profiles of Mollisols, and in other circumstances to the specific profiles of Spodosols, or certain Alfisols (i.e. brown forest soils), etc. (Ponomareva, 1969).

The formation and development of soils are closely associated with the action of different forms of organic matter on soil-forming parent material. The most important link in this biogeochemical process is the entry into soil of fresh organic matter, its decomposition and partial mineralization with the liberation of carbon dioxide and the elements of nitrogen and ash.

Although much of the carbon dioxide escapes into the atmosphere, some dissolves in water to form weak carbonic acid. The acidified water may percolate through the soil to gradually cause soil acidity. Percolating waters continuously move small amounts of  $H^+$ , which replace solubilized basic cations of calcium, magnesium, potassium, sodium, etc. (Donahue et al, 1983).

Organic matter transformation is primarily accomplished by the abundant soil organisms. For example, in one gram of soil there may be found: one billion bacteria, several hundred million actinomycetes, ten to twenty million fungi, ten thousand to three million algae, up to one million protozoa and fifty nematodes (Stevenson, 1982). However, a part of the fresh organic matter entering the soil as a result of complex biochemical and physiochemical processes is transformed into a complex of peculiar organic compounds called humus substances (Tyurin and Kononova, 1962).

To the father of Russian soil science, soil formation is the process of the synthesis and destruction of organic matter. According to Vil'yams the synthesis and destruction of organic matter is the basis of life (Ponomareva, 1974).

### Mountain Studies

Many studies have been made of mountain soils which have been concerned with determining the change in soil properties with elevation. Although changes in organic carbon and nitrogen contents are commonly considered only a few studies have evaluated the nature of the organic matter in more detail.

Kuz'min and Chernegova (1981) found that the humic-fulvic acid ratio was close to one for eight soils ranging in elevation from 500 to 1900 m in soils from four vegetation zones but that the humus fractional composition was dissimilar. The climates ranged from cold arid steppes to cold humid taigas and tundras and according to them accounted for the shallow humus horizons and specific composition and properties of organic matter. The humic-fulvic acid ratio varied with 0.8 to 1.3 and was considered of little diagnostic value for their soils.

According to Orlov et al (1979) (cited by Kuz'min and Chernegova, 1981) the group composition of humus varies in a zonal-genetic soil series. The intensity of

biochemical processes in soils determines the accumulation of humus with a high-quality humate composition. The nature of the humified material, or the depth of humification, is a function of the total amount of plant and animal residues, the rate of the biochemical reactions and of their duration. Explicit quantitative characteristics for evaluating the biological activity of soils have not been developed because of its dependence on many factors.

Kuz'min and Chernegova (1981) concluded that the fractional composition of humus, which reflects the relation between organic and mineral components, clearly reveals the ecological and genetic characteristics of the soils. They reported that under grass, despite the contrast of hydrothermal conditions in Steppe and Alluvial soils, the transformation of organic matter results in the formation of calcium humates, whereas under forest and shrub vegetation it promotes the formation of alumino-iron compounds. The migration capacity of organic matter is manifested in an increase in the amount of "aggressive" fulvic acid in the illuvial-humus horizons of the Tundra soils. This is consistent with the abundant atmospheric precipitation and the nature of the ground cover.

Vladychenskiy and Borovkova (1982), in another mountain soil study which covered soils between 1400 and 1900 m in the northwestern Caucasus, found that elevation

had no direct effect on the composition or properties of the humus. The abundance of grass cover and the composition of the litter had an incomparably greater effect on the formation of the humus of the Brown Mountain-Forest soils. The soils had profiles typical of Brown Mountain-Forest soils. The granite was the parent material and responsible for the shallowness of the soil profile, its stoniness and the large proportion of large separates in the stone fraction.

They found that the humus content in the soils, all of which had over 10 % organic carbon in the humus-accumulative horizon, varied within the gradation, increasing with elevation from the soils of the beech forest to the soils of the moss-forb fir forest. The reason was because of the change with elevation of hydrothermal humification conditions, which promote greater conservation of organic matter in the form of humus.

Their study also examined the humic-fulvic acid ratio with depth. They found that because the proportion of fulvic acids increased with depth, the ratio decreased. They also found low E4/E6 values and concluded that the humic acids present had a relatively simple makeup although the degree of humification of organic matter was high in the humus-accumulation horizon.

In an earlier soil mountain study, Assing (1960), covered seven vegetation zones over elevations from below 650 to 3400 m. The zones, described as soil-vegetation belts and found in the northern Tyan'-Shan', were: a wormwood-thistle desert on light and grey-brown Sierozems, a desert steppe zone of sheep's fescue with wormwood on light Chestnut soils and ordinary Sierozems, a steppe zone of feather and motley grasses or feather and sheep's fescue on mountain ordinary Chernozems and dark Chestnut soils, a deciduous forest zone with meadow-steppe lands of miscellaneous grasses on grey forest Podzolized soils and leached Chernozems, a spruce forest, tall-grass meadow, and scrub steppe zone on mountain forest dark non-podzolized or deeply podzolized soils, an alpine and sub-alpine mountain-meadow and high mountain-meadow steppe zone and a perpetual snow, glacier and rock zone .

Assing (1960) concluded that there was a gradual increase of humus content in the soil, from the foothill desert light Sierozems to the high mountain alpine meadow soils which had a particularly high humus content. He also concluded that unlike lowland soils, mountain soils do not undergo a reduction in humus content in passing from mountain Chernozems to mountain-forest and on to mountain-meadow soils, as in the northern taiga soils. The humus content remains as high as in the highly humic Chernozems

or even increases. He also concluded that in transition from mountain Chernozems to mountain-forest and mountain-meadow soils, the humic-fulvic acid ratio changes in favor of the fulvic acids and at the same time the humus and humic acid content remains high.

Similar results were found by Rublin and Dzhumagulov (1977) who studied mountain soils of Kirghizia having a cold continental climate. The elevations ranged from 2000 to 4000 m. All the soils studied were generally similar in humus composition, having predominantly fulvic acid type of humus. Chestnut soils were somewhat different with the humus in their uppermost horizons more often of the humic acid type of humus. The most mobile humic and fulvic acid fractions occupied an important place in the composition of the humus of all soils. The E4/E6 ratio varied considerably by soil groups and also within soil groups was generally very low and indicated the humus was less complex in mountain than in lowland soils.

A fractional composition and characteristics study (Luo and Xiang-Lan 1979) in soils of Tai Bai mountain in China from the foot to the summit of the mountain, found that the surface layer of all the soils had humic-fulvic acid ratios of  $\sim 1$ . The ratio was found to decrease with depth because the proportion of fulvic acids increased simultaneously. Using optical density, coagulation and

electrophoretic tests, they found the humic acids to be relatively active and possessing low aromaticity. They concluded that the cool and humid climate retarded the condensation of the humic substances.

Other soil mountain studies worth mentioning include Mikhaylova's (1970) mountain-taiga soils in the Urals, Kuz'min and Chernegova's (1976) brown mountain-taiga and sod forest soils in the Baykal region and Muktanov's (1978) mountain soils in the Urals.

## CHAPTER 3

### METHODS

#### Field

Sites representing 19 elevations were selected for sampling on the south face of the Santa Catalina Mountains along the Mount Lemmon highway. The analytical work consisted of chemical analyses of duplicate soil samples from six soils selected at each of the 19 elevations. A horizons of the six soils were collected to a depth of 15 cm within an area of about 300 m<sup>2</sup>. The analyses were conducted after familiarity with the procedures from a year of practice.

Soils were sampled without regard to aspect, at 100 m intervals between 900 and 2700 m. A Paulin System altimeter was used to determine the elevations. The altimeter was adjusted at the beginning of each collection day by setting the known elevation at a bench mark at the base of the mountain. Other benchmarks located along the transect served as checks on the accuracy of the instrument over the span of daily sampling.

Samples were collected in the spring of 1982. Soils sampled at each elevation included the range of microclimates present such as under trees and in the open

uncanopied areas. A three-kilogram composite sample of soil was collected from each site made up of the six samples.

The soils were photographed for vegetation, location and topographic information. The soils were air dried in a greenhouse and sieved to separate the fine earth (< 2 mm) material from the many to common coarse fragments. A topographic map showing the roads was marked to locate the sites along the roads. The soils were visited in the fall of 1984 for classification, aspect and vegetation.

#### Laboratory

The methods are a hybrid of several well known techniques. Kononova and Belchikova (1965) have worked out a rapid method for humus composition. Although the method is rapid, it is considered to be reliable for humus fractionation and carbon determination in the various fractions for numerous sample analysis. A similar method was described by Lowe (1980) and was used in characterizing the soils shown on the field trips associated with the International Congress of Soil Science held in Canada in 1978.

The above authors use an extraction solution of 0.1 molar sodium pyrophosphate and sodium hydroxide in place of Tyurin's method of repeated extraction of the humic substances with 0.1 molar sodium hydroxide from the decalcified soil. The ratio of the humic acids to fulvic

acids in both methods is nearly the same. The method is further modified by using the Walkley and Black heat of dilution method (Metson, 1979) to determine the C content instead of by the Tyurin method in Simakova's (1957) modification.

An additional modification by Metson et al, (1979) is that the green color of the reduced (trivalent) chromium is measured spectrophotometrically at 600 nm rather than measuring the residual dichromate with the more conventional titrametric method.

Subsamples (about 35 g) of the soils were sifted and cleaned of raw organic matter such as rootlets, bugs, charcoal and seeds. The cleaning method suggested by Belchikova and Kononova was modified by using water to float the organic matter before removal by screening with tissues. These treated samples were then ground to pass a 0.29 mm sieve.

A gram of this finely cleaned soil was oxidized with acid chromate to yield the total or humus carbon. Ten grams more was used in the extraction of the alkali soluble fractions. Aliquots of the extraction solution were taken for the extractable organic carbon and for the acid fractionation of humic and fulvic acids. After evaporation each was oxidized with acid chromate. The humin carbon was determined from subtraction of the extractable organic

carbon from the total carbon. The fulvic acid carbon was determined from subtraction of the humic acid carbon from the extractable organic carbon. The humic-fulvic ratio was then formulated. E4/E6 ratios were determined by taking a small aliquot of the humic acid solution and diluting it with 0.05 N NaOH and then neutralizing with .05 N H<sub>2</sub>SO<sub>4</sub> followed by spectrophotometric absorbance readings at 465 and 665 nm. The two readings were expressed as a ratio.

## CHAPTER 4

### THE SOILS AND THEIR ENVIRONMENT

#### The Mountains

The Santa Catalina Mountains, located a few kilometers north of Tucson, range in elevation from 850 to 900 m at their base to 2800 m at Mount Lemmon, the high point of the range. Mount Lemmon is located about 64 kilometers from the city by a highway which provided access up the south slope for this study. The range is favorable for research because of a wide range of elevation, vegetation, relatively undisturbed conditions and accessibility (Whittaker, 1968).

The mountains have been stream-eroded to topographic maturity, with mostly moderate to steep slopes. There is a dissected upland of lower relief above 2100 m. Parent materials on the south side are relatively homogeneous with the Catalina gneiss complex forming most of the surface (Whittaker, 1968).

#### Vegetation

The determination of the vertical limits of species by slope exposure is particularly striking in the Santa Catalina Mountains because of the transition from desert

into forested country. The steep climatic gradient and varied topography create alternating vegetation of constant departures from the theoretical vegetation if the mountain were a smooth sided pyramid. Slope exposure is the topographic control of the physical factors which form the environment and most affects young plants and seedlings (Shreve, 1915).

The present elevational limit of a species, after thousands of years, is the average point at which a particular feature of its physiological activities is stopped by particular environmental conditions, not competition. The physical factors of temperature, moisture and radiation, which slope exposure controls, are the factors which cause the elevational differentiation of the vegetation of the entire mountain (Shreve, 1915).

The vegetation pattern of the south slope of the range is dominated by the combined effects of increasing precipitation and decreasing temperature toward higher elevations. The vegetation appears as a series of vegetation-types from subalpine forest near the summit to desert scrub near the base of the mountain (Whittaker, 1968).

Figure 2, page 8, shows schematically the distribution of plant communities in the Santa Catalina Mountains. It should be emphasized, however, that these

types intergrade continuously and that the vegetation of the mountains should be conceived as a complex population continuum, i.e., a single pattern of continuously intergrading communities (Whittaker, 1968).

A series of trends in community characteristics relate the various community types along the elevation gradient (Whittaker, 1968). From top to bottom, these trends include: (1) Decreasing productivity and biomass. Above-ground net primary production in the fir forests is 900 to 1200 g/m<sup>2</sup>/yr, and decreases progressively down the mountain to 200 to 500 g/m<sup>2</sup>/yr in woodlands and to lower values in deserts. As a means of comparison, Kononova (1975), has estimated that the total phytomass production can range from 400 g/m<sup>2</sup>/yr for the extremes of tropical deserts to 50,000 g/m<sup>2</sup>/yr for humid tropical forests (cited by Tate and Theng, 1970).

(2) Vegetation coverage. The sums of coverage percents for all plant strata in the fir forests are 100 to 120 %, those in many woodlands of middle elevations 60 to 80 % and those in deserts of the lower mountain slopes 30 to 50 % (Whittaker, 1968). The vegetation grades from forests with full tree cover, nearly full litter covered shaded soil to deserts with sparse vegetation cover and litter where the soil is mostly exposed to unimpeded diurnal heating and cooling.

(3) Changing growth-form dominance. Proportions of the various growth-forms in the vegetation change continuously toward lower elevations, from strong dominance of fir to pines, to pines and evergreen oaks, to oaks with pinyon pine and juniper, to increasing proportions of grass, to grass with desert shrubs, to desert shrubs and semishrubs.

(4) Changing floristic composition. Toward lower elevations, (a) richness of the vegetation in numbers of plant species increases, (b) proportions of Raunkiaer life-forms shift and (c) geographic affinities of the floras shift.

The topographic moisture gradient from ravines through lower and north facing slopes to east and west facing and dry south and southwest facing slopes is a complex gradient along which many environmental factors change. Increasing aridity and increasing temperatures are conspicuous among these changes.

### Climate

Mean annual precipitation at Tucson in desert in the Santa Cruz Valley at 730 m elevation is 27.8 cm; that at Oracle in desert grassland, on the northern base, at 1370 m, is 49.2 cm (Whittaker, 1968); that at Sabino Canyon, in the main drainage basin of the south side, is 27.4 cm (Smith, 1956). Precipitation records at high elevations in the

mountains include an average of 85 cm for six years at 2400 m and one of 81 cm for three years at 2770 m (Whittaker, 1968).

Analysis of rainfall records gives increases in both summer and winter rainfall, 1.6 and 1.3 cm per 100 m elevation increase, respectively. Shreve (1915) showed that the rate of evaporation decreased with increasing elevation and that summer soil moisture contents changed little below 2100 m, but increased rapidly above that elevation to 9 % on a south slope at 2750 m.

Mean monthly temperatures for January and July, and mean annual temperatures are: 10.0, 30.1 and 19.6° C at Tucson; 7.7, 26.5, and 16.7° C at Oracle (Whittaker, 1968); 9.0, 31.1 and 20.3° C at Sabino Canyon (Smith, 1956). Temperature measurements by Shreve gave an average decrease of temperature with elevation of 7.5° C per 1000 m rise.

The year round soil temperatures, at 20 cm depth, from a Whittaker (1968) study gave a steeper mean decrease of 8.9° C/1000 m rise, but markedly different rates of decrease in winter and summer. The winter rate (December through February) was 5.4° C decrease per 1000 m rise and the summer rate (June through August) was 12.6° C decrease per 1000 m rise.

Because of the desert location and steep moisture gradient of the Santa Catalina Mountains, a particularly

steep temperature gradient is to be expected (Whittaker, 1968). Amplitude of annual soil temperature fluctuation decreases toward higher elevations because of: (1) the effects of cold air drainage in winter, (2) desert heating in summer at low elevations combined with the moderating effects of humidity, (3) vegetation and snow cover, and (4) exposure to upper prevailing winds at higher elevations (Whittaker, 1968).

The temperature and moisture gradients interact in a complex fashion. The increased moisture, and the vegetation cover supported by it, reduce temperature contrasts toward higher elevations. These lowered temperatures toward higher elevations increase the effectiveness of a given amount of precipitation and intensify the effect of the precipitation gradient (Whittaker, 1968).

The topographic moisture gradient involves comparable interactions between topographically determined moisture conditions and temperatures (Whittaker, 1968). As indicated by their vegetation, the topographic moisture gradients resemble, but are not the same as, portions of the elevation gradient (Whittaker, 1968).

### Soils

The soils of the Santa Catalina Mountains are predominantly shallow Entisols and Inceptisols with a few Aridisols and Mollisols. The soils examined are examples of soil formations ranging from those with humus existing under sparse bush litter in the O horizons in the desert to those with a profile, albeit shallow, that contains an even distribution of soil humus. Profile development is limited, and the soils are immature in relation to zonal profile characteristics. With the exception of the subalpine fir forest, they are believed to be mature in the sense of stabilization of soil characteristics in relation to the present environment of the soil, including its topographic situation (Whittaker, 1968).

The restricted areas of alluvial soil in the desert and lower mountain regions are of a fine sand or sandy loam and possess considerable humus, in contrast to the residual soils of the slopes (Shreve, 1915). At the forested elevations the soil is similar to that of the evergreen oak region. The soil of the lower pine belt is similar in depth and humus content to that of the upper oak region (Shreve, 1915).

Above 2300 m, however, the amount of humus, as well as the amount of surface litter, increases with the increasing density of the stand of pines. On the north

facing slopes, which are clothed with fir forest, the soil is not much if at all deeper than in the heavy stands of pine, but is notably higher in organic matter (Shreve, 1915).

The most striking feature of the soil profiles is their shallow depth to bedrock, except in colluvial areas. Illuvial horizons are absent in most of the profiles. The A horizon often rests directly over the R horizon. An unconsolidated horizon, best named a C horizon and consisting of partially weathered bedrock, can be found between the A horizon and the bedrock in several profiles (Whittaker et al, 1968).

From top to bottom the content of organic matter decreases in an apparent curvilinear relationship (Whittaker, 1968). A fitted regression line gives a mean rate of change of 3.2 % decrease in organic matter per 1000 m elevation decrease below 2000 m and a higher rate in the coniferous forests of the upland above 2000 m (Whittaker, 1968).

The trend may be judged primarily a consequence of the trend of decreasing community productivity, and hence of the rate of addition of organic matter to the soil, toward lower elevations (Whittaker, 1968). Two additional factors may, however, tend to intensify this effect, (1) increasing temperatures toward lower elevations, as they increase the

rate of decomposition, and (2) growth-form trends which imply increasing prevalence of leaves resistant to decomposition toward higher elevations (Whittaker, 1968).

Correlated with the content of organic matter in the surface soil is the decreasing thickness and coverage of litter toward lower elevations (Whittaker, 1968). In the highest elevations, litter covers more than 90 % of the ground with an average depth of 5 cm of identifiable needles and twigs and an additional 1 to 3 cm of decomposing organic material. Litter is thinner, 0 to 2 cm and of incomplete to sparse cover in woodlands, and very meager and largely localized around bases of shrubs in the desert (Whittaker, 1968).

The soils sampled are mainly loamy skeletal with mixed mineralogy. The temperature regimes ranged from thermic at the lower elevations through mesic to frigid at the high elevations. Table 8 describes the vegetation and soil classification with elevation. The classifications with increasing elevation are: Lithic Haplargids, Lithic Torriorthents, Lithic Ustorhents, Lithic Haplustolls, Typic Ustorhents, Typic Ustochrepts, Haplaborolls, Typic Eutrochrepts, Typic Haplumbrepts and Typic Haplaborolls.

Table 8. Vegetation descriptions and soil classification with elevation, south slope, Santa Catalina Mountains, 15 cm depth

elevation (meters)	aspect	vegetation	classification
900	SE	prickly pear, paloverde, mesquite, saguaro	Lithic Haplargid loamy skeletal, mixed, thermic
1000	SE	prickly pear, paloverde, mesquite, saguaro	Lithic Haplargid loamy skeletal, mixed, thermic
1100	S	shin daggers, saguaro, cholla, mesquite	Lithic Torriorthent loamy skeletal, mixed, thermic
1200	S	desert broom, prickly pear, ocotillo	Lithic Torriorthent loamy skeletal, mixed, thermic
1300	SE	mazanita, oak, yucca	Lithic Ustorthent loamy skeletal, mixed, mesic
1400	S	desert broom, oak, yucca, grasses	Lithic Ustorthent loamy skeletal, mixed, mesic
1500	S	manzanita, shin daggers, grasses, oak	Ustorthent or Haplustoll
1600	W	alligator juniper pinyon pine, oak, manzanita, pine	Lithic Haplustoll loamy skeletal, mixed, mesic
1700	SE	manzanita, agave, alligator juniper, ponderosa pine,	Lithic Ustorthent loamy or sandy skeletal mixed, mesic
1800	NE	juniper, yucca, pinyon pine, oak, manzanita, pine	Lithic Ustorthent loamy or sandy skeletal mixed minerals

Table 8. Vegetation descriptions and soil classification with elevation, south slope, Santa Catalina Mountains, 15 cm depth continued

elevation (meters)	aspect	vegetation	classification
1900	E	manzanita, oak, pinyon pine	Lithic Ustorthent sandy skeletal, mixed, mesic
2000	WSW	pinyon pine, oak, manzanita	Typic Ustorthent
2100	NE	manzanita, oak, ponderosa pine, alligator juniper	Lithic Ustorthent loamy skeletal, mixed, mesic
2200	S	pine, fir	Typic Ustochrept loamy skeletal, mixed, mesic
2300	S	ponderosa pine, oak, fir	Typic Ustochrept loamy skeletal, mixed, mesic
2400	S	ponderosa pine, oak, grasses, fir	Haplaboroll or Typic Eutrochrept or Typic Haplumbrept
2500	N	pine, fir, blue spruce, ferns	Typic Haplumbrept
2600	N	blue spruce, fir, Douglas fir, pine (old)	Typic Haplaboroll or mixed Typic Haplumbrept loamy, mixed
2700	NW	ponderosa pine, grasses, ferns, aspen, pine, blue spruce, fir	Typic Haplumbrept or Typic Haplaboroll loamy, mixed

## CHAPTER 5

### RESULTS

The raw data, given in Appendix A, were recalculated into mean values before the least square method of statistical analysis was performed. The fitted equations of the curves were used to calculate carbon values and subsequently these were plotted against the experimental ones to obtain  $R^2$  values. Curves were drawn from graphs plotted of the calculated carbon values vs elevation using the Msustat program (Lund, 1983). The curves were traced onto the plotted graphs of the experimental values and appear as figures 4 through 10. The data are presented in tables 9 and 10.

The  $R^2$  values and curvilinear equations are presented in table 11. In all parameters, except the humic-fulvic acid ratio, correlation is high. The  $R^2$  values were greater than or at least .78 excluding the  $R^2$  value of .05 for the humic-fulvic acid ratio. The slope is also positive in all those cases except for the E4/E6 ratio, which is negative except for the highest elevations. This indicates that all forms of carbon, as well as the total organic carbon, in the soils increase with elevation. The

uncorrelated humic-fulvic acid ratio indicated no  
proportional trend of humic and fulvic acids with elevation.

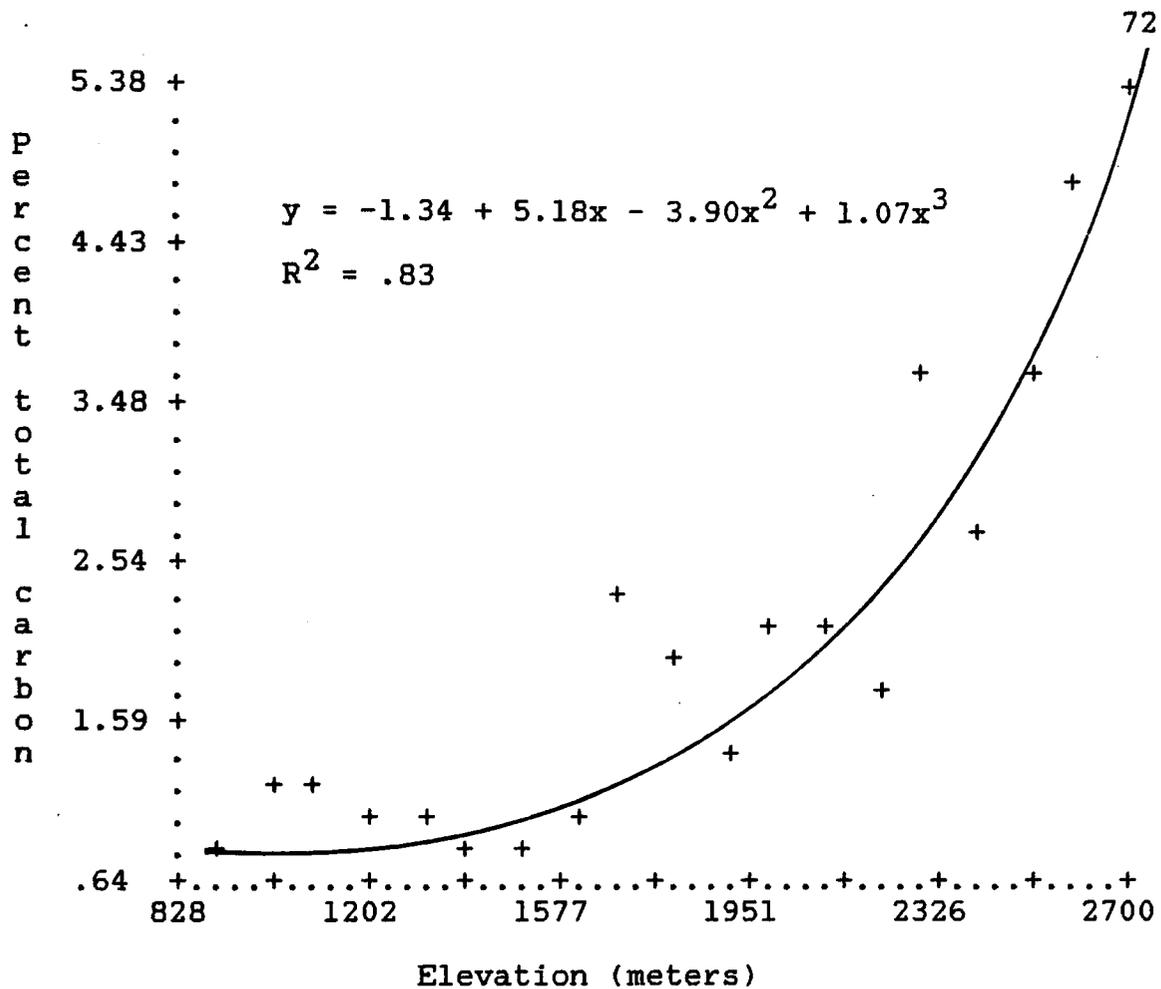


Figure 4. Percent total carbon vs elevation

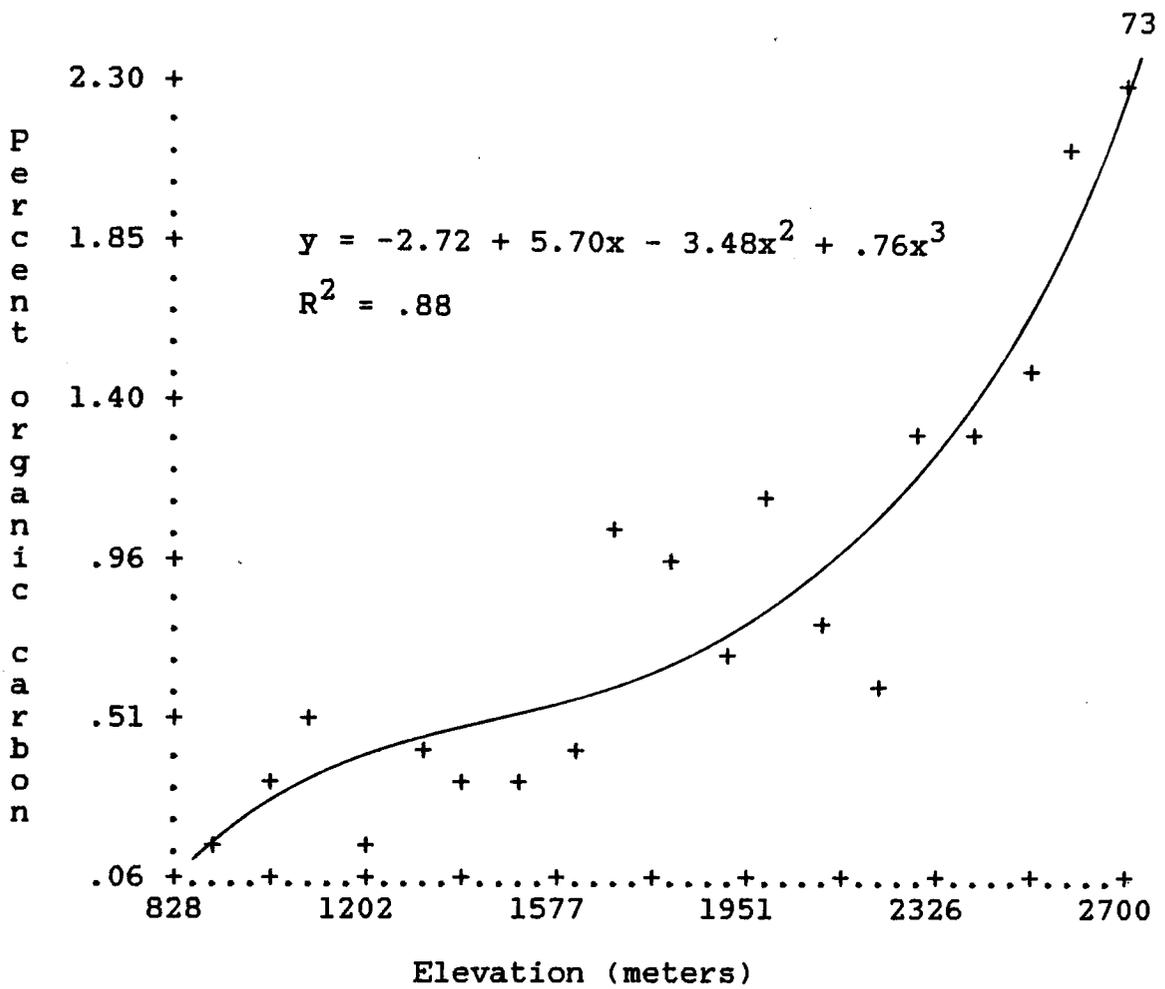


Figure 5. Percent extractable organic carbon vs elevation

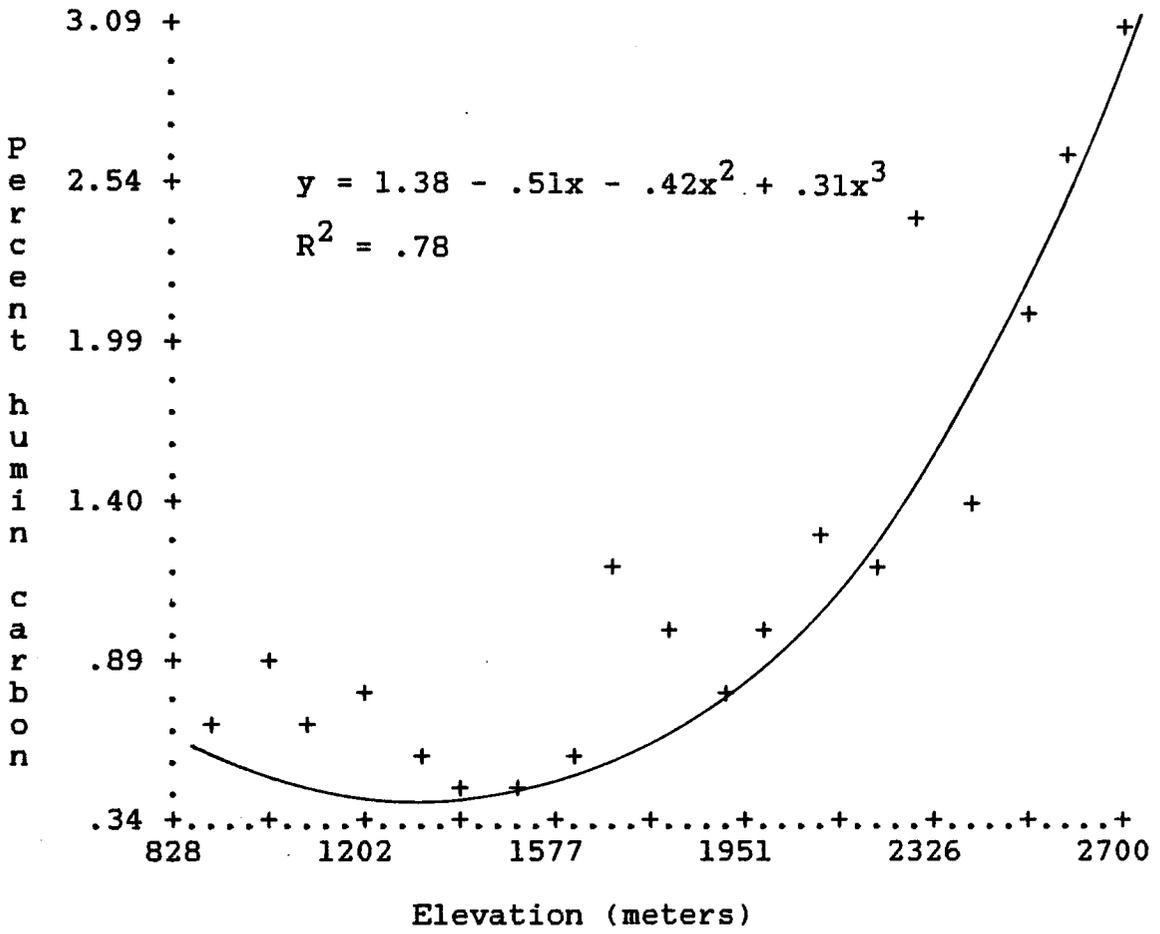


Figure 6. Percent humin carbon vs elevation

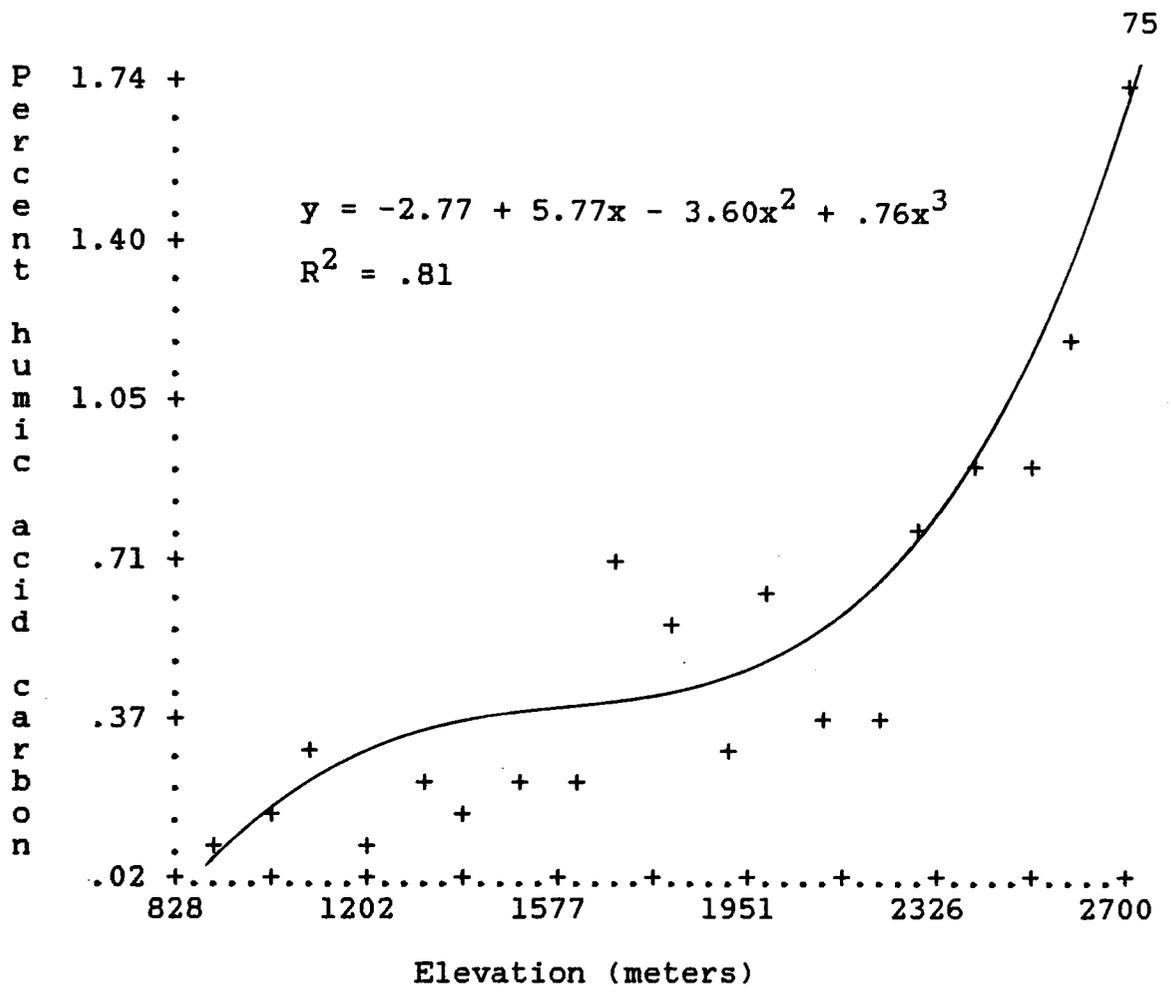


Figure 7. Percent humic acid carbon vs elevation

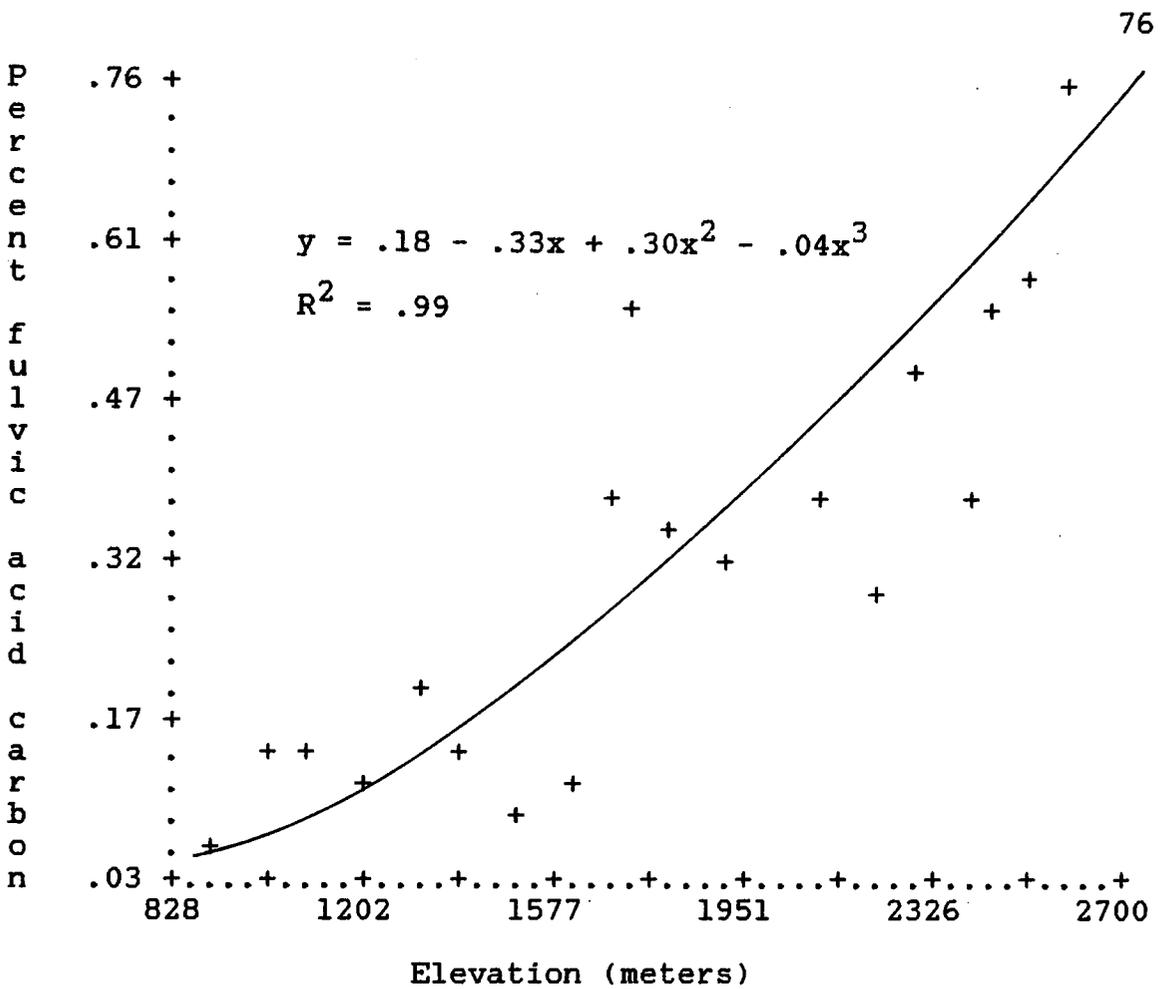


Figure 8. Percent fulvic acid carbon vs elevation

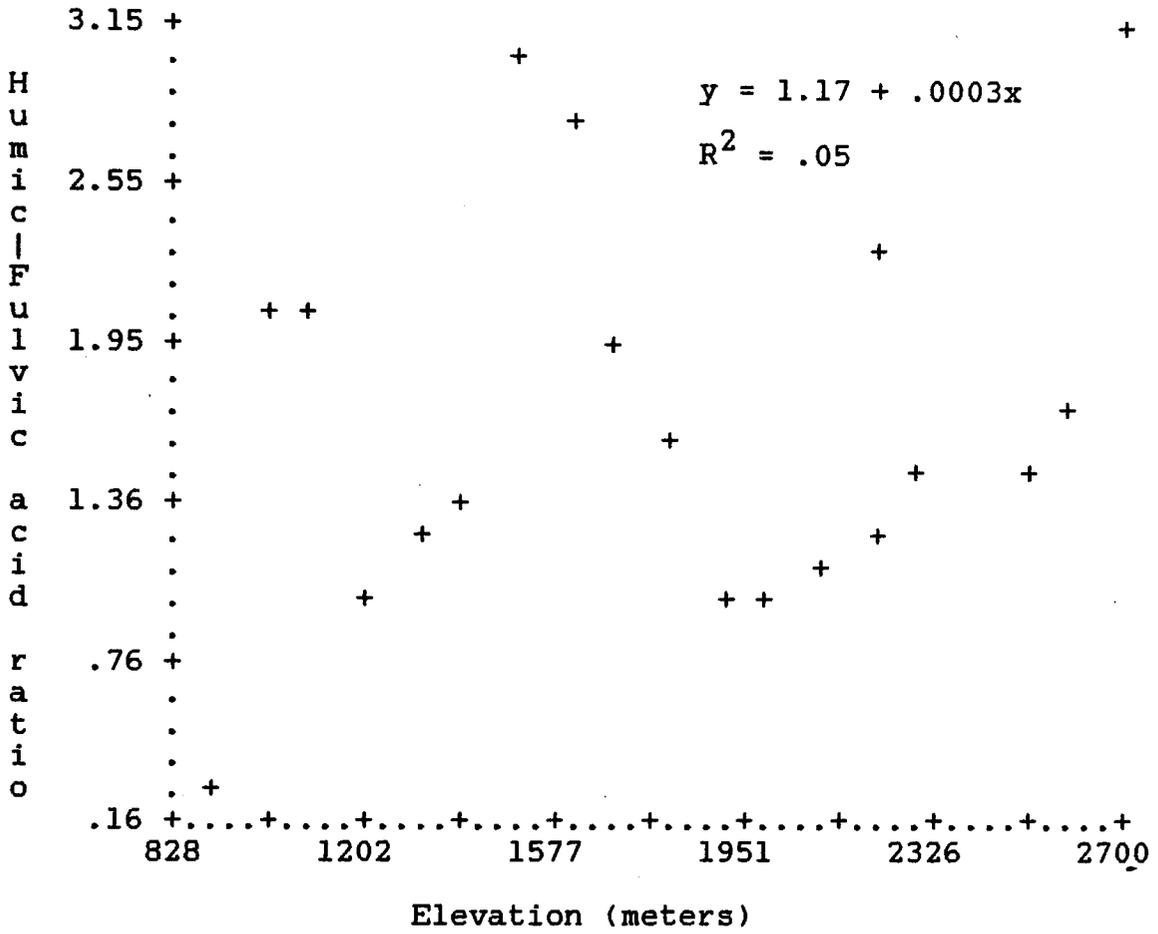


Figure 9. Humic-Fulvic acid ratio vs elevation

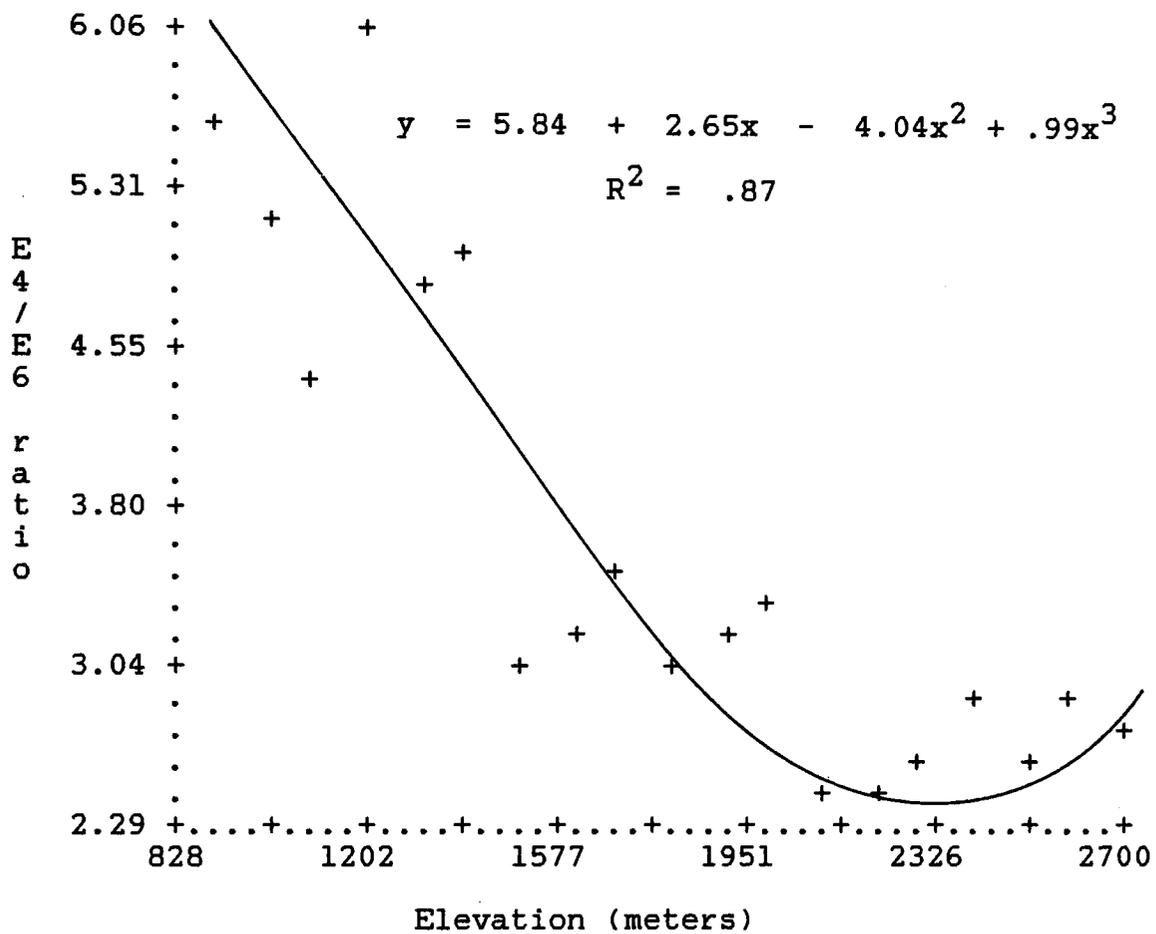


Figure 10. E4/E6 ratio vs elevation

Table 9. Changes in forms of carbon (mean percent) and changes in the E4/E6 ratio with elevation, south slope, Santa Catalina Mountains

elevation (meters)	total	extractable	humin	E4/E6
900	.82	.15	.67	5.69
1000	1.30	.36	.94	5.21
1100	1.23	.51	.73	4.54
1200	1.07	.22	.85	6.06
1300	1.03	.45	.58	4.92
1400	.83	.38	.45	5.00
1500	.91	.38	.53	3.14
1600	1.01	.42	.60	3.23
1700	2.44	1.12	1.32	3.61
1800	2.04	.99	1.05	3.06
1900	1.51	.69	.82	3.29
2000	2.28	1.22	1.06	3.45
2100	2.16	.82	1.35	2.54
2200	1.91	.67	1.24	2.43
2300	3.77	1.34	2.44	2.60
2400	2.87	1.32	1.54	2.99
2500	3.71	1.53	2.18	2.71
2600	4.85	2.17	2.68	2.98
2700	5.38	2.30	3.09	2.82

Table 10. Changes in forms of carbon (mean percent) and the humic-fulvic acid ratio with elevation, south slope, Santa Catalina Mountains

elevation (meters)	humic acid	fulvic acid	humic-fulvic
900	.09	.06	.27
1000	.22	.16	2.15
1100	.35	.16	2.14
1200	.10	.12	1.06
1300	.25	.21	1.26
1400	.22	.17	1.37
1500	.28	.10	3.03
1600	.29	.13	2.82
1700	.73	.40	2.00
1800	.62	.38	1.68
1900	.36	.34	1.06
2000	.65	.57	1.10
2100	.43	.39	1.14
2200	.37	.30	1.26
2300	.83	.51	1.50
2400	.94	.39	2.36
2500	.93	.60	1.57
2600	1.25	.76	1.79
2700	1.74	.56	3.15

Table 11. Curvilinear equations and  $R^2$  values for forms of carbon with elevation, south slope, Santa Catalina Mountains

carbon form	equation	$R^2$
total	$y = -1.34 + 5.18x - 3.90x^2 + 1.07x^3$	.83
extractable organic	$y = -2.72 + 5.70x - 3.48x^2 + 0.76x^3$	.88
humic	$y = 1.38 - 0.51x - 0.42x^2 + 0.31x^3$	.78
humic acid	$y = -2.77 + 5.77x - 3.60x^2 + 0.76x^3$	.81
fulvic acid	$y = 0.18 - 0.33x + 0.30x^2 - 0.04x^3$	.99
humic-fulvic	$y = 1.17 + 0.0003x$	.05
E4/E6	$y = 5.84 - 2.65x - 4.04x^2 + 0.99x^3$	.87

## CHAPTER 6

### DISCUSSION AND CONCLUSIONS

It was not surprising to find that there was no correlation between the humic-fulvic acid ratio and elevation given the diverse nature of the mountain soils and associated climates. However, it would seem likely that there would be a trend since the other carbon forms correlated with elevation. An explanation for the observation is lacking. High and low values occurred across the range of elevations. They may result from laboratory methods that selectively favor certain humus components over others or shift equilibria of the fulvic and humic acids before separation.

As the carbon accumulates in soils it is stored in different forms which may be affected by elevation and or physical conditions. Along this elevational continuum are located soils which contain increasingly high levels of humic acids of the older, larger and more aromatically concentrated form. These soils dry out during the year and permit the condensation reactions to take place producing water as a by-product.

E4/E6

Although the humic-fulvic acid ratio may be used as a means for characterizing soil humus, the E4/E6 ratio has been widely used for characterization purposes too. The E4/E6 ratio for humic acids are usually  $< 5.0$ ; those for fulvic acids range from 6.0 to 8.5 according to Chen et al, (1977) cited by Stevenson (1982). The ratio decreases with increasing molecular weight and concentration of aromatic constituents and is believed to serve as an index of humification.

A low ratio indicates a relatively high concentration of aromatic constituents; a high ratio reflects a low concentration and infers the presence of relatively more aliphatic structures. An inverse relationship has been observed between this ratio and the mean residence time of humic material; the humic material with the highest E4/E6 ratio has the lowest mean residence time, indicating the more humified and highly aromatic substances are of more ancient origin (Campbell et al, 1958) as cited by Stevenson (1982).

A detailed study by Chen, Senesi and Schnitzer (1977), showed that measurement of the E4/E6 ratio is (1) mainly governed by particle weight, (2) affected by pH, (3) correlated with the free radical concentration, (4) not directly related to the relative concentration of condensed

aromatic rings and (5) independent of humic acid concentration in the 100 to 500 ppm range. Chen et al, were in agreement with Kononova (1966), that the ratio should be determined between pH 7 and 8, best done by dissolving the humic material in 0.05 N NaHCO<sub>3</sub> at concentration of 200 to 400 ppm.

It is frequently suggested in the soil science literature that the magnitude of the E4/E6 ratio of humic substances is related to the relative concentration of condensed aromatic rings in these substances (Chen et al, 1977). A low E4/E6 ratio is related to a high concentration of condensed aromatic rings and a high ratio to a low concentration of condensed aromatic rings. From extensive chemical degradation studies (Schnitzer, 1976) cited by Chen (1977) and viscometric investigations (Chen and Schnitzer, 1976) cited by Chen (1977) humic and fulvic acids contain aromatic rings but not as highly condensed structures and that they behave like flexible, linear, synthetic polyelectrolytes. Chen et al (1977) conclude that humic and fulvic acids contain numerous linkages about which free rotation can occur.

The E4/E6 ratio values correlated with elevation and are in accordance with the increasing organic matter. It is interesting to note the change in slope for elevations 2300 through 2700 m. The values increase over these elevations

and indicate the possible interference of leaching waters in the condensation of humic acids. Nevertheless, the values are less than those at the lower elevations.

#### Other Measurements

Measurements not taken in this study but taken by Whittaker (1968), are summarized in table 12. Nitrogen increased .05 % with 1000 m increase in elevation. The rapid decrease in soil organic matter toward lower elevations resulted in the carbon/nitrogen ratio decreasing at 11.7 units per 1000 m (Whittaker, 1968).

The pH values ranged from 7.0 to 4.5, decreasing toward higher elevations at a mean rate of 1.3 units per 1000 m. Base saturation percents decreased toward higher elevations at a rate of 37 percent per 1000 m. The most acid soils were those of the pine forests. The subalpine fir forest, though more humid than the pine forest, was less acid, and its values for pH and exchange capacity were anomalous in relation to the elevational trend (Whittaker, 1968).

Whittaker et al (1968) also found that exchange capacities of the soils increase toward higher elevations. The mean rate approximated 7.5 units per 1000 m. The three major cations, Ca, Mg and K showed decreasing percents of exchange capacity toward higher elevation, but not in parallel with one another. Percent Ca showed a strong

Table 12. Other measurements, south slope, Santa Catalina Mountains, 13 cm depth (Whittaker, 1968)

elevation (meters)	vegetation	percent organic matter	percent N	percent C/N
960	spinose desert	1.75	.09	11.5
1200	desert grassland	2.22	.12	11.7
1200	shrub phase desert	2.52	.13	11.2
1330	open oak woodland	.98	.06	9.6
1330	open oak woodland	2.04	.10	11.6
1525	open oak woodland	2.28	.07	18.9
1525	pygmy conifer-oak	2.15	.10	12.0
1680	pygmy conifer-oak	1.38	.04	19.0
1680	Arizona cypress woods	3.96	.13	17.7
1890	pygmy conifer-oak	1.02	.04	15.5
2020	pygmy conifer-oak	1.38	.05	15.7
2020	pine-oak woodland	4.10	.13	18.2
2140	pine-oak forest	17.50	.33	30.7
2500	pine forest	3.69	.08	21.7
2500	montane fir forest	6.89	.17	23.0
2710	mixed pine forest	4.98	.10	12.5
2650	subalpine fir forest	8.45	.31	35.9

Table 12. Other measurements, south slope, Santa Catalina Mountains, 13 cm depth continued

elevation (meters)	CEC meq/g	percent of CEC				percent base saturation	pH
		Ca	Mg	K	Na		
960	0.08	76.9	13.0	3.3	0	93.2	7.0
1200	0.17	74.5	15.4	3.5	0	93.4	6.5
1200	0.11	69.1	14.4	6.9	0	90.4	7.0
1330	0.14	65.7	10.2	2.2	0	78.1	6.0
1330	0.13	64.3	12.9	2.8	0	80.0	7.0
1525	0.16	65.6	14.2	1.9	0.9	82.6	6.5
1525	0.10	56.3	11.4	2.5	0	70.2	6.7
1680	0.07	44.2	14.4	2.8	0	61.4	6.0
1680	0.20	69.6	5.6	1.5	0	76.7	7.5
1890	0.08	48.3	10.4	2.7	0	61.4	6.5
2020	0.08	33.2	12.7	2.6	0	48.5	5.5
2020	0.17	62.6	7.4	1.8	0	71.8	6.5
2140	0.35	24.2	6.9	1.7	0.2	33.0	4.5
2500	0.16	22.9	11.8	2.5	0	37.2	4.8
2500	0.24	21.4	8.0	2.5	0	31.9	5.2
2710	0.16	13.4	10.9	2.1	0.8	27.2	4.5
2650	0.39	63.7	7.3	3.7	0	74.7	6.0

relation to elevation, decreasing at 38 % per 1000 m toward higher elevations. Mg and K showed weaker trends.

### Color

Historically light has been used to analyze humus. The rich dark color of humus in solution stimulated its own analytical examination using light over 60 years ago (Kononova, 1961). Humus is composed of stable, polycondensates of biological origin and are found in many visible colors.

Fractionation with acid produces a color division of a sort but chromatography on cellulose powder emphasizes division with a resulting green humic acid (McLaren and Skujins, 1971). The color of the extracted organic matter is also used in the classification of Histosols (Soil Survey Staff, 1975). The color ratio of optical density has been discussed above. Since the E4/E6 ratio was correlated with elevation but not the humic-fulvic acid ratio, a further humus color breakdown study is indicated.

A possible future study could be of the affect that elevation has on the colors of humus. This study could employ a laser beam and a computer for precise and accurate color measurement. Such a study focuses on a useful parameter and develops the science logically. These colors compared to one another using a least significant difference test or correlation with elevation should explain more of

the biological differences between the soils on a mountain or across a continent.

A study of optical properties of humic compounds distributed throughout soil profiles may provide interesting information on their synthesis and degradation as well as on their interactions with inorganic soil constituents.

### Reagents

Of the various neutral reagents,  $\text{Na}_4\text{P}_2\text{O}_7$  has been the most widely used. The amount of organic matter recovered, when less than 30 %, is considerably less than with caustic alkali, but less alteration occurs. To minimize chemical modification of the humic material, extraction should be carried out at pH 7. The method used in this study was at pH 13 for quantitative speed. Humic acids recovered from soil by extraction with sodium pyrophosphate usually contain Fe and Al as contaminants (Stevenson, 1982).

When the concentration of sulfuric acid, used to separate the humic from the fulvic acids, is 0.6 N or higher, there occurs a gradual increase of organic matter in the precipitate, i.e., the fraction of fulvic acid is converted into a fraction of humic acids. When the environment is strongly alkaline, the humic acids are converted into fulvic acids, according to Nikolaevskay (1961). Therefore when working with humus substances,

qualitatively, high concentrations of either alkalis or acids must be avoided (Ponomarova, 1969).

### Conclusions

From this soil study of mountain soils from the base to the summit, all organic matter components except the humic-fulvic acid ratio were correlated with elevation. I conclude that the humic-fulvic acid ratio, based on classical organic matter separation, is not a descriptively useful means for characterizing a range of climatically different soils. On the other hand, it would be more useful to use the E4/E6 ratio to investigate soil genesis via composition. This ratio relates directly to organic matter properties, i.e. molecular size of the humic acid fraction. In addition, this ratio may be employed with fulvic acids as well as other fractions of the extractable organic carbon.

APPENDIX A

RAW DATA OF HUMUS COMPONENTS,  
SANTA CATALINA MOUNTAINS,  
PIMA COUNTY, ARIZONA

Table A. Raw data of changes in forms of carbon (percent) and changes in the E4/E6 ratio with elevation, south slope, Santa Catalina Mountains

elevation (meters)	total	extractable	humic	E4/E6
900	0.77	0.20	0.57	5.43
	1.13	0.34	0.79	6.25
	0.36	0.04	0.32	5.21
	0.54	0.06	0.48	5.93
	1.16	0.12	1.04	5.61
	0.95	0.12	0.83	5.00
1000	0.77	0.18	0.59	5.09
	2.80	0.83	1.97	6.05
	1.61	0.44	1.17	4.93
	1.31	0.36	0.95	4.78
	0.65	0.16	0.49	5.23
	0.65	0.18	0.47	5.19
1100	1.01	0.32	0.69	4.35
	0.68	0.20	0.48	4.81
	1.37	0.40	0.97	4.11
	2.08	1.19	0.89	4.02
	1.49	0.60	0.45	4.71
	0.77	0.32	0.45	5.22

Table A. Raw data of changes in forms of carbon (percent) and changes in the E4/E6 ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	total	extractable	humin	E4/E6
	0.63	0.20	0.43	6.69
	0.57	0.19	0.38	6.03
1200	1.27	0.37	0.90	6.90
	2.26	0.15	2.11	4.64
	1.10	0.22	0.88	6.17
	0.57	0.16	0.41	5.93
	1.07	0.47	0.60	4.59
	0.79	0.39	0.40	4.65
1300	2.14	0.85	1.29	5.78
	0.35	0.17	0.18	5.07
	0.74	0.38	0.36	4.68
	1.10	0.43	0.67	4.76
	1.28	0.60	0.68	4.86
	0.57	0.25	0.32	5.04
1400	1.12	0.22	0.70	4.87
	0.51	0.22	0.29	4.96
	1.52	0.54	0.98	5.78
	0.68	0.26	0.42	4.46

Table A. Raw data of changes in forms of carbon (percent) and changes in the E4/E6 ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	total	extractable	humin	E4/E6
	1.37	0.64	0.73	3.36
	0.33	0.14	0.19	2.48
1500	0.47	0.19	0.28	3.24
	0.39	0.16	0.23	3.13
	0.67	0.27	0.40	3.23
	2.22	0.85	1.37	3.42
	1.54	0.61	0.93	3.20
	1.01	0.42	0.59	3.13
1600	1.16	0.48	0.68	3.45
	0.73	0.30	0.43	3.07
	0.97	0.40	0.57	3.15
	0.67	0.29	0.38	3.39
	2.89	1.15	1.74	4.00
	1.36	0.53	0.83	2.90
1700	2.74	1.25	1.49	3.90
	4.38	2.56	1.82	4.15
	1.88	0.62	1.26	3.46
	1.37	0.59	0.78	3.27

Table A. Raw data of changes in forms of carbon (percent) and changes in the E4/E6 ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	total	extractable	humin	E4/E6
1800	4.09	1.95	2.14	3.13
	1.64	0.85	0.79	3.07
	1.66	0.79	0.87	3.05
	2.08	0.98	1.10	3.05
	1.28	0.62	0.66	3.07
	1.49	0.73	0.76	2.96
1900	3.38	1.30	2.08	3.41
	1.18	0.56	0.62	3.54
	0.45	0.24	0.21	2.68
	0.66	0.35	0.31	3.41
	1.22	0.63	0.59	3.41
	2.17	1.07	1.10	3.34
2000	1.64	0.92	0.72	3.63
	1.52	0.93	0.59	3.19
	3.01	1.71	1.30	3.31
	3.51	1.84	1.67	3.39
	1.28	0.68	0.60	3.56
	2.70	1.21	1.49	3.62

Table A. Raw data of changes in forms of carbon (percent) and changes in the E4/E6 ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	total	extractable	humin	E4/E6
2100	1.57	0.56	1.01	2.65
	2.05	0.80	1.25	2.71
	2.32	0.91	1.41	2.54
	2.16	0.85	1.31	2.56
	3.16	1.23	1.93	2.46
	1.72	0.55	1.17	2.31
2200	2.95	1.06	1.89	3.03
	1.79	0.67	1.12	2.68
	1.55	0.58	0.97	2.69
	1.43	0.49	0.94	2.12
	2.08	0.72	1.36	2.11
	1.67	0.50	1.17	1.95
2300	4.79	1.69	3.10	3.06
	1.58	0.35	1.23	2.03
	4.88	1.79	3.09	3.11
	2.10	0.73	1.37	2.54
	5.64	2.13	3.51	2.16
	3.65	1.34	2.31	2.72

Table A. Raw data of changes in forms of carbon (percent) and changes in the E4/E6 ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	total	extractable	humin	E4/E6
2400	3.69	1.89	1.80	2.92
	1.64	0.80	0.84	2.70
	2.56	1.52	1.04	2.75
	2.41	0.96	1.45	2.85
	2.29	1.12	1.17	2.85
	4.61	2.08	2.53	4.00
2500	3.27	1.32	2.26	2.54
	3.60	1.34	2.26	2.63
	3.21	1.43	1.78	2.75
	6.40	2.44	3.96	2.94
	3.51	1.63	1.88	2.75
	2.26	1.00	1.26	2.63
2600	4.85	2.10	2.75	2.99
	6.34	2.84	3.50	3.08
	7.08	3.08	4.00	2.97
	5.42	2.44	2.98	2.97
	1.13	0.50	0.63	2.90
	4.26	2.06	2.20	2.88

Table A. Raw data of changes in forms of carbon (percent) and changes in the E4/E6 ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	total	extractable	humin	E4/E6
	6.34	2.78	3.56	2.62
	5.18	2.17	3.01	2.78
2700	5.00	2.09	2.91	2.80
	5.06	2.10	2.96	2.74
	5.15	2.29	2.86	3.00
	5.57	2.35	3.22	2.97

Table B. Raw data of changes in forms of carbon (percent) and changes in the humic-fulvic acid ratio with elevation, south slope, Santa Catalina Mountains

elevation (meters)	humic acid	fulvic acid	humic-fulvic
900	0.12	0.08	1.50
	0.18	0.16	1.15
	0.06	-0.02	-3.00
	0.06	0.00	0.00
	0.06	0.06	1.00
	0.06	0.06	1.00
1000	0.12	0.06	2.25
	0.42	0.41	1.00
	0.30	0.14	2.10
	0.27	0.19	3.50
	0.09	0.07	1.80
	0.12	0.056	2.25
1100	0.24	0.08	3.00
	0.18	0.02	9.00
	0.33	0.07	6.00
	0.77	0.42	1.85
	0.39	0.21	1.90
	0.18	0.14	1.40

Table B. Raw data of changes in forms of carbon (percent) and changes in the humic-fulvic acid ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	humic acid	fulvic acid	humic-fulvic
	0.09	0.11	0.85
	0.09	0.10	0.91
1200	0.18	0.19	0.95
	0.08	0.08	2.04
	0.09	0.13	0.69
	0.08	0.09	0.94
	0.26	0.22	1.21
	0.26	1.14	1.98
1300	0.45	0.40	1.13
	0.08	0.10	0.80
	0.23	0.17	1.33
	0.23	0.20	1.10
	0.35	0.26	1.35
	0.15	0.10	1.52
1400	0.27	0.10	1.20
	0.12	0.10	1.20
	0.27	0.27	1.00
	0.15	0.11	1.36

Table B. Raw data of changes in forms of carbon (percent) and changes in the humic-fulvic acid ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	humic acid	fulvic acid	humic-fulvic
	0.54	0.10	5.69
	0.09	0.05	1.80
1500	0.15	0.04	4.00
	0.12	0.04	3.00
	0.15	0.12	1.26
	0.60	0.25	2.40
	0.39	0.22	1.78
	0.26	0.17	1.57
1600	0.33	0.15	2.24
	0.24	0.06	5.67
	0.30	0.10	3.00
	0.21	0.08	2.67
	0.68	0.47	1.45
	0.36	0.17	2.12
1700	0.86	0.39	2.22
	1.64	0.96	1.81
	0.45	0.17	2.65
	0.38	0.22	1.75

Table B. Raw data of changes in forms of carbon (percent) and changes in the humic-fulvic acid ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	humic acid	fulvic acid	humic-fulvic
1800	1.22	0.73	1.67
	0.53	0.33	1.62
	0.51	0.28	1.82
	0.57	0.41	1.40
	0.35	0.28	1.26
	0.51	0.22	2.32
1900	0.71	0.59	1.20
	0.27	0.29	0.93
	0.13	0.11	1.26
	0.17	0.19	0.92
	0.32	0.32	1.01
	0.54	0.53	1.03
2000	0.45	0.47	0.97
	0.41	0.53	0.77
	1.01	0.70	1.45
	1.10	0.74	1.49
	0.33	0.35	0.95
	0.60	0.61	0.99

Table B. Raw data of changes in forms of carbon (percent) and changes in the humic-fulvic acid ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	humic acid	fulvic acid	humic-fulvic
2100	0.32	0.25	1.29
	0.44	0.37	1.18
	0.38	0.52	0.73
	0.45	0.54	1.12
	0.67	0.56	1.21
	0.32	0.24	1.32
2200	0.57	0.49	1.18
	0.36	0.31	1.15
	0.36	0.22	1.69
	0.27	0.22	1.21
	0.41	0.32	1.27
	0.26	0.25	1.03
2300	1.07	0.62	1.74
	0.15	0.20	0.75
	1.21	0.57	2.11
	0.38	0.36	1.05
	1.48	0.66	2.24
	0.70	0.64	1.08

Table B. Raw data of changes in forms of carbon (percent) and changes in the humic-fulvic acid ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	humic acid	fulvic acid	humic-fulvic
2400	1.42	0.47	3.02
	0.53	0.28	1.91
	0.65	0.39	1.67
	0.60	0.36	1.67
	0.83	0.34	2.47
	1.61	0.47	3.44
2500	0.76	0.57	1.34
	0.73	0.62	1.18
	0.89	0.54	1.65
	1.55	0.89	1.75
	1.04	0.59	1.76
	0.63	0.37	1.71
2600	1.33	0.77	1.72
	2.07	0.78	2.68
	1.91	1.18	1.63
	1.66	0.79	2.12
	0.23	0.28	0.82
	0.31	0.75	1.75

Table B. Raw data of changes in forms of carbon (percent) and changes in the humic-fulvic acid ratio with elevation, south slope, Santa Catalina Mountains continued

elevation (meters)	humic acid	fulvic acid	humic-fulvic
	2.13	0.66	3.25
	1.72	0.46	3.78
2700	1.49	0.60	2.49
	1.55	0.55	2.82
	1.66	0.64	2.61
	1.88	0.48	3.95

APPENDIX B

COMMON AND SCIENTIFIC NAMES OF  
MENTIONED VEGETATION,  
SANTA CATALINA MOUNTAINS,  
PIMA COUNTY, ARIZONA

Table A. Common and scientific names of mentioned vegetation, Santa Catalina Mountains, Pima County, Arizona

common name	scientific name
agave	<u>Agave palmeri</u>
alligator juniper	<u>Juniperus deppeana</u>
aplina fir	<u>Abies lasiocarpa</u>
Arizona oak	<u>Quercus arizonica</u>
aspen	<u>Populus tremuloides</u>
blue spruce	<u>Picea pungens</u>
Chihuahua pine	<u>Pinus leiophylla</u>
cholla	<u>Opuntia spinosior</u>
desert broom	<u>Baccharis sarothroides</u>
Douglas fir	<u>Pseudotsuga menziesi</u>
Emory oak	<u>Quercus emoryi</u>
Engelmann spruce	<u>Picea engelmanni</u>
fern	<u>Pteridium aquilinum</u>
manzanita	<u>Arctostaphylos pungens</u>
mesquite	<u>Prosopis juliflora</u>
Mexican blue oak	<u>Quercus oblongifolia</u>
ocotillo	<u>Fouquieria splendens</u>
paloverde	<u>Cercidium floridum</u>
pinyon pine	<u>Pinus cembroides</u>

Table A. Common and scientific names of mentioned  
vegetation, Santa Catalina Mountains, Pima County,  
Arizona continued

common name	scientific name
ponderosa pine	<u>Pinus ponderosa</u>
prickly pear	<u>Opuntia chlorotica</u>
prickly pear	<u>Opuntia phaeacantha</u>
saguaro	<u>Carnegiea gigantea</u>
shin daggers	<u>Agave schottii</u>
silverleaf oak	<u>Quercus hypoleucoides</u>
yucca	<u>Yucca arizonica</u>
yucca	<u>Yucca schottii</u>

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