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PROJECT REPORT

SUBSURFACE CHARACTERIZATION:
PREDICTION OF REACTIONS BETWEEN GEOLOGIC MATERIALS AND ORGANIC POLLUTANTS.

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ABSTRACT

It is generally implied that for hydrophobic pollutants soil organic matter, clay minerals and possibly amorphous hydroxides are the primary earth materials that influence the attenuation of organic pollutants in the subsurface environment. Determining the distribution of these materials, both vertically and areally, requires quantitative estimates of these compounds in a wide number of samples. Scanning electron microscopy is a common method of characterizing clay minerals from the deeper subsurface, but the dehydration of soil organic matter in soils without destroying their structure is difficult at best and probably will require special freeze drying equipment. Quantitative x-ray diffraction is a viable method for simple mixtures of well crystalline compounds, but it becomes at best semi-quantitative for multicomponent mixtures, and next to useless for amorphous or poorly crystalline materials. Fourier Transform Infrared Spectrometry although used extensively to characterize extracted humic and fulvic acids lacks the sensitivity to detect the much smaller amounts present in unextracted soil samples. Raman microprobe techniques can yield information about material characterization that has been incompletely provided by conventional techniques, such as information on the molecular nature of the components of a sample and their distribution in the sample.

To date four sites in various parts of the Continental United States have been chosen as study areas. These are: the former creosote waste disposal lagoon in Conroe, Texas, the D'Imperio Dump in Atlantic County, New Jersey, the Apple Creek drainage basin in Burleigh County, North Dakota, and north central Payne County, Oklahoma.

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SECTION 1

INTRODUCTION

Since the early 1970's ground water pollution has received much attention from the public. In most ground-water pollution investigations, samples of water and, much less frequently, earth materials are collected for chemical analysis. The results may indicate that a problem exists, but they do not indicate why the problem exists, other than that a contaminant has reached the water table. Presently, many regulatory agencies must predict what will happen to a contaminant in ground water with respect to space and time. This prediction, however, is useful and valid only in a very general way because we simply do not know what controls contaminant movement. What is the role of the geologic medium with respect to the attenuation of a pollutant? Does it depend only on the type of clay mineral, organic matter, or hydroxide present, or on the relative percentages of these compounds acting in concert? What role is played by micro-organisms in the subsurface, what controls their presence or survival and what factors influence their biodegradation activities.

Answers to questions such as these are not available because no one has made a concerted effort to find out. Furthermore, until recently, no one thought there was any reason to do so. Recent research has shown unequivocally that it will be impossible to predict the transport and fate of materials in the subsurface without this knowledge.

The travel of synthetic organic chemical pollutants from the surface of the earth to an aquifer, particularly one that serves as a source of drinking water, is of fundamental concern to all citizens. The sources of these pollutants are many and varied, ranging from local spills or discharges into creeks, through large scale spraying of crops with pesticides, herbicides, or sewage, to seepage from a variety of waste disposal sites (Pettyjohn and Hounslow, 1982). The principal objective of the Environmental Protection Agency Ground Water Research Strategy, known as "subsurface characterization," is to predict the movement of these pollutants in the subsurface. Most present studies examine particular soils and specific pollutants, and because of the impracticality of studying the effects of 40,000 organic compounds on 5,000 different types of geologic materials, the fundamental principles and mechanisms of the reactions that take place must be understood and quantified (Hounslow, 1981). The following concepts must be considered when examining pollution movement: 1) chromatography, which is the process whereby differential solute movement results when a solution moves through a porous solid, such as when polluted groundwater moves through sediments; 2) adsorption, which is described quantitatively by an adsorption isotherm (a graph of the amount of material, in this case a pollutant, absorbed/ gram by the solid versus the concentration of the pollutant in solution)--the constant in the equation describing this graph is known as the adsorption coefficient; and 3) mass transport equation, which enables the concentration of a pollutant to be determined at a specified place after a specified time. This equation incorporates estimates of ground water velocity, disfusion, biodegradation, and adsorption--the last term which is the subject of this report. Following a general introduction to these concepts, this report will discuss how these concepts are applied to the movement of pollutants through the soil.

CHROMATOGRAPHIC MOVEMENT

The flow of fluids through porous media has received considerable attention in both field and laboratory, however the behaviour of the dissolved constituents (solutes) during this process has received little attention outside the analytical chemistry laboratory. The following discussion is intended to show that chromatography is a complex multifaceted process and not the simplistic one usually chosen to explain pollutant movement. It cannot be overemphasized that a critical evaluation of the model selected is essential if reliable predictions of pollutant movement are to be made.

Chromatography is the process such that when a solution of a compound (mobile phase) moves through porous solid (stationary phase) some solutes appear to move more rapidly than others. The process that controls the rate at which a particular compound moves relative to that of the fluid is called adsorption or partition. Adsorption is the term used if the stationary phase is a solid, and partition if the stationary phase is a gel or a liquid (whose support may be an inert porous solid phase).

In analytical chemistry, chromatography is commonly used to separate compounds. It was first used in 1906 by Tswett to separate colored substances in plant materials, hence the name. The process is based on the fact that some solutes move more rapidly than others, that is, they distribute themselves between the mobile and the stationary phases in proportions that vary from one substance to another. Chromatographic movement is influenced by the following criteria:

A. The nature of the stationary phase
  1. Solid - adsorption chromatography
  2. Liquid (or gel) - partition chromatography
B. The composition of the mobile phase, (Stock and Rice,1963)
  1. Pure solvent - elution chromatography
  2. A solution added continuously - frontal chromatography
  3. A solute more strongly adsorbed than any of the compounds of the mixture - displacement chromatography

Stationary Phase

The stationary phase may be an active solid (solid stationary phase) or a liquid supported by porous inert solids (liquid stationary phase).

The Liquid Stationary Phase--

This phase may be a true liquid supported by an inert (non' reacting) porous solid or, in some cases, a gel. The rate of movement of a dissolved constituent depends on the relative solubility of this solute in the stationary phase and in the model to the movement of radiostrontium in soils. Fissel and Poelstra further extended the theory in 1963. King and McCarty (1968) applied this model to the movement of organic phosphate pesticides in a variety of soils and added an additional term to cover pesticide degradation. Their model was confined to linear adsorption coefficients.

The Solid Stationary Phase--

This phase is an active solid that reacts with solutes in the liquid phase and results in the process known as adsorption chromatography. It refers to a surface effect that takes place at the boundary between the moving and stationary phases.

Weiss (1943) proposed a theory for elution chromatography (qv) of a single solute based on a differential equation for the adsorption process. He derived equations for the determination of solute concentrations with depth using linear and non linear adsorption isotherms, band widths, solute movement and shape of the adsorption band. Weil-Malherbe (1943) verified the Weiss theory experimentally and determined that the tailing of an elution curve is a function of the Freundlich exponential coefficient. That is, for linear adsorption isotherms the elution curve is virtually symmetrical, whereas if the exponent is less than 1, a tail develops on the eluted solute band.

Mobile Phase

Chromatographic movement can also be classified according to the manner by which the solute moves through the porous medium. The terms elution, frontal and displacement are used to describe the different types of conditions.

Elution_chromatography--

This refers to the transport of a solute previously added to a chromatographic column by means of the application of pure solvent Figure 1. If it is assumed that there are no stationary phase mobile-phase interactions, then the more weakly adsorbed substances travel more rapidly than the more strongly adsorbed substances. A common phenomena with this technique, is that of tailing, which results in wider, diffuse and overlapping bands. In the other two processes this does not occur. A point source contaminated site leached by rain water would be an example of this phenomena, as is thin layer chromatography.

Frontal chromatography--

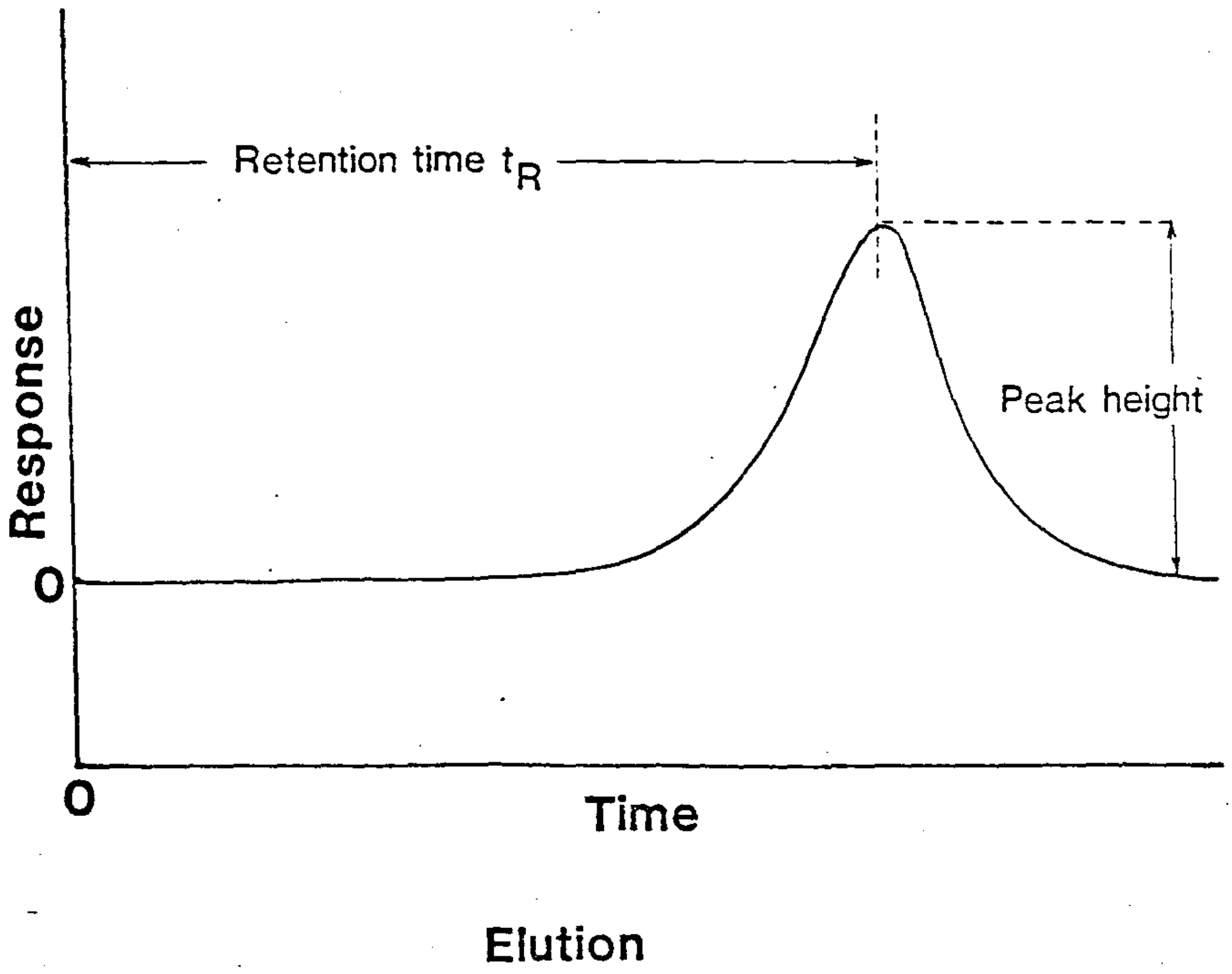


Figure 1. Elution chromatography refers to the transport of a solute previously added to a chromatographic column by the application of pure solvent.

This type of chromatography occurs when a solution of the mixture is added continuously. If there are a number of components in the mixture each having different adsorption characteristics, a number of zones will be formed. The leading edge of each zone is called a front. The first (leading) zone will contain the least adsorbed solute whereas the other zones will contain mixtures of the various solutes Figure 2. Eventually however, the effluent from the system becomes identical in composition to the sample entering the system. A land treatment disposal site could well illustrate this phenomena.

Displacement_chromatography--

This results when the mobile phase contains a substance more strongly adsorbed than any of the components of the mixture. This substance is known as the displacer. A mixture of solutes moves down the column at the same rate as the displacer is added and resolves itself into bands of pure components. The order of these bands is the order of the strength of adsorption on the stationary phase. Each pure band acts as a displacer of the less adsorbed component ahead of it Figure 3. The regeneration of a water softener by sodium chloride illustrates this process.

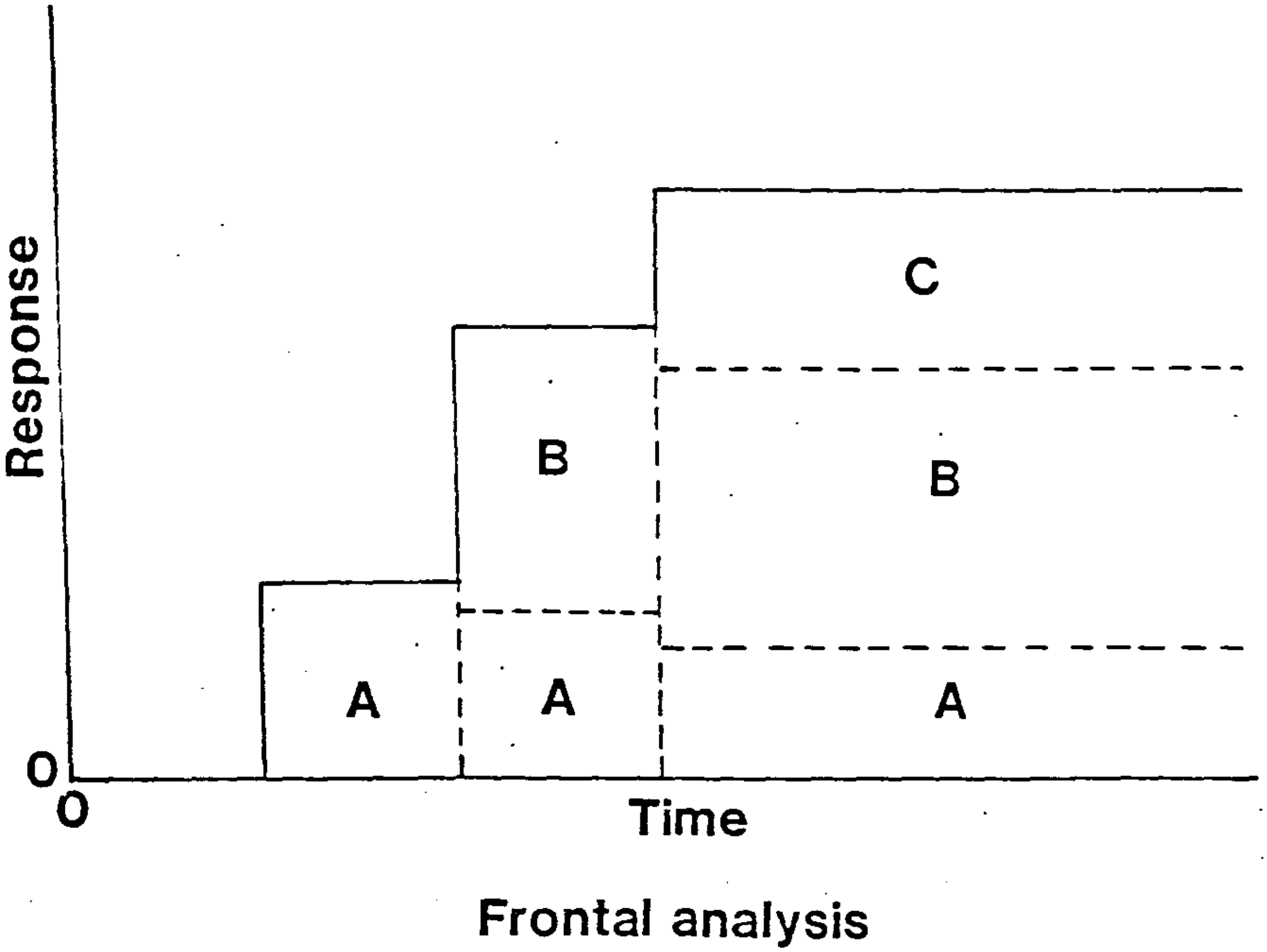


Figure 2. Frontal chromatography occurs when a solution of the solute is added continuously. After passage of the leading zone the effluent from the column becomes identical in composition to the sample entering the system.

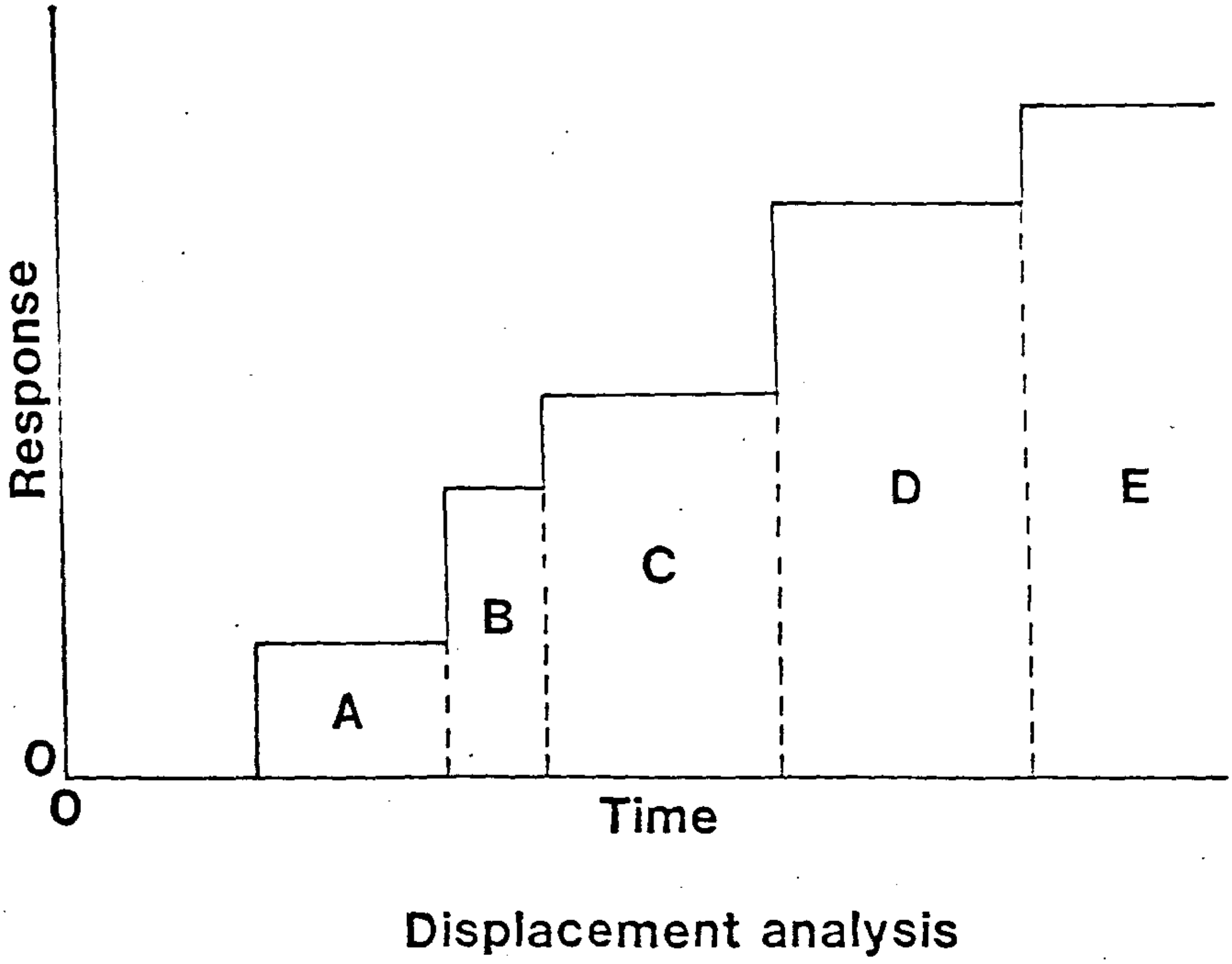


Figure 3. Displacement chromatography results when the mobile phase contains a substance more strongly absorbed than any of the components of the mixture. The solute mixture resolves itself into bands, each acting as a displacer of the less adsorbed component ahead of it.

ADSORPTION

Adsorption describes the distribution of a solute between a liquid and a solid phase; it is of paramount importance in all chromatographic studies. It is generally considered to be the result of either an affinity for the solid or a lack of affinity for the liquid, Weber 1972.

If the adsorption is a consequence of the lyophobic (solvent-disliking) character of the solute relative to a particular solvent, then the solute displays a low solubility in that liquid. This inverse relationship between adsorption and solubility is still invoked as the primary theory for explaining the movement of pesticides in soils. In aqueous systems this phenomena is called hydrophobic adsorption. On the other hand the solute may have a high affinity for the solid phase. Three types of surface phenomena must be considered.

(a) physical adsorption results from van der Waals forces, that is fluctuations in electron distributions producing instantaneous dipoles. Adsorbed molecules are not fixed to a specific site but are free to move within the interface.

(b) chemisorption represents a chemical interaction with the adsorbent and the bonding occurs at specific sites on the surface of the adsorbent.

(c) exchange adsorption is a process in which ions of one substance concentrate at a surface as a result of electrostatic attraction to changed sites at the surface. The charge on the ion is the determining factor for exchange adsorption. Generally the higher the charge and the smaller the ion the stronger the adsorption. The molecular size or hydrated radius must however, be the parameter considered.

Adsorption Isotherms - Equations

The adsorption coefficient is not always a constant and it may vary with the concentration of the solute in the liquid phase. The graph that allows the adsorption coefficient to be obtained at different concentrations is known as an adsorption isotherm.

An adsorption isotherm determined experimentally is a plot of the amount of material adsorbed per gram of adsorbant versus the concentration of the adsorbate in solution. The result may be a straight line or an exponential curve (that is, a straight line on a log-log plot).

Linear adsorption isotherms--

These isotherms result when the distribution coefficient is independent of concentration, that is:

S = Kd.C

where S is the amount of solute adsorbed by the solid phase.

C is the concentration of solute in the liquid phase.

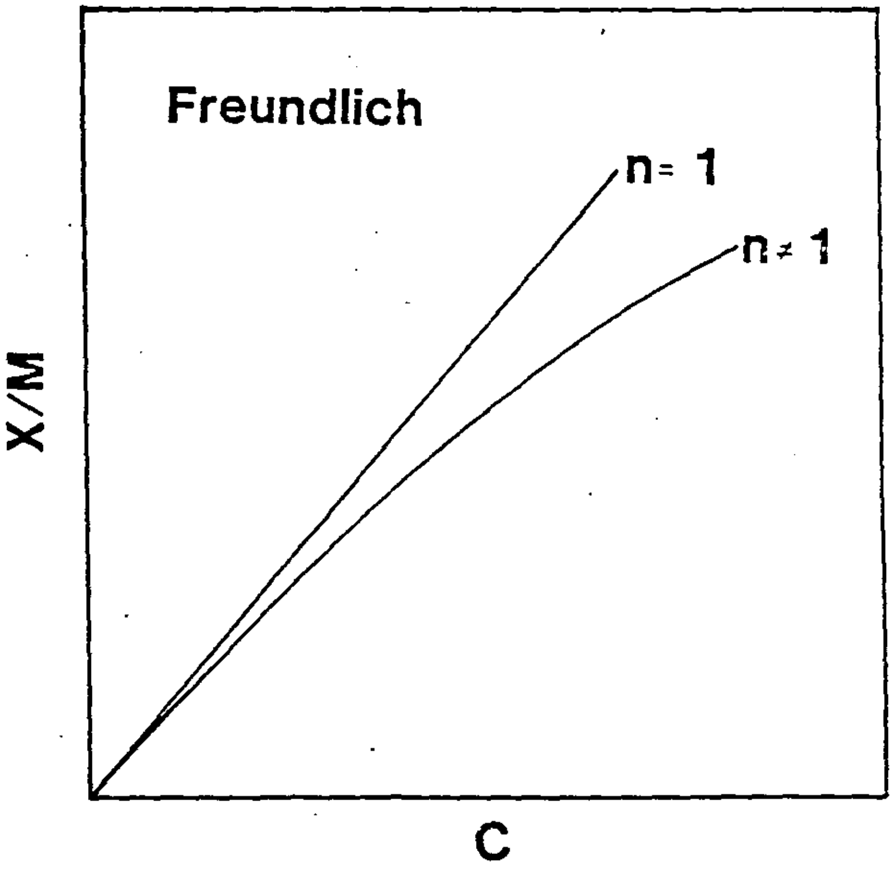
Kd is the distribution coefficient, (linear adsorption coefficient)

This is commonly the relationship observed where partition occurs between two liquid phases up to their solubility limit. Most chromatography models used for describing pollutant transport assume this model.

Freundlich isotherms--

These isotherms are primarily an empirical attempt to describe non-linear relationships. They are defined by the equation

S = KC**n (Figure 4).



$$X/M = KC^n$$

Figure 4. Freundlich isotherms, linear when n equals 1 and non linear when n does not equal 1.

where K and n are constants. It is usually presented in the linear form:

$$\log S = K + n \log C$$

where n is the slope of the line and K the adsorption coefficient (Figure 5).

Although generally considered an empirical relationship Sposito (1980) derived it theoretically for the trace adsorption of an ion participating in an exchange reaction.

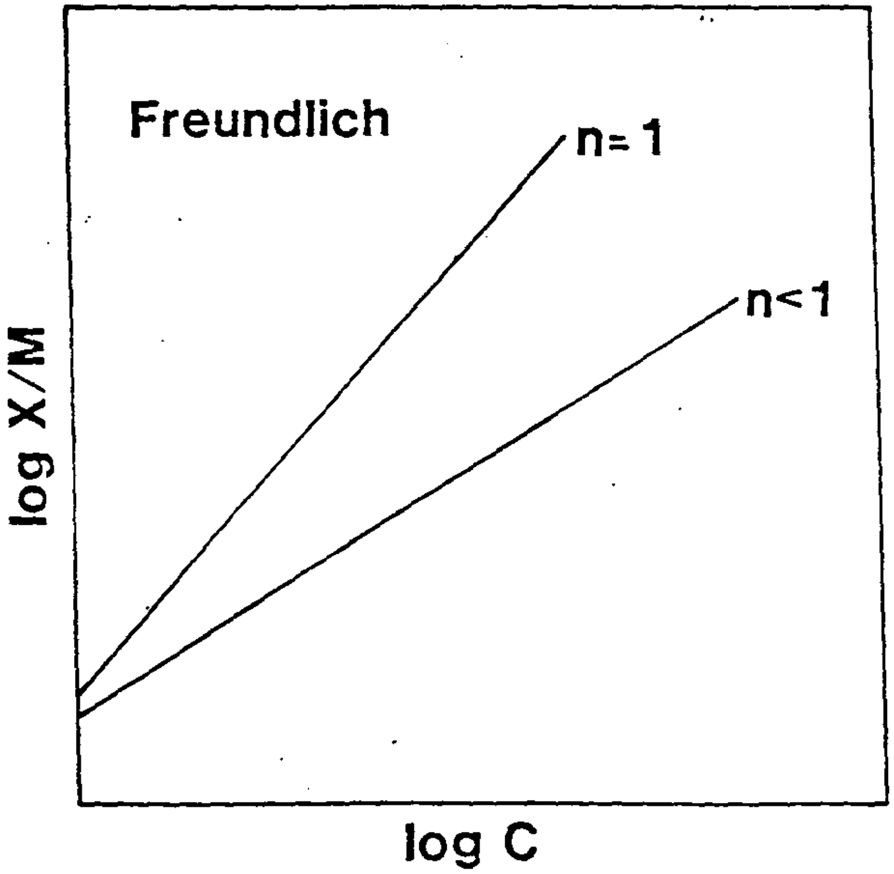
Elution curves illustrating the phenomena of tailing for isotherms where $n = 1$, $n < 1$ and $n > 1$ are shown in Figures 6, 7 and 8.

Langmuir isotherms--

These isotherms were developed by Langmuir (1918) to describe the adsorption of gases by solids. It has a valid theoretical base and assumes monolayer adsorption, and that the solid possesses a finite number of adsorption sites. The general equation is:

$$S = (Sm.b.C)/(1 + b.C)$$

where: S is the number of moles of solute adsorbed per gram of adsorbent,



$$\log X/M = \log K + n \log C$$

Figure 5. Freundlich isotherms becoming linear when plotted on log-log scales. Plots of isotherms with two values of n are shown.

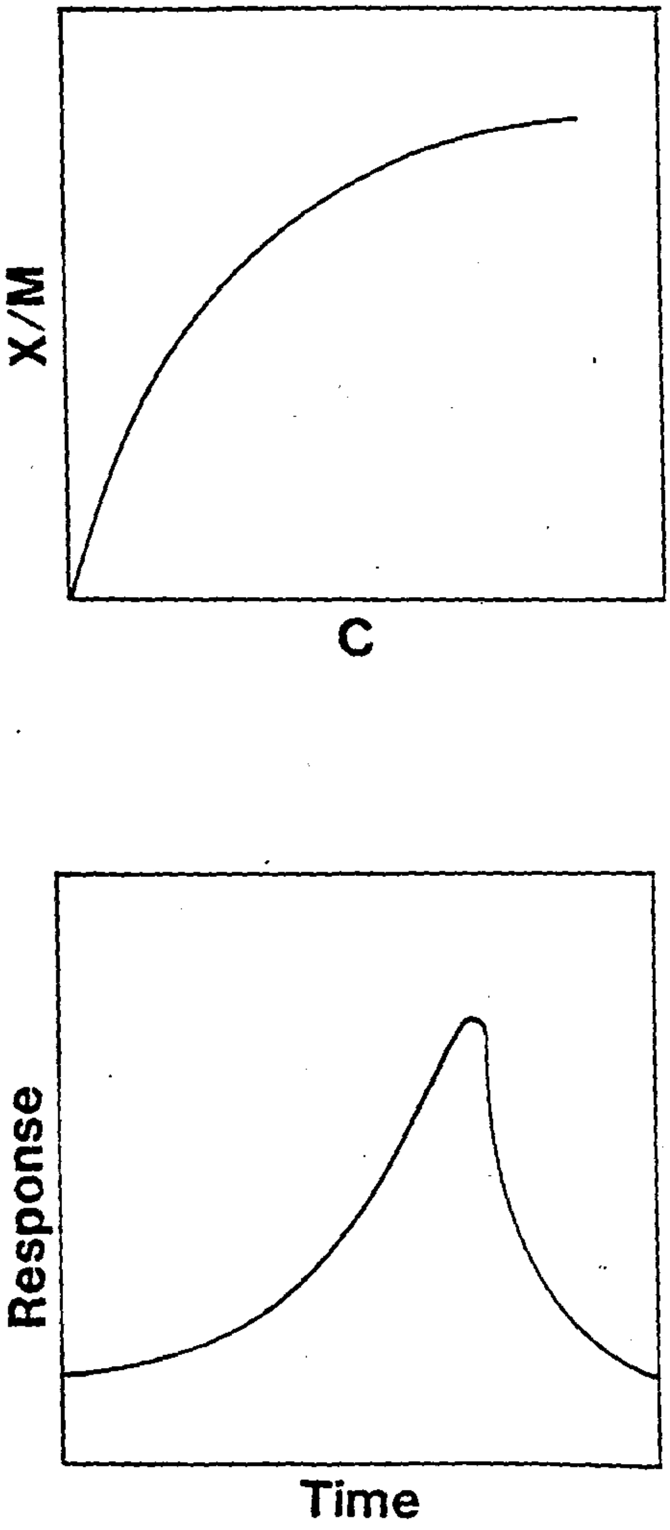


Figure 7. A non-linear adsorption isotherm, concave down with the Freundlich n less 1, showing tailing towards the source.

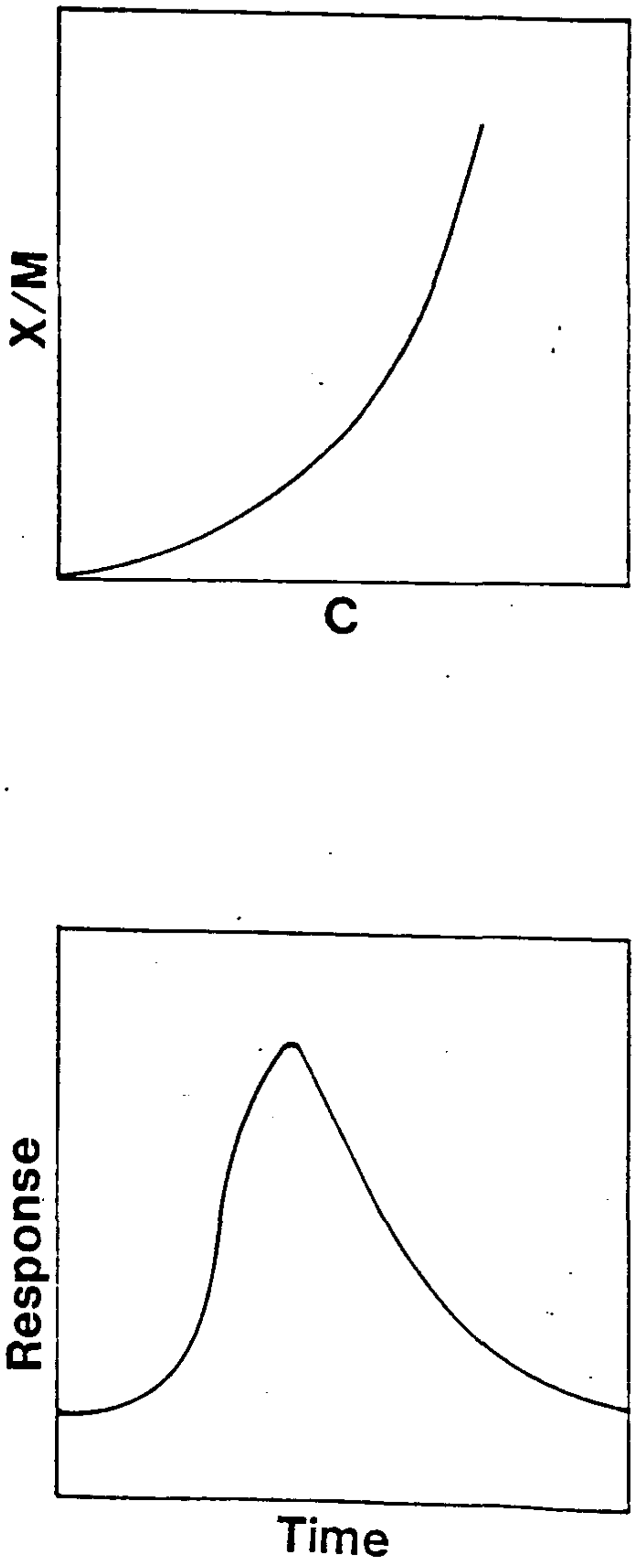


Figure 8. A non-linear adsorption isotherm, convex down with Freundlich n greater than 1, showing tailing towards the effluent direction.

Sm is the number of moles of solute adsorbed per gram of adsorbent in forming a complete single layer of adsorbed solute molecules on the surface of the adsorbent (monolayer).

C is the concentration of solute in the liquid phase, and b is a constant.

Expressed in linear form $1/S = 1/Sm + 1/(b.Sm.C)$

where: $1/Sm$ is the intercept and $1/(b.S)m$ is the slope, Figure 9.

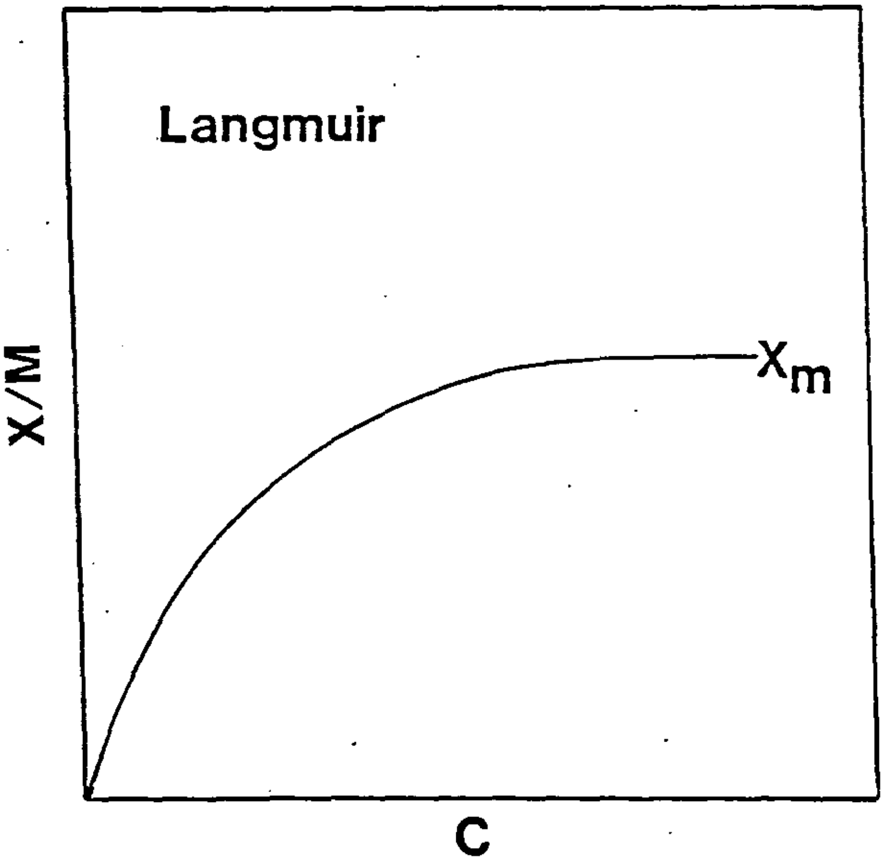
B.E.T. isotherms--

These isotherms were developed by Brunauer, Emmett and Teller (1938) to include systems in which a vapor is adsorbed as several layers of solute on the adsorbent surface (multilayers). They obtained the equation

$$P/(V(Po-P)) = 1/(Vm.C) + P(C-1)/(Po.Vm.C)$$

where V is the volume of gas adsorbed at pressure P,

Vm is the volume adsorbed in the first completed monolayer,



$$X = \frac{X_m bc}{1 + bc}$$

Figure 9. Langmuir adsorption isotherm illustrating monolayer adsorption with the solid having a maximum concentration of solute of Xm. This is also called an L-curve.

Po is the saturation pressure of the vapor

C is a constant = exp ((E1-L)RT)

where E and L are the heat adsorption in the first layer and the latent heat of condensation respectively. T is the absolute temperature and R is the gas constant.

A plot of P/(V(Po-P)) versus P/Po should be linear.

Adsorption Isotherms - Shapes

Studies of adsorption isotherms have indicated that their shapes may give some insight as to the nature and possibly the mechanism of the substrate-solute-solvent interactions, (Giles et. al., 1960, Giles 1970). This is of prime interest to those studying natural systems where many of the parameters are poorly understood, or even unknown.

It has been shown that for a given solute different shaped isotherms result from different combinations of solvent and substrate. The primary factors are the polar or non polar nature of the solvent and substrate as well of the polar nature or monofunctionality of the solute.

Giles et. al. (1960) proposed a fourfold division of adsorption isotherms based on the slope of the initial part of the curve, and a further subdivision according to the shape of the curve further from the origin.

The initial slope depends on the rate of change of site availability with increase in solute adsorbed. The plateau or inflection point on the curves represents the first degree of saturation, that is, further adsorption can only take place on new surfaces. If the adsorbed molecules of the monolayer are so oriented that the new surface they present to the solution has low attraction for more solute molecules, the curve has a long plateau. If they are oriented such that the new surface has high attraction for more solute, the curve rises steadily and has no plateau.

The four main classes of isotherms are:

L-curves--

These are the normal or "Langmuir" isotherms, Figure 9, and are characteristically convex near the origin. Thus the more solute taken up the less chance that a solute molecule will find a suitable site on which it can be adsorbed. The types of systems which give this curve have one of the following characteristics:

i. the adsorbed molecules are most likely to be adsorbed flat, or ii. adsorbed end on with little solvent competition, found in cases where:

- a. highly polar solute and substrate and a non polar solvent.
- b. monofunctional ionic substances with very strong intermolecular attraction.

H-curves--

These are high affinity curves in which the solute has such a high affinity for the substrate in dilute solution which is completely adsorbed, or at least there is no measurable amount remaining in solution Figure 10. This is usually indicative of chemisorption or ion exchange. The initial part of the isotherm is therefore vertical. The adsorbed species are either:

- i. large units such as ionic micelles or polymeric molecules, or
- ii. single ions with a high exchange capacity.

S-curves--

These curves describe those systems where the greater the amount of solute already adsorbed, the easier it is for aditional solute to become adsorbed. These curves are characteristically

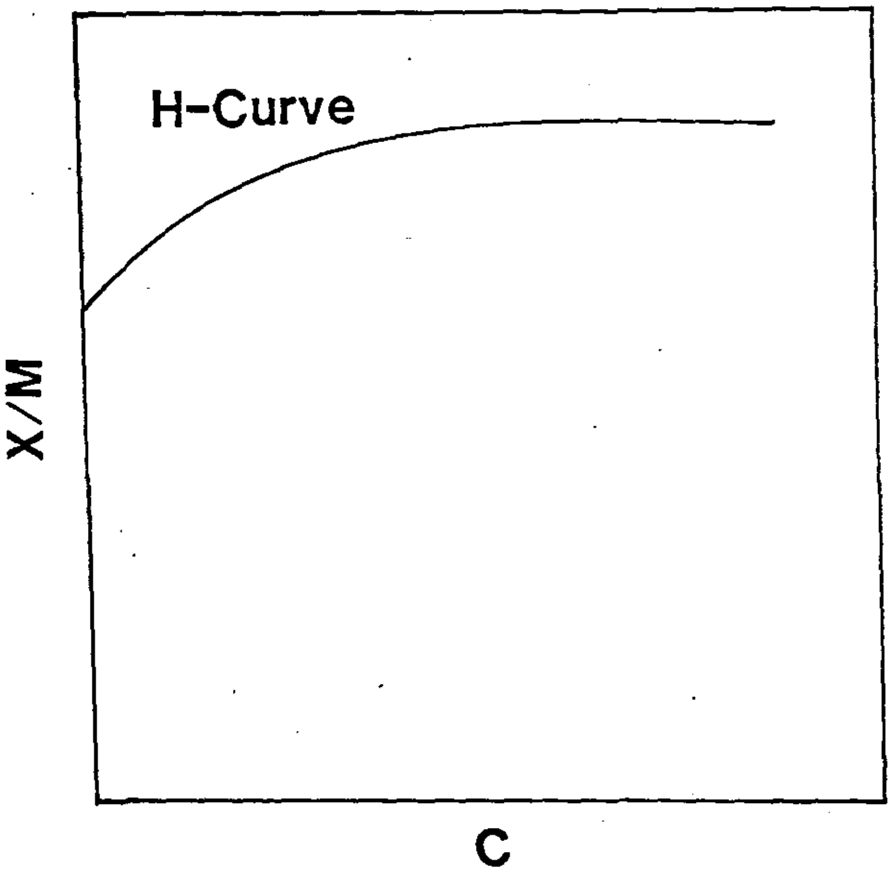


Figure 10. High affinity type of adsorption isotherm where the solute in dilute solution is completely adsorbed. This usually indicates chemisorption or ion exchange.

concave near the origin, Figure 11, and are generally considered to indicate the vertical orientation of adsorbed molecules at the surface. This is the typical adsorption isotherm for monofunctional solutes with moderate intermolecular attraction, adsorbed on a polar substrate from a polar solvent. It indicates a tendency for large adsorbed molecules to associate rather than to remain as isolated units. This has also been called co-operative adsorption.

C-curves--

These are constant partition curves or linear isotherms where the availability of sites remains constant at all concentrations up to saturation Figure 12. It is typical of the curve obtained for the partition of a solute between two immiscible solvents. The implication is that the solute is penetrating regions of the substrate that are inaccessible to the solvent.

It must be emphasized that isotherms may change in shape with a change in conditions. Thus the common organic chemical phenol, a monofunctional solute will give an S-curve from polar solvents such as water on polar substrates, an L-curve on polar

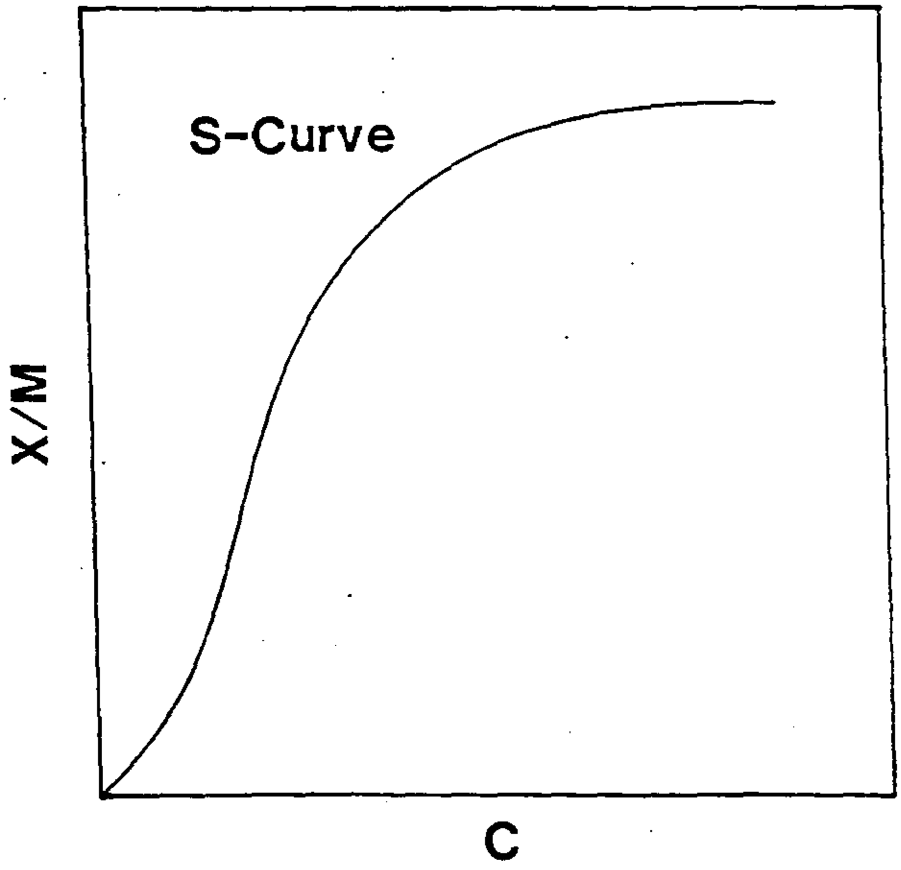


Figure 11. Typical S-curve where initially the greater the amount of solute already adsorbed, the easier it is for further solute to become adsorbed.

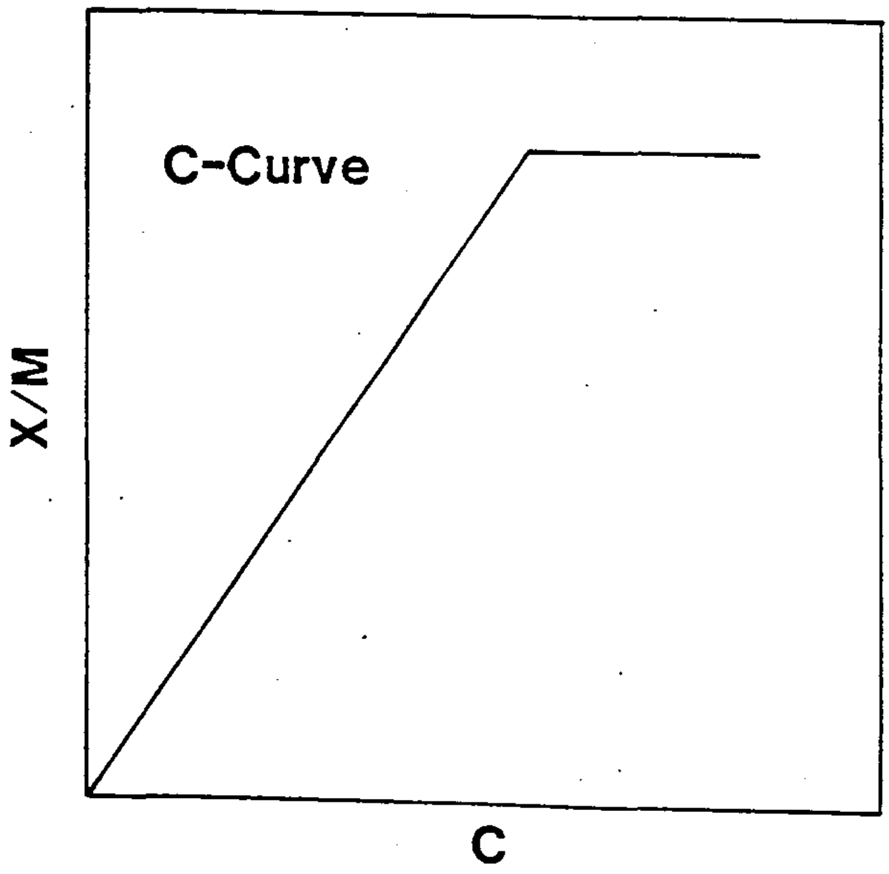


Figure 12. The C-curve or constant partition curve where the availability of sites remains constant at all concentrations up to saturation.

substrates from non-polar solvents and a c-curve on hydrophobic polymers from an inert liquid (which does not swell the substrate).

MASS TRANSPORT EQUATION

The primary purpose of the mass transport equation is to determine the concentration of a pollutant at a specified place after a specified time. Four different processes are incorporated into this equation:

1. advection or the transport of the pollutant at the ground-water velocity;
2. dispersion or the spreading of the concentration front because of aquifer inhomogeneity and molecular diffusion;
3. biodegradation or the disappearance of the solute because of microbial action;
4. adsorption or retention of the solute in the soil phase because of partitioning between the solid and liquid phases.

The only term to be discussed in this paper is the last one, adsorption.

Adsorption Term

The total mass of solute per unit volume of porous medium is the sum of the solute in solution plus that adsorbed on the soil. If the porous medium is 100% saturated with solution, the volume of solution per unit volume of porous media is equal to the effective porosity, n. Further the mass of soil per unit volume of porous medium is B, the bulk density. Thus if the total mass of solute per unit volume is Ct then

$$Ct\ (\text{total}) = n.C\ (\text{liquid}) + B.Cs\ (\text{solid}) \qquad (1)$$

where C is the solution concentration and Cs is the adsorbed mass concentration.

In general Cs is a function of C, that is, a relationship defined by the adsorption coefficient.

The change in the mass of solute adsorbed on the solid (Cs) with time can be expressed as

$$Cs/\ \ t \quad = \quad dCs/dC\ .\ \ C/\ t \qquad (2)$$

After combining (1) and (2) the change in total mass of solute per unit volume of porous medium with time is

$$Ct/\ \ t = n.\ \ C/\ \ t + B.dCs/dC.\ \ C/\ t$$

$$= \quad C/\ \ t(n + B.dCs/dC)$$

$$= n.\ \ C/\ \ t(1 + B/n.dCs/dC)$$

where the term $1 + B/n.dCs/dC \qquad (3)$

is defined as the retardation coefficient Rd.

Thus $Ct/\ \ t = Rd.n.\ \ C/\ t. \qquad (4)$

The Retardation Coefficient

This coefficient as defined in (3) above contains two readily obtainable terms n, the effective porosity and B the bulk density of the soil. The third variable is the ratio dCs/dC, which is derived from the adsorption coefficient, Kd.

Thus the retardation coefficient, Rd = 1 + Kd. B/n , represents a ratio of the velocity of the water over the velocity of the solute. Thus if a solute having a retardation Rd = 10 has travelled 10 ft., the water has travelled 100 ft.

The reciprocal of Rd which is the chemical Rf factor is more readily understood because solute movement is defined in terms of the water movement. That is, during the time that water has moved a distance x the solute has moved a distance Rf times x. Thus assuming an Rf of 0.1 and a water movement of 100 ft. the solute has moved 100 x 0.1 = 10 ft.

APPLICATION TO THE SOIL-SEDIMENT SYSTEM

Once a general understanding of adsorption chromatography is obtained, it must be applied to the problem of predicting the rate of movement of chemical pollutants in the soil-sediment environment. The mobile phase is, of course, water, and the solid phase is soil. Soil is a complex multiphase system where components vary considerably from one area to another. The three solid phase constituents most likely to be important in the adsorption reactions are soil organic matter, clay minerals and amorphous hydroxides of iron, aluminum, and manganese.

Soil organic matter (SOM) is a mixture of complex organic polymers of doubtful composition that is generally assumed to have a large number of phenolic -OH and carboxylic acid groups attached to it. It may be physically and chemically separated into three main components: alkali soluble fulvic and humic acids, and insoluble humin. The interactions between the soil organic matter-clay minerals and amorphous hydroxides that may affect the adsorption chracteristics are essentially unknown.

A vast amount of literature has developed over the last three decades on the adsorption of organic compounds (primarily herbicides and pesticides) by soil components. In 1954, Sherburne and Freed published one of the earliest papers to report experimental data that showed an unequivocal correlation between adsorption of a specific organic compound and soil organic matter. Since then many papers have been written expanding the number of organic compounds for which this relationship holds true.

Normalized Adsorption Coefficients

Recently, it has become a fairly common practice to normalize adsorption coefficients obtained from soils to their organic matter or organic carbon content, as in the following equation.

$$Koc = K.100/ \%OC$$

where Koc is the normalized adsorption coefficient and K is the adsorption coefficient obtained using a soil containing OC% organic carbon.

The sorbing medium is thus considered to be the soil-organic matter rather than the total mass of soil. Lambert (1967), Furmidge and Osgerby (1967) normalize to %SOM whereas Karickhoff normalizes his distribution coefficient to percent of organic carbon. It has been found empirically that soil organic matter contains 58% organic carbon and thus Koc can be derived from Ksom.

Although soil organic matter has been shown to be the primary factor in many adsorption experiments, it is not the only one. Subsequently in 1960, Leopold et. al. showed that for 17 of the chlorinated derivatives of phenoxyacetic acid there was a strong inverse correlation between their adsorption and solubility. In a more practical mode, Harris (1964) noted that whereas in most soils the adsorption (inactivation) of insecticides is proportional in the organic content of the soil, in dry soils, this inactivation is related to the adsorption capacity of the mineral fraction. Bailey & White (1964) presented the first review of the adsorption and desorption of organic pesticides by soil colloids; including soil organic matter, clays, and amorphous hydroxides. A considerable discussion on the effect of soil moisture is included in this review.

Stevenson (1976) reviewed many aspects of organic matter-pesticide reactions in soils. His discussion is based on the premise that adsorption by organic matter has been shown to be a large factor in the behavior of many pesticides in soil. He also stated that the mechanisms of pesticide-organic matter interactions will remain obscure until more is known about the nature of chemical composition of the organic fraction of soils.

Stevenson also divides soil organic matter into humic and non-humic fractions, discusses the probable structure of humic and fulvic acids and speculates on organic matter-clay interactions' suggesting that they may function more as a unit than as a separate entities, even though the clay still provides an organic surface for adsorption.

He emphasizes that although it is commonly believed that soils differ greatly in their organic matter contents, it is not generally appreciated that major qualitative differences also exist.

Various adsorption mechanisms are also discussed in some detail. Khan (1978) further reviews the nature and classification of pesticides and various mechanisms that have been proposed for their adsorption by soil organic matter.
For example, 2-4D is strongly adsorbed by humic acid although the effect of illite may be important (Hague, 1975). Similarly - napthol is primarily adsorbed by soil-organic matter although a high montmorillonite/soil-organic matter ratio has a significant effect on the adsorption isotherm (Hasset et. al., 1981).

Estimates of adsorption coefficients

Estimates of adsorption coefficients are commonly attempted by using parameters, such as solubility, or simplified techniques, such as octanol/water partition coefficients rather than the difficult and time consuming determination of adsorption isotherms.

Solubility--

Some solubility estimates are Cassidy (1951), who remarks that many investigators have noted that the solubility of a substance in a given solvent may be expected to affect its absorbility. He further cautions that correlations between solubility and adsorption onto a solid surface should not be expected unless the adsorbent does not play a role in the process.

Various equations have been prepared for this relationship. Lundelius, 1920 (Cassidy 1951) proposed that the Freundlich K is inversely proportional to the solute in question i.e.

$\log K = A-n \log S$ where n is the Freundlich exponent).

The constants in the equations are largely dependant on the solubility units used and to a lesser extent on the group of compounds investigated.

Kenaga and Goring (1978) collected data for 106 organic chemicals, primarily pesticides, and obtained a regression equation.

$$\log K_{oc} = 3.64 - 0.55 \log S \text{ (ppm)}$$

S was reported in ppm. They estimated the results would be within +1.23 orders of magnitude from the actual value, assuming 95% confidence limits.

Chiou et. al. (1979) obtained a relationship between distribution coefficients and solubility for a large number of nonionic organic compounds. Their relationship covers more than seven orders of magnitude in S and four orders of magnitude in Koc. They found that: $\log K_{som} = 4.040 - 0.557 \log S$ (micromoles/liter) where S is in micromoles/liter. Assuming that SOM = 58%oc,

$$Koc = 3.80 - 0.557 \log S.$$

Karickhoff et. al. (1979) found the relationship to be

$$\log Koc = 0.44 - 0.54 \log S \text{ (mole fraction)}$$

where S is expressed as a mole fraction, and only hydrophobic compounds such as aromatic hydrocarbons and chlorinated hydrocarbons were considered.

Means et. al. (1980) found a relationship

$$\log Koc = 4.070 - 0.82 \log S \text{ (mg/ml)}$$

where S is in mg/ml.

Karickhoff (1981) gives

$$\log Koc = - 0.197 - 0.594 \log S \text{ (mole fraction solubility)}$$

where S = mole fraction solubility. Karickhoff also recommended the incorporation of a crystal energy term in the equation.

Octanol-water partition coefficients--

The partitioning of a solute between water an an immissible organic solvent has been used extensively to estimate biological concentration tendency solutes. Generally, octanol-water partition coefficients are those most commonly measured and Leo et. al. (1971) made an extensive compilation of these coefficients in 1971.

Ward and Holly (1966) found a linear relationship between amount of sorption and the degree of partitioning between cyclahexane and water of S- triazines. They showed this to be a better index of sorption for these compounds than their solubilities.

Chiou et. al. (1977) used octanol/water partition coefficients to obtain better estimates of solubility, that is,

log Kow = 5.00 - 0.670 log S (micro moles/ liter)

where Kow equals the octanol/water partition coefficient and S equals the aqueous solubility in micro moles/ liter. These equations were found to be valid over 6 orders of magnitude in Koc (10 - 10**7).

Karickhoff et. al. (1979) examined 10 hydrophobic pollutants with water solubilities ranging from 1 ppb to 1000 ppm and obtained excellent correlations of Koc versus Kow and poor correlation between Koc and solubility. One of the following equations was suggested:

log Koc = 1.00 log Kow - 0.21 or Koc = 0.63 Kow

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Means et. al (1979) obtained similar partition coefficients for pyrene and DMBA respectively

$$K_{oc} = .53\ K_{ow} \text{ and } 0.50\ K_{ow}$$

Banerjee et. al. (1980) correlated n-octanol/water partition coefficients with solubility and found that

$$\log K_{ow} = 5.2 - 0.68 \log S \text{ (micro moles/ liter)}$$

Where S is in micro moles/ per liter. For solids with known melting points they suggest

$$\log K_{ow} = 6.5 - 0.89 \log S - 0.015 \text{ (mp)}$$

Chiou and Schmedding (1980) state that most inaccurate data on water solubility and partition coefficient are generated with impure compounds or solvents. They discuss methods of ensuring purity of phases and suggest at a minimum that a melting point of a solid phase is minimal and that poor phase separations or persistant emulsions are often an indication of undesirable solvents. Experimentally they found, for 36 organics that ranged over 6 orders of magnitude, that

$$\log K_{ow} = -0.862 \log S \text{ (moles/ liter)} + 0.710$$

with S is moles/ liter.

Kenaga and Goring (1980) obtained the relationship following relationship for 45 organics:

$$\log K_{oc} = 1.377 + 0.544 \log K_{ow}$$

Karickhoff (1981) obtained the equation for hydrophobic solutes: $\log K_{oc} = 0.989 \log K_{ow} - 0.346$.
The near unity of the coefficient suggest that $K_{oc} = 0.411 K_{ow}$ is a good approximation.

Briggs (1981) gives the relationship

$$\log K_{om} = 0.52 \log K_{ow} + 0.64.$$

He presents the data of Felsot and Dahn (1979) in the form,

$$\log K_{om} = 0.52 \log K_{ow} + 0.78$$

the data of Lord et. al. (1978) as,

$$\log K_{om} = 0.53 \log K_{ow} + 0.98$$

and his own earlier data as

$$\log K_{om} = 0.52 \log K_{ow} + 0.62.$$

Brown and Flagg (1981) found another empirical equation for 9 compounds:

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006.$$

Soil Thin Layer Chromatography (TLC)--

A direct method for determining retardation of pesticides in soil termed "soil thin-layer chromatography" was proposed by Helling and Turner (1968). This quantitative index of relative pesticide mobility which is based on Rf values, correlated well with published data on movement.

Further refinements of this technique were published by Helling (1971a) together with applications (Helling, 1971b), as well as the influence of soil properties (Helling, 1971c). One correlation found, was that pesticide mobility tended to be directly related to increased water flux.

A comparison of the various methods for determining the mobility of organic pollutants in the laboratory reveal that TLC is one of the least expensive techniques (Helling and Dragun, 1980).

High Performance Liquid Chromatography (HPLC)--

McCall et. al. (1980) suggested that the retention time on HPLC may be directly related to a Koc value.

Integration of the Concepts with the Mass Transport Equation

The primary objective of the preceding discussion is to describe chramotographic movement, the role of the adsorption coefficient, and the various methods of obtaining estimates of this parameter. In this section the manner in which the adsorption coefficient is integrated into the mass transport equation is examined.

Retardation Coefficient--

The retardation coefficient term in the mass transport equation contains the variable dCs/dC, which is directly related to the adsorption coefficient. It equals Kd in the linear case but the relationship becomes more complex for non-linear isotherms. In the linear case where

$$Cs = Kd.C$$

$$dCs/dC = Kd$$

the adsorption obeys the Langmuir isotherm:

$$Cs = Kd.Cm.C/(1 + KC)$$

where Cm is the limiting concentration when the monolayer is filled: $dCs/dC = Kd.Cm/(1 + Kd.C)**2$

In the Freundlich case where

$$Cs = Kd.C**n$$

POROSITY = .2 DENSITY = 2.65 % OC = .1

CHEMICAL	Koc	KD	R	Rf x 52800 ft	Rf
DICAMBA	0.4	0.00	1	52577	0.996
2-4 D ACID	20.0	0.02	1	43564	0.825
PARATHION	24.0	0.02	1	42092	0.797
ETHYLENE DIBROMIDE	44.0	0.04	1	36007	0.682
2-4-5 T	53.0	0.05	2	33807	0.640
BENZENE	83.0	0.08	2	28088	0.532
ALDRIN	410.0	0.41	5	9877	0.187
LINDANE	911.0	0.91	11	4955	0.094
NAPHTHALENE	1300.0	1.30	15	3572	0.068
HEXACHLOROBENZENE	3914.0	3.91	42	1243	0.024
PARAQUAT	15473.0	15.47	165	320	0.006
ANTHRACENE	26000.0	26.00	277	191	0.004
METHOXYCHLOR	80000.0	80.00	849	62	0.001
PHENOL	82000.0	82.00	870	61	0.001
PYRENE	84000.0	84.00	891	59	0.001
DDT	238000.0	238.00	2524	21	0.000
224444 HEXACHLOROBIPHENYL	1200000.0	1200.00	12721	4	0.000

Table 1. Examples or retardation coefficients. Organic chemicals having a wide range of K_D values showing their retardation and R_f values. The calculations assume a porosity of 0.2, a rock mineral density of 2.65 and 0.1% organic carbon.

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dCs/dC = n.Kd.C**(n-1)

Retardation Calculations--

Assuming linear isotherms, a pore fraction n and a bulk density B, the retardation Rd = 1 + Kd .B/n
and as B = D(1 - n) where D = specific gravity of rock minerals.
Koc is defined as 100.Kd / %oc therefore,

Kd = %oc.Koc/100

the retardation Rd becomes Rd = 1 + (1-n) . Koc.%oc/(100.n)

As a guide, a number of organic chemicals with normalized adsorption coefficients ranging 8 orders of magnitude are listed in Table 1. With these data are listed the calculated Kd value for 1%oc, retardation coefficients Rd, Rf values and the amount they may be considered to have moved if the water moved a distance of 10 miles. It must be understood that linear adsorption is assumed, and that degradation and diffusion are ignored.

SECTION 2

SUMMARY AND CONCLUSIONS

The following concepts must be considered when examining pollution movement: 1) chromatography, which is the process whereby differential solute movement results when a solution moves through a porous solid, such as when polluted groundwater moves through sediments; 2) adsorption, which is described quantitatively by an adsorption isotherm (a graph of the amount of material, in this case a pollutant, absorbed/ gram by the solid versus the concentration of the pollutant in solution)--the constant in the equation describing this graph is known as the adsorption coefficient; and 3) mass transport equation, which enables the concentration of a pollutant to be determined at a specified place after a specified time. This equation incorporates estimates of ground water velocity, disfusion, biodegradation, and adsorption-

It is generally implied that for hydrophobic pollutants soil organic matter, clay minerals and possibly amorphous hydroxides are the primary earth materials that influence the attenuation of organic pollutants in the subsurface environment. One of the primary objectives of our present research is to establish the distribution of these materials both vertically and areally and to obtain quantitative estimates of these compounds in a wide number of samples. Because the materials being studied are some of the most complex in nature and because of the difficulty of determining the behavior of pollutants in contact with soil, the soil and its components must be characterized, or at least catagorized. The inorganic parts consist of clays, amorphous hydroxides and oxides. The organic fraction, on the other hand, is composed of literally millions of complex organic compounds generated from the chemical and biological degradation of plant and animal residues. These compounds are known collectively as soil organic matter (SOM), or humic substances.

These inorganic and organic fractions can form complexes with each other, and with toxic wastes (both organic and inorganic) and thus they affect the transportation, concentration and distribution of any toxic materials in contact with them.

Scanning electron microscopy is a common method of characterizing clay minerals from the deeper subsurface, but the dehydration of soil organic matter in soils without destroying their structure is difficult at best and probably will require special freeze drying equipment. Quantitative x-ray diffraction is a viable method for simple mixtures of well crystalline compounds, but it becomes at best semi-quantitative for multicomponent mixtures, and next to useless for amorphous or poorly crystalline materials such as some clays, natural organic matter and amorphous hydroxides. Fourier Transform Infrared Spectrometry although used extensively to characterize extracted humic and fulvic acids lacks the sensitivity to detect the much smaller amounts present in unextracted soil samples. Raman microprobe techniques can yield molecular bond information that is not obtainable by conventional techniques. Information on the molecular nature of the components of a sample, the distribution in the sample, and the chemical and physical character of the matrix are characteristics that may be explored.

CHROMATOGRAPHY

Chromatography is the name given to the movement of a dissolved chemical compound whose solution (mobile phase) moves through a porous solid (stationary phase). The process that controls the rate at which the compound moves relative to that at which the solvent moves is called adsorption if the stationary phase is a solid, or partition of the stationary phase is a liquid. Three types of solute movement can occur depending on whether or not the mobile phase is a pure solvent, a solution of the solute added continuously or a solution of a substance more strongly adsorbed than the solute(s) under investigation. If the mobile phase is a pure solvent, the shape of the moving adsorption band depends on the Freundlich exponential coefficient. If this is less than 1 a tail develops on the eluted solute band. If the solution of solute is added continuously, once equilibrium is attained, the effluent from the system becomes identical in composition to the solution entering the system. When the mobile phase contains a substance more strongly adsorbed then any of the compounds of the mixture the solutes resolve themselves into bands that move at the same rate as the mobile phase. The order of these bands is the order of the strength of adsorption and each band acts as a displacer of the less adsorbed component ahead of it.

ADSORPTION

Adsorption is generally considered to be the result of two processes, a lack of affinity of the solute for the solvent or an affinity of the solute for the solid. The first explains the inverse relationship between adsorption and solubility, the second includes the various types of surface phenomena such as physical adsorption, chemisorption and exchange adsorption. Experimental determination of adsorption result in a graph known as an adsorption isotherm, a plot of the amount of material adsorbed on the adsorbent versus the concentration of the solute in solution. If the amount adsorbed is independent of concentration in solution it is termed a linear isotherm. Non linear relationshps are usually defined by an exponential function, the Freundlich isotherm. The shapes of adsorption isotherms may give some insight as to the nature and possibly the mechanics of the adsorption interactions.

ADSORPTION - APPROXIMATIONS

One of the more confusing issues that may confront an investigator trying to obtain an approximation to an adsorption coefficients is the diversity of units used in the various equations.

The adsorption coefficient may be obtained from data using mass units or using mole units, if the isotherm is linear it will not matter which, however, if n is not equal to 1 then

$$K(\text{moles}) = K\ (\text{mass}) \times Mn/M$$

where M is the molecular weight of the compound (Osgerby, 1970)

The adsorption coefficient may refer to the total weight of soil or it may be

(i) normalized to the organic matter content

$Ksom = K/(\%SOM)$, or

(ii) normalized to the organic carbon content

$Koc = Ksom/1.724$

assuming 58% oc in SOM.

If the adsorption coefficient is to be derived from solubility data then it should be determined what units the solubility data are in and what the correlation equation uses. They may be expressed in mg/l, micromoles/l, or mole fraction.

$$\text{micromoles/l} = \text{mole fraction} \times 55.56 \times 103$$

$$\log S(\text{micromoles/l}) = \log S(\text{mole fraction}) + 4.74$$

As a guide, the various equations advanced for obtaining Koc from solubility have the form

$$\log Koc = A - B \log S$$

If S is in micromoles/liter

$A = 3.6$ to 5

$B = .54$ to $.59$

The equation for obtaining Koc from the octanol water partition coefficients have the form

$$Koc = C\ Kow$$

where $C = .4$ to $.6$

MASS TRANSPORT EQUATION

The mass transport equation is that equation used to determine the concentraion of a pollutant at a specified place after a specified time. The four processes incorporated in it are advection, dispersion, biodegradation and sorption. Only the latter is discussed here.

RETARDATION

The sorption term in this equation is defined as the retardation coefficient (Rd) that is

$$Rd = 1 + B/n.\ dCs/dc$$

where B is the bulk density of the soil, n is the effective porosity, and dCs/dC is the change in adsorption with concentration of pollutant. It is usually assumed that adsorption is linear and that

$$dCs/dC = Kd$$

where Kd is the linear adsorption coefficient, and therefore,

$$Rd = 1 + BKd/n$$

The chromatographic Rf factor is defined as the velocity of the point of maximum concentration of the solute over the average linear velocity of the ground water that is Rf = 1/Rd for linear isotherms.

A direct determination of the Rf value, the reciprocal of R_d, may be obtained using soil thin layer chromatography.

METHOD DEVELOPMENT

Soil organic matter, clay minerals and possibly amorphous hydroxides are the primary earth materials that influence the attenuation of organic pollutants in the subsurface environment. One of the primary objectives of this research is to establish the distribution of these materials both vertically and areally, thus it is imperative to be able to obtain quantitative estimates of these compounds in a wide number of samples. Although methods have been reported in the literature for these compounds none are really satisfactory because of the number of assumptions made in the methodology, or because of the specific nature of our samples. For example, quantitative x-ray diffraction is a viable method for simple mixtures of well crystalline compounds, but it becomes at best semi-quantitative for multicomponent mixtures, and next to useless for amorphous or poorly crystalline materials such as some clays, natural organic matter and amorphous hydroxides. Similarly, organic matter determinations often contain an arbitary factor, which will vary from site to site. Further a lack of sensitivity is common when fractions of a percent are present. The determination of amorphous hydroxides depends primarily on differential solution which is complicated by the fact that some clays also dissolve under these conditions and if the hydroxides become partly microcrystalline their solution characteristics also change.

Thus the materials being studied are some of the most complex in nature. In order to begin to understand the difficulty of determining the behavior of pollutants in contact with soil, the soil and its components must be characterized, or at least catagorized. And, the soil components are easily catagorized into inorganic and organic parts. The inorganic parts consist of clays, amorphous hydroxides and oxides, and any trace elements which may be present in the particular area.

The organic fraction, on the other hand, is composed of literally millions of compex organic compounds generated from the chemical and biological degradation of plant and animal residues. These compounds are known collectively as soil organic matter (SOM), or humic substances.

These inorganic and organic fractions can form complexes with each other, and with toxic wastes (both organic and inorganic) and thus they affect the transportaion, concentration and distribution of any toxic materials in contact with them. They are the "chromatograph" stationary phase to the mobile phase of the toxic materials of interest. As such, their properties are of considerable interest.

CHEMICAL METHODS

Inorganic Fractions

1) Clays: These fine grained, crystalline, poorly crystalline or amorphous compounds are of particular importance in geochemistry due to their singular ability to form complexes with toxic organics and with SOM. This ability is an effect of both composition and surface area.

Depending on the type of clays, their amounts, and the pH of the fluid phase clays are known to have negatively charged sites, and so can accomodate cations, or positively charged ions on their surfaces (Brady 1974) which can be exchanged with other cations of greater affinity just as is done in a laboratory column with ion exchange chromatography. The clays are characterized in this respect by analyzing for the cation Exchange Capacity (CEC).

2) Amorphous Hydroxides: These are the oxides and hydroxides of various common metals, with those of aluminum and iron being the most universally found as soil constituents (Brown et. al., 1978). They are found intermixed with the silicate clays; a good example being the hydroxide allophane which is an amorphous combination of silica and aluminum. These hydroxides and oxides are often insoluble collodial materials, which like clays, accumulate negative charges, and thus exchangeable cations on their surfaces. Little work has been done on the interactions of these hydroxides with clays, som, or organics.

Organic Fractions:

The SOM or humic substances are widely distributed in soils, natural waters, marine and lake sediments, peat, lignite, oil shales, and coal (Stevenson and Goh, 1971). They have the ability to act as pH buffers in the soil and are important to the transportation and concentration of a variety of mineral substances (Stevenson and Butler, 1969) and heavy metals (Kononova, 1966). These compounds which are produced in soils range from yellowish to black in color and have molecular weights which range from 500 to 300,000 (Schnitzer and Kahn, 1978)

Total organic carbon or percent organic matter are merely different ways of reporting the amount of carbonaceous material present in a sample of SOM. They are actually estimates based on an assumption that fifty eight percent of the SOM is organic carbon.

In addition, it was found in the literature that since the decomposition of the soil organic matter is not 100% efficient a factor (f) is added to make up the difference. Choosing a value for htis factor is based on the experimenter's experience and also must vary from area to area. Since the soils tested reflect different soil orders as well as different areas, direct comparison of results probably not warranted. The TOC and POM measurement can be made either by 1) combustion techniques involving the collection of the evolved CO2, 2) gravimetric combustion, as with the plasma ash furnace, or 3) by oxidation-reduction reactions involving the oxidation of the SOM by excess dichromate ion followed by a titration to determine the amount of unreacted dichromate ion left after the reaction (Allison, 1965).

1) The combustion techniques such as using a LECO furnace initially involve the removal of the inorganic carbonates, followed by the combustion of the sample , trapping the CO2 and measuring the amount evolved.

2) The plasma ash technique is a method for completely oxidizing carbonaceous materials at a low temperature. The primary advantage of this technique for this study is that the clay minerals and amorphous hydroxides should be minimally affected due to the lower temperatures maintained during the ashing of the organic fraction of the soil. Major disadvantages is the inaccuracy in the weighing and the long time for the combustion to go to completion.

3) The dichromate oxidation procedure is generally the most convenient method but partial oxidation is still a major analytical problem.

Cation Exchange Capacity (CEC) and Exchangeable Cation Determination
(ECD)

Clays, amorphous hydroxides, and SOM all have the ability to attract and adsorb soluble cations present in the soil. These cations 'adhere' to the negatively charged sites present on the various soil fractions. The bonds are probably of the van der Waals tyupe and so are not permanent, and so are "exchangeable". The number of negatively charged sites as found by the CEC and the types and concentrations of the actual exchangeable cations present may help determine the susceptability of an organic chemical to 'adhere' to a soil particle.

INSTRUMENTAL METHODS

The instrumental techniques utilized in this study have been scanning electron microscopy (SEM) to observe the shapes and distributions of soil constituents, including SOM; x-ray diffraction for the qualitative and quantitative analysis of the crystalline soil constituents; Fourier Transform Infrared Spectroscopy (FTIR) and Raman Microprobe, for the molecular bond characterization of soil constituents.

SCANNING ELECTRON MICROSCOPY

Numerous researchers have studied various aspects of soil formation, micromorphology, and mineralogy using the SEM, but few have included an examination of soil organic matter.

The examination of the soil using scanning electron microscopy without some type of freeze drying invariably led to spattering when probed by an electron beam. With the freeze drying techniques we used, including rapid cooling in liquid nitrogen before the actual freeze drying no obvious organic structures were observed. This led us to the conclusion that the only way that this technique could be used was using the technique advocated by Gilliott (1969) who concluded that a quick-freeze followed by a freeze-drying at less than -130 C is the most effective method for preserving the original soil structure without creating ice artifacts on the sample (a technique used extensively on biological specimens). The drawbacks to this technique are that it is a very slow process, and that it would involve the purchase of some expensive state -of -the -art equipment.

X-RAY DIFFRACTION

Powder x-ray diffraction analysis is an excellent technique for the quantitative analysis of simple crystalline-mixtures. The intensity of each component's pattern is proportional to the amount present, except for a correction factor due to absorption. If a mixture contains both a weak absorber and a strong absorber the signal due to the weak absorber will be attenuated, while the peaks of the strong absorber will be even further enhanced over those of the pure unmixed samples, even if those are run under identical conditions. This differential absorbtion is not random and calculations may be made which will predict characteristic absorption coefficients for separate components.

The method used for quantitative x-ray diffraction analysis is the one developed by Hooton and Giorgetta (1977) who assume that a constant for an instrument with a given configuration and with a constant Beam intensity can be determined for each mineral. If it is assumed that the sum of the weight fractions is equal to 100% then it is possible to determine weight fractions of individual components, without references to calibration curves and mixing standards. An easy method to determine relative values of H is to select one mineral as a reference standard, assign a value to H for that mineral, and determine H for all other minerals by mixing them in known proportion with the standard and using the appropriate equations.

Quantitative x-ray diffraction using an external standard system requires extreme machine stability and the availability of pure samples of all the constituents. This is not the case when one is dealing with mixed layer clays, or those that are not perfectly crystalline. This unfortunately is the usual case with soil clays. The final limitation is the presence of amorphous constituents in the sample, especially those like amorphous oxides and hydroxides of iron and manganese which are particularly string absorbers, and which in addirtion give rise to fluorescence effects.

SPECTROMETRY

Whereas X-ray diffraction is a result of the total crystal structure, infrared spectroscopy looks at individual bonds, making it one of the few tools available for characterizing amorphous constituents such as natural organic matter, amorphous hydroxides and synthetic organic pollutants.

FOURIER TRANSFORM INFRARED SPECTROMETRY - FTIR

A recent development of infrared spectroscopy is the availability of Fourier Transform Infrared Spectroscopy (FTIR) which has higher sensitivity than the older wavelength instruments as well as having computerized data manipulation capabilities including spectral stripping. The latter is essentially the non-chemical separation of mixtures using difference or subtraction spectroscopy.

Common FTIR instrumental configurations are simple specular reflectance, attenuated total reflectance (Harrick, 1981), photo-accoustics (Rockley, 1980, Rockley et. al. 1981, and Krishnan, 1981), diffuse reflectance and transmission methods.

The spectral reflectance or attenuated total reflectance method although very fast was prone to severe absorption effects that dramatically distorted the spectral peaks (Christiansen effect); the photoacoustic detector lacked the sensitivity essential for the concentrations we were seeking and required too long a purging time; the diffuse reflectance method required too great a dilution such that the resulting sensitivity was inadequate for our purpose. Standard transmission FTIR techniques using pressed KBr pellets were tried and high quality spectra were obtained in a relatively short time, primarily determined by the sample preparation time . Given all the previous considerations, this measurement technique is probably the optimum choice. In summary the presence of moisture in the samples was a major problem, and the method essentially lacked the sensitivity to detect natural organic matter less than about 1%.

The conclusion is that the examination of clay-SOM-organic-pollutant complexes will require the thorough purification and characterization of various humic and fulvic acids and that the spectroscopic measurement of chemical bonds formed between pollutants and the substrate--what ever these bonds are--will be mandated to define the mechanism for chemical adsorption from ground waters. This research will be a tedious and difficult with a low probability of success.

LASER RAMAN MICROPROBE

The most recent addition to the study is the Raman Laser Microprobe, which is ideally suited to the examination of soil organic material and some of the other soil inorganic components.

Major advantages of the Raman method are that it is nondestructive and requires little sample preparation time. Sample may be analyzed in situ. It is molecularly specific, and samples may include all states of matter, and thus any type of molecule organic, inorganic, or biological may be identified. Further, it does not require the use of a vacuum or other type of sample pretreatment. One final advantage is that water, which is a major limitation of Infrared technique, exhibits only a very small Raman signal, and it does not matter if the sample contains or is examined in water.

Major limitations of the Raman method are the inherent weakness of the Raman effect, the weak signals being difficult to detect and thus placing strenuous requirements on the spectrometer. Local heating effects caused by a buildup of heat in the sample from the laser radiation may exist, although examining the sample in water or by reduced laser beam intensity may ameliorate this problem. The weak Raman signal may be difficult to detect when the sample also emits flourescence. Using a quenching technique may eliminate the problem. Finally lack of standard reference spectra (because of the newness of the analytical technique) makes identification of unknowns more time consuming.

The Laser Raman Microprobe has been in use only a limited time and we have not as yet been able to carry out many of the investigations we hope to do. At this point we have made an effort to characterize some of the standard clays, including montmorillonite and several kaolinites. In time, we hope to be able to identify an adsorbed organic pollutant and to determine whether its substrate is an organic or inorganic fraction of the soil. Our immediate objective is to the mode of distribution of the natural organic matter in the various soil types.

The ultimate limits of detection, quantitation of individual species present, sample size, sample heating and fluorescence, and the compositional complexity of sample are questions whose answers must wait for increased understanding that will come from future studies.

SITE CHARACTERIZATION

To date four sites in various parts of the Continental United States have been chosen as study areas. These are: the former creosote waste disposal lagoon in Conroe, Texas, the D'Imperio Dump in Atlantic County, New Jersey, the Apple Creek drainage basin in Burleigh County, North Dakota, and north central Payne County, Oklahoma.

Various aspects of subsurface characterization are being considered in each area. The first two sites represent point-source ground water pollution problems where in-depth studies over restricted areas will be undertaken. The third site represents a region, where subsurface conditions on a greater areal scale will be examined. At the fourth site, a study of macropores and their effect on the transmission of surface recharge to a ground water system is being conducted.

SECTION 3

RECOMMENDATIONS

The primary emphasis for the next phase of this reseach is to conduct a series of experiments using the Raman Microprobe, as the instrument has only been on line as of February 1984. The Ramanor U-1000 Laser Raman Microprobe is an instrument which combines the high information content characteristic of the Raman vibrational spectra with the ability to microscopically examine individual areas of homogeniety in a macroscopically heterogeneous sample. This type of instrument under specific circumstances can be a very powerful tool in the investigation of the fate or organic pollutants in the soil.

The Raman Microprobe does have its limitations. One of these difficulties is one common to all spectroscopic methods, and it is in the analysis of very complex mixtures. As is the case with all similar methods, a Raman spectrum of a mixture is a summation of all the symmetric vibrational modes of each component. The situation is further complicated if two or more of the components have identical functional groups. The same functional groups will absorb vibrational energy at the same frequencies. The intensities of these bonds is simply the summation of the intensities of each.

There are various software packages which are able to deconvolute complex mixture spectra. These rely on the ability of a computer to recognize and identify absorption patterns and then to subtract that pattern from the mixture spectrum. The next pattern is then identified from the resultant spectrum, an operation made easier by the previous subtraction, then it too is subtracted. This can be done with a mixture of perhaps as many as fifty spectra in the most advanced routines (R. Kroutil, 1983). Unfortunately all of these routines depend on computer libraries of known compounds. This means that if any of the compounds in the mixture are not in the computer library, they will either not be identified or mis-identified, depending on the routine. Further, all of these advanced routines, to date, are tailored for infrared spectra only. Because of this, we feel that it is much more promising at this time to use the Microprobe to determine fundamental interactions between specific organic compounds, cations and water with specific soil components.

Clay studies: It is well known that soils and clays complex with both cationic and organic species (Theng, 1974). These adsorptive interactions in soils are the summation of the interactions of each component, the clays, amorphous hydroxides, and the soil organic matter. Of the three, the first two are the easiest to approach with the Raman Microprobe at this time. The following recommendation is designed to determine the extent, location, and type of bonding of species adsorbed on clays, and later, amorphous hydroxides. If the type of bonding between a specific clay and the specific functional group of a known organic compound can be determined, a solidly based estimate of the adsorptive retentiveness of that clay to an organic pollutant having that functional group should be obtainable.

For this approach, the Raman Spectra of the clays, without interlamellar species, and with specific replaced species must be fully characterized and compared, as has been done in the case of zeolites (Egerton et al. 1976).

For our model organic adsorbed species we plan to use pyrene to determine the bond type (Hendra et al. 1971) and a yet to be determined nitrophenol species, a pollutant metabolite which should be detectable at very low concentrations due to the resonance Raman effect (Grasselli, Snavely and Bulkin, 1981).

We have already begun to characterize montmorillonite clays for this purpose. These clays have been stripped of the naturally included cations and have been replaced with ammonium, calcium and sodium ions. This study will be continued with the model organic compounds and expanded to include the amorphous hydroxide and oxide soil fractions. The effects of adsorbed water will be investigated with each sample. Finally, the identity of each species will be established with the powder x-ray instrument.

An expansion of the more fundamental clay study will be to map the distribution and retention of an organic model compound on completely characterized but natural clay-bearing sandstones or completely characterized soil beds. The organic model compound will be chosen so as to make use of the enhancement gained by the resonance Raman effect. This should allow us to test the results of the clay study on natural, but well characterized soils. We expect to do this study in conjunction with the efforts at the RSKRL on soil column leaching.

Microorganism-Pesticide Study

A further recommendation is the investigation of pesticide bioaccumulation in native soil microorganisms. It is known that some microorganisms such as colpidium Campylium (Delhaye et al. 1979) accumulate and concentrate organic pesticides in their digestive vacuoles.

This should allow the aeral mapping of some pesticide types as well as pesticide metabolites with the use of the Raman Microprobe. The microorganisms could accumulate the pesticides from originally unmeasurable concentrations to concentrations detectable by the microprobe. This particular type of study is admirably suited to microprobe analysis with the aid of the high power microscopic objective and directly without extraction. Populations of the target organism and their pesticide up-take ability could not only give an estimate of the pesticide concentration, its location over the ground surface, but also could help determine the rate of the biometabolism of the pesticide to some less toxic metabolite.

Spectral Library

In conjunction with these studies we expect to accumulate a library of Raman Spectra of soil components , basic mineral types, and common pollutants and their metabolites. The identity of these standard samples will be confirmed by their powder x-ray spectra in order to insure accuracy.

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SECTION 4

METHODS DEVELOPMENT

In an earlier chapter it was shown unequivocally that soil organic matter, clay minerals and possibly amorphous hydroxides are the primary earth materials that influence the attenuation of organic pollutants in the subsurface environment. Considering that one of the primary objectives of this research is to establish the distribution of these materials both vertically and areally, it is imperative to be able to obtain quantitative estimates of these compounds in a wide number of samples. Although methods have been reported in the literature for these compounds none are really satisfactory because of the number of assumptions made in the methodology, or because of the specific nature of our samples. For example, quantitative x-ray diffraction is a viable method for simple mixtures of well crystalline compounds, but it becomes at best semi-quantitative for multicomponent mixtures, and next to useless for amorphous or poorly crystalline materials such as some clays, natural organic matter and amorphous hydroxides. Similarly, organic matter determinations invariably contain an arbitary factor, which will vary from site to site, in addition to showing a lack of sensitivity when fractions of a percent are present. The determination of amorphous hydroxides depends primarily on differential solution which is complicated by the fact that some clays also dissolve under these conditions and if the hydroxides become partly microcrystalline their solution characteristics also change.

It rapidly became apparent that a considerable part of this phase of our research would have to be concentrated on developing methods applicable to the problem in hand. Some are chemical, others are instrumnental. Of the instrumnetal methods attempted both SEM and FTIR were investigated in some detail, but eventually they were discarded for a variety of reasons which are discussed below. Some x-ray diffraction was done but because of instrumental problems (now hopefully corrected by the manufacturer) only qualitative results were obtained. The Raman microprobe was obtained but was not opperational during the period of this report.

Materials:

The materials used in this study are some of the most complex in nature. In order to begin to understand the difficulty of determining the behavior of pollutants in contact with soil, the soil and its components must be characterized, or at least catagorized. And, the soil components are easily catagorized into inorganic and organic parts. The inorganic parts consist of clays, amorphous hydroxides and oxides, and any trace elements which may be present in the particular area.

The organic fraction, on the other hand, is composed of literally millions of compex organic compounds generated from the chemical and biological degradation of plant and animal residues. These compounds are known collectively as soil organic matter (SOM), or humic substances.

These inorganic and organic fractions can form complexes with each other, and with toxic wastes (both organic and inorganic) and thus they affect the transportaion, concentration and distribution of any toxic materials in contact with them. They are the "chromatograph" stationary phase to the mobile phase of the toxic materials of interest. As such, their properties are of considerable interest.

Inorganic Fractions

1) Clays: These fine grained, crystalline, poorly crystalline or amorphous compounds are of particular

importance in geochemistry due to their singular ability to form complexes with toxic organics and with SOM. This ability is an effect of both composition and surface area.

Depending on the type of clays, their amounts, and the pH of the fluid phase clays are known to have negatively charged sites, and so can accomodate cations, or positively charged ions on their surfaces (Brady 1974) which can be exchanged with other cations of greater affinity just as is done in a laboratory column with ion exchange chromatography. The clays are characterized in this respect by analyzing for the cation Exchange Capacity (CEC).

In the laboratory the clay fractions in the soil are separated by size with a settling procedure followed by centrifugation. This clay size fraction is then further characterized by CEC, X-ray diffraction, Raman Spectroscopy, and Scanning Electron Microscopy (SEM).

2) Amorphous Hydroxides: These are the oxides and hydroxides of various common metals, with those of aluminum and iron being the most universally found as soil constituents (Brown et. al., 1978). They are found intermixed with the silicate clays; a good example being the hydroxide allophane which is an amorphous combination of silica and aluminum. These hydroxides

and oxides are often insoluble collodial materials, which like clays, accumulate negative charges, and thus exchangeable cations on their surfaces. Little work has been done on the interactions of these hydroxides with clays, som, or organics. So, quantifying the amount of the hydroxides present in the soil is a first step towards determining their importance to the transport and fate of organic chemicals in the subsurface. The hydroxides are generally separated from the other components by selective dissolution in dilute acids, followed analysis using Atomic Absorption techniques.

3) Trace Elements: These represent the smallest contribution to the inorganic soil fraction. They are usually found in solid solution in minerals or adsorbed onto various colloidal particles. They may include various toxic heavy metals such as lead and mercury, but more usually they are just trace amounts of the more common metals. They may be determined by atomic adsorption if specific ones are being sort, or subjected to a semi-quantitative x-ray fluorescence scan if a general idea of those present is required.

Organic Fractions:

The SOM or humic substances are widely distributed in soils, natural waters, marine and lake sediments, peat, lignite, oil shales, and coal (Stevenson and Goh, 1971). They have the ability to act as pH buffers in the soil and are important to the transportation and concentration of a variety of mineral substances (Stevenson and Butler, 1969) and heavy metals (Kononova, 1966). These compounds which are produced in soils range from yellowish to black in color and have molecular weights which range from 500 to 300,000 (Schnitzer and Kahn, 1978)

Humic substances are generally divided into three groups based on their solubilities:

1. The most soluble fraction is called fulvic acid. It is soluble in both acid and base, and has the lowest average molecular weights.
2. Humic acid is base soluble but is not soluble in acid.
3. Humin is insoluble in both acids and bases and has the highest average molecular weight with the greater proportion of the humic fraction of the soils most likely being humic and fulvic acids closely bound to the inorganic fractions in the soil (Stevenson and Baker, 1969).

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The reader should note that these divisions are only operational. They are merely arbitrary groupings of a heterogeneous mixture of literally millions of different organic compounds having every conceivable functional group (Felbeck, 1965). There is in reality a continuous gradation among these compounds from high to low molecular weight, and from high to low solubility, with no sharp divisions. The humic substances also vary in composition from one site to another.

The SOM or humic soil fractions are characterized in this study with CEC, their mass after ashing, as elemental carbon reported as either Total Organic Carbon (TOC) or Percent Organic Material (POM) and by such instrumental methods as IR, FTIR, FTIR-PAS, SEM and Raman Spectroscopy.

Methods Used in this Study:

In this study we are characterizing both the bulk sample as well as a variety of different size fractions of each sample using both non-instrumental chemical analyses and instrumental methods. Each sample is first catagorized according to its bulk characteristics. Chemical and instrumental techniques are then used to try to determine and to perhaps quantify those parameters which most affect the bulk characteristics of the soil sample. Preliminary results have been obtained for most of these methods on samples of the major soil groups and on the North Dakota soil samples. Work is continuing on samples from the other study areas.

The methods used in this research are discussed under sampling techniques, non-instrumental methods and instrumental methods.

Sample Collection & Preparation

Various methods were used in the collection of soil and sediment samples. Surface samples were collected primarily through the 'scoop and bag' method. Deeper samples were collected by different drilling rigs depending on the area. A portable split spoon sampler was also used with little success.

Different experiments required varying preparation techniques. The only common method is that all of the samples were dried. This was accomplished by oven and air-drying techniques.

Collection-

The collection methods described below were site specific in some respects, and thus they will be discussed by area.

Apple Creek Basin, North Dakota

Surface samples were collected by the 'scoop and bag' method. At first a small hole was dug to define the major soil horizons. Shoveled samples were taken of the major layers and placed in 'zip-loc' plastic bags. In particular instances, gravel pits allowed a more enhanced view of some soil profiles.

Samples down to two feet below land surface were collected by sledge hammer-driven split spoon and shelby tube samplers. It was found that the soil columns could not be removed from the shelby tube intact so this method was discarded. Split spoons were only effective in the sandier soils.

Vadose zone samples down to 15.5 feet (4.72m) were collected by a shelby tube sampler pressed into the ground by a drilling rig. The soils were extracted using a press. The columns were then wrapped in plastic to prevent contamination. The cores are 1.5 in. (3.8cm) in diameter.

D'Imperio Dump Site New Jersey

Two holes were drilled using a mud-rotary drill rig. Continuous split spoon samples were collected to a depth of 45 feet

(13.7m) in a hole down-gradient of the site and to 37 feet (ooo m) in an up-gradient hole. The diameter of the cores collected is 1.5 in. (3.8cm). These samples were preserved in mason jars, sealed with wrapping tape, and shipped by air to Oklahoma State University in Coleman coolers.

Abandoned Creosote Lagoon, Conroe Texas

During June of 1983, numerous test borings were dulled at the Conroe site by personnel from Robert S. Kerr Environmental Research Laboratories. A 6-inch hollow stem auger rig was used for both drilling and collection of split spoon samples. Sediment was obtained for subsurface characterization work from 4 holes; one assumed to be at the up-gradient boundary of the lagoon, two assumed to be near the edge of the contaminated zone in a sidegradient direction, and the fourth in a supposed background area. In one hole (sidegradient), samples were collected continuously to a depth of 26 feet; samples from the other holes were obtained where changes in lithology of the sediments occurred. Three soil samples were collected from a wooded area approximately 1000 feet off-site, using a shovel to dig and loosen the material. All samples were packed in mason jars or heavyweight plastic bags and sealed with strapping tape immediately after collection. They were then stored in coolers prior to and during shipment to OSU.

Preparation

All of the samples collected were dried before they were analyzed. Oven drying took place at temperatures between 176 and 212oF (80-100oC). Air drying generally occured over a few weeks period during which the samples were sheltered from falling dust.

Analyses of the soils occurs in two parts. Initially, bulk properties are determined. To investigate the micro properties, the soils are then sieved into several size fractions and re-analyzed.

Clay Extraction and Identification:

The crushed sample is dispersed in a dilute Calgon solution using an ultrasonic disaggregator, transfered to a one liter measuring cylinder and thoroughly mixed. After settling for the appropriate time required by Stokes law the < 2 micrometer fraction is syphoned off.

A small amount of this aqueous suspension is filtered through a Millipore filter which is then glued to the x-ray diffractometer sample holder. After one scan the sample is then exposed to ethylene glycol and re x-rayed. In some cases where doubt still exists as to the clays present some of the clay suspension is filtered onto a ceramic plate, dried in an oven, heated to 550 degrees C in a muffle furnace and x-rayed once again.

For some samples the calcium carbonate, iron oxide and organic matter may be removed using the procedure of Kittrick and Hope, 1963.

Non-instrumental Methods:

We have adopted the classical agronomic methods of bulk soil characterization. These include determinations of soil type, moisture content, clay separations and extractions, amorphous hydroxide and oxide extractions, determinations of the amount of SOM present, and finally the ability of each soil component to take up and exchange cations. Several methods of performing each determination available. A complete listing of all the techniques is found in "Methods of Soil Analysis-Part 2" Black, et. al. However, none of these methods have been tested for their applicability to hydrogeochemical studies. This led our laboratory to use the methods of Agronomic Services Lab at Oklahoma State University as Supplied by Emeritus Professor Lester W. Reed, and the methods described by Baker and Blocker et. al. (1975). The applicability of other bulk methods will be done during the follow up research.

Moisture Content:

The moisture content of the soil samples were obtained by sample dessication and weighing, and were done at the Dept. of Geology water lab at Oklahoma State University.

The results for the moisture content of the major soil groups are listed in appendix---- while the North Dakota core samples are listed in appendices ----and-----. It can be seen that while some soil groups such as Williams loam yield a narrow range of moisture content others show little similarity as is seen in the correlation of moisture content with depth in the North Dakota samples.

The determination of the amount of organic matter in soils.

Organic Matter in Soils:

TOC and POM

These two parameters are merely different ways of reporting the amount of carbonaceous material present in a sample of SOM. They are actually estimates based on an assumption that fifty eight percent of the SOM is organic carbon.

In addition, it was found in the literature that since the decomposition of the soil organic matter is not 100% efficient a factor (f) is added to make up the difference. Choosing a value for htis factor is based on the experimenter's experience and also must vary from area to area. Since the soils tested reflect different soil orders as well as different areas, direct comparison of results is probably not warranted. The results of appendix----- use an f value of 1.33.

The TOC and POM measurement can be made either by 1) gravimetric combustion, as with the plasma ash furnace, or 2) by oxidation-reduction reactions involving the oxidation of the SOM by excess dichromate ion followed by a titration to determine the amount of unreacted dichromate ion left after the reaction (Allison, 1965).

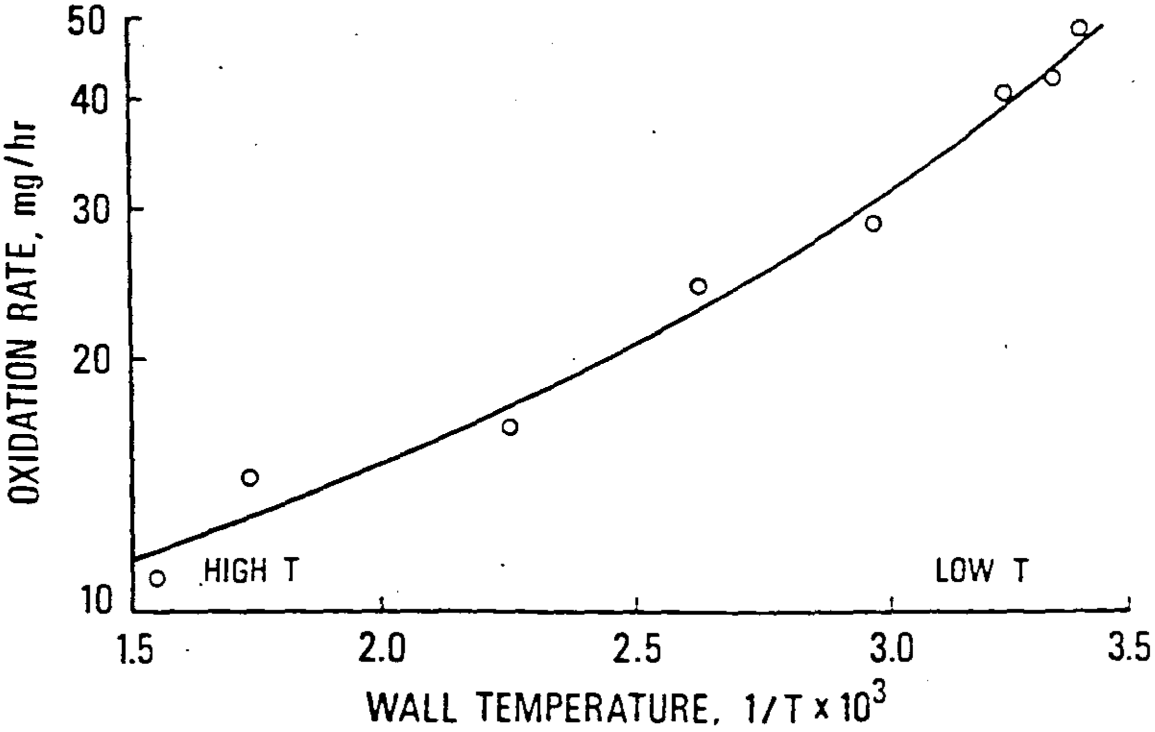
1) The plasma ash technique

This is a method for completely oxidizing carbonaceous materials at a low temperature. The primary advantage of this technique for this study is that the clay minerals and amorphous hydroxides should be minimally affected due to the lower temperatures maintained during the ashing of the organic fraction of the soil.

Plasma ashing is an effect that occurs when a gas at low pressure is exposed to an intense radiofrequency field. Under these conditions the gas, oxygen in this case, exists as a plasma, a partially ionized mixture of atomic as well as molecular oxygen. The atomic oxygen in the plasma field acts as a powerful oxidizing agent at low temperatures. The rate of oxidation is dependant on several variables. Hollahan and Bell (1979), in a text on plasma chemistry, state that the oxidation rate decreases with increasing reactor well temperature (Figure 13) and pressure (Figure 14). The oxidation, however, increases with increasing sample surface area (Figure 15), rf power (Figuer 16), and flow rate (Figure 17).

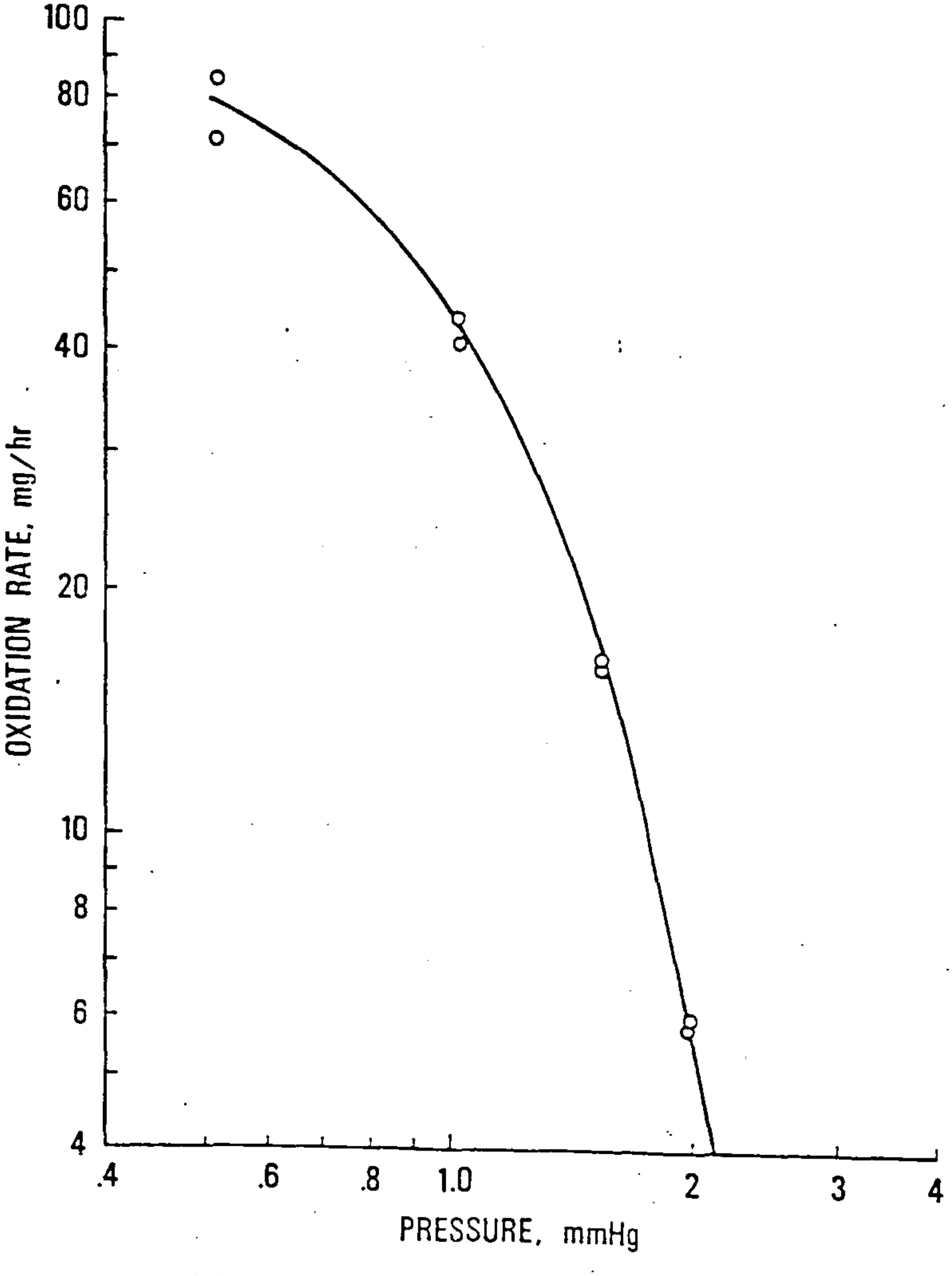
The technique has been used for coal analyses (La Flamme, 1979) as well as in the examination of clay-size fractions of two podzolic soils (De Kimpe, Miles, Laverdieve, La Flamme, 1982).

In our project, this technique will also be used for



Effect of wall temperature on the oxidation rate of graphite.
(After Hollahan, 1974)

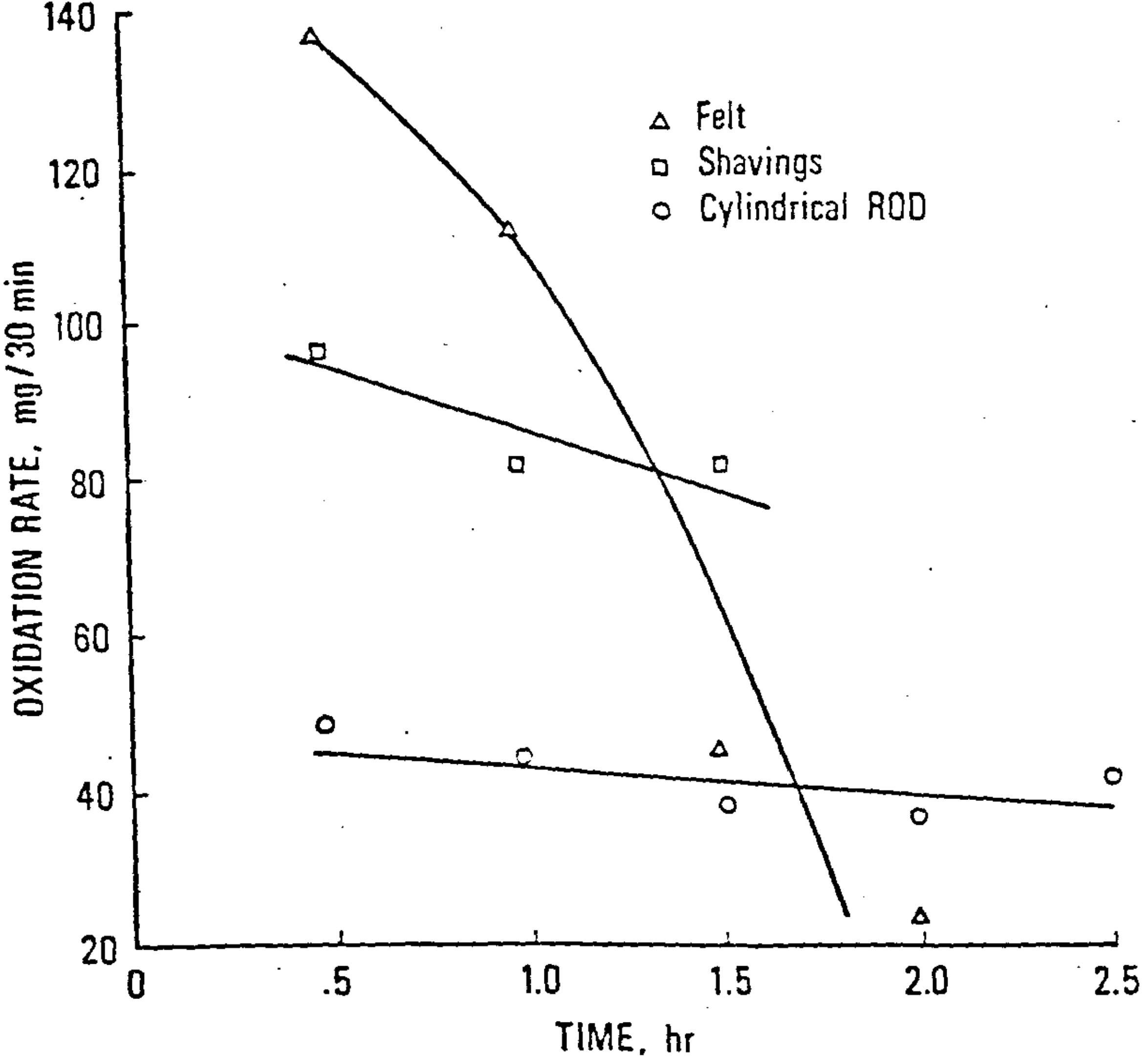
Figure 13



Oxidation rate of sucrose as a function of gas pressure: rf power, 20 W; flow rate, 15 cm³/min; sample location, 10 cm.

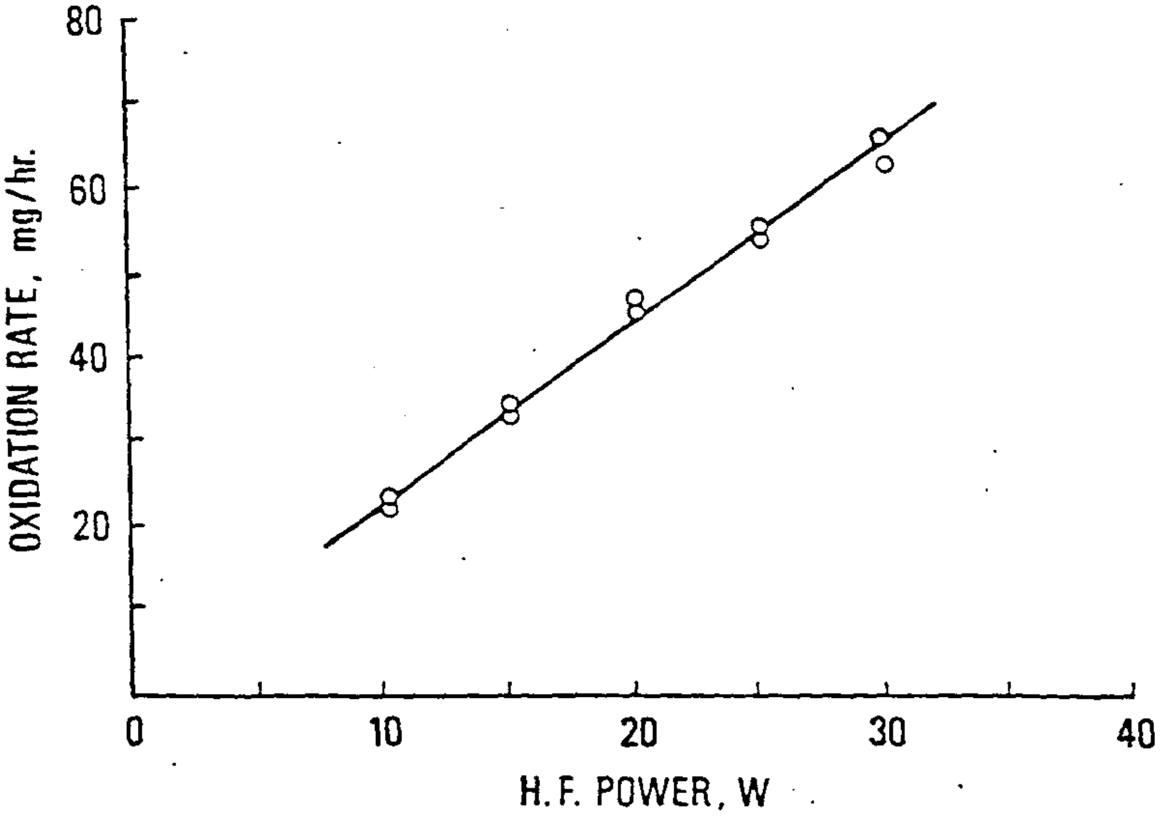
(After Hollahan, 1974)

Figure 14



Effect of surface area on oxidation rate,
maximum temperature 100°C.
(After Hollahan, 1974)

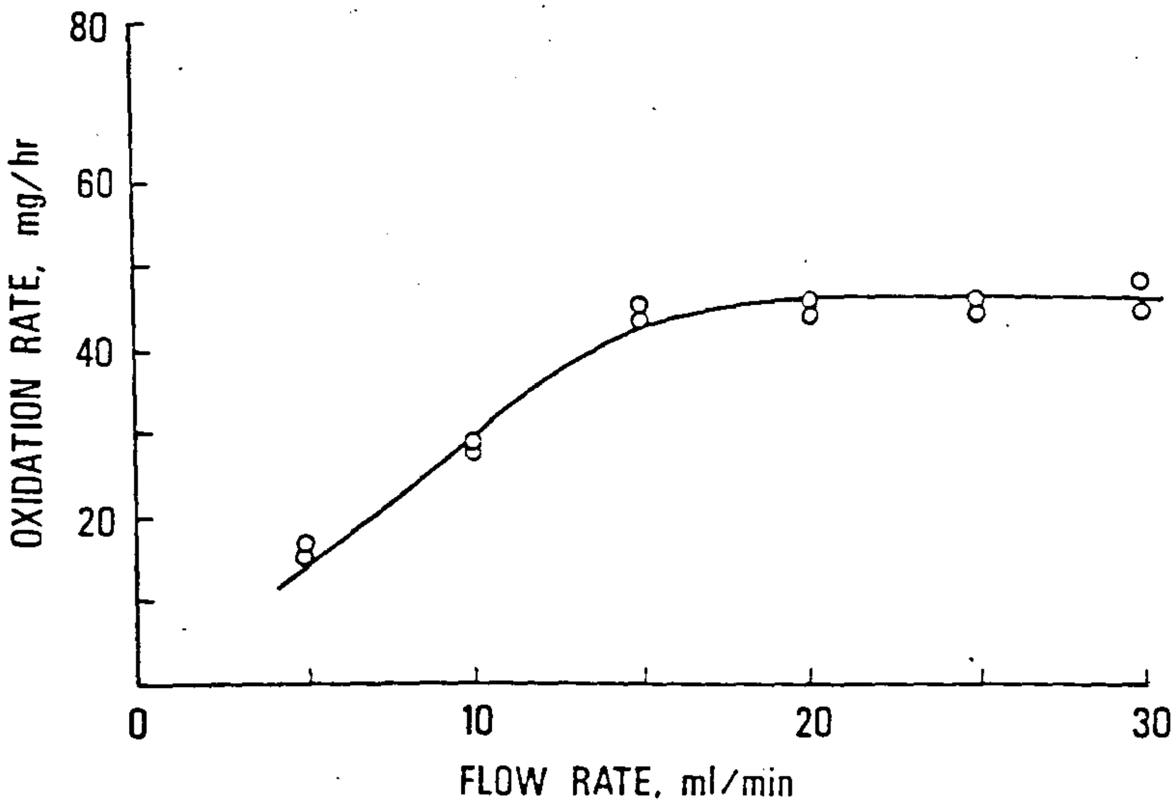
Figure 15



Oxidation rate of sucrose as a function of rf power; pressure, 1 torr; flow rate, 15 cm^3/min; sample location, 10 cm downstream from end of inductive coil.

(After Hollahan, 1974)

Figure 16



Oxidation rate of sucrose as a function of flow rate: pressure, 1 torr; rf power, 20 W; sample location, 10 cm.

(After Hollahan, 1974)

Figure 17

comparison studies using FTIR, Raman, and various chemical techniques on soil samples before and after the removal of SOM by plasma ashing. It is hoped that the organic fraction can be characterized from the differences in the before and after spectra. It is also proposed that plasma ashed samples could be used as controls for the adsorption isotherm work being done at RSKERL.

Oxidation Reduction

2) V Reaction method to determine TOC and POM

This method is based on the oxidaiton of the SOM by the dichromate ion. The amount of SOM is then determined by titration of the dichromate ion left over after the reaction takes place. Three titrations were tried. The first which used barium diphenyl sulfonate (BDS) as an indicator and the second which used ferrous ammonium sulfate as an indicator proved to have difficult and time consuming procedures and yielded erraatic results as well even though they are listed as standard procedures. A third method from the Agronomic services at Oklahoma State University was finally used. This titration used orthophenanthrolene as an indicator, proved to be rapid and to yield reproducible results.

Cation Exchange Capacity (CEC) and Exchangeable Cation Determination (ECD)

Clays, amorphous hydroxides, and SOM all have the ability to attract and adsorb soluble cations present in the soil. These cations 'adhere' to the negatively charged sites present on the various soil fractions. The bonds are probably of the van der Waals tyupe and so are not permanent, and so are "exchangeable". The number of negatively charged sites as found by the CEC and the types and concentrations of the actual exchangeable cations present may help determine the susceptability of an organic chemical to 'adhere' to a soil particle. These procedures have only just been implemented and preliminary results are as yet unavailable.

Instrumental Methods

The instrumental techniques utilized in this study have been Atomic Absorption Spectrophotometry, for the determination of trace elements; x-ray diffraction for the qualitative and quantitative analysis of soil constituents; scanning electron microscopy (SEM) to observe the shapes and distributions of soil constituents, including

(SOM); Fourier Transform Infrared Spectroscopy (FT1R) and Raman Microprobe, for the characterization of soil constituents, including buinding of som to other soil fractions possibly.

Trace element analyses by Atomic Absorption

Atomic Absorption Spectroscopy is based on the observaiton that elements in the atomic state can absorb or emit discrete frequencies of light according to the well known Planck Equation. This procedure is almost entirely utilized to identify metals, and has a practical range down to ppb concentrations, after proper sample concentration steps.

Physically the method is simple. A sample is digested to a liquid in a suitable acid in order to obtain free cations. The sample is then sprayed through a flame vaporize the cations, and exposed to a beam of light at one of the metals absorption or excitation frequencies. The loss of light intensity is measured and related to the amount of metal present in the sample.

In our study the types and amounts of trace elements present in each soil sample are determined by atomic absorption spectrometry (AA). The procedure is a straightforeward digestion of the sample by hydrochloric acid and hydrogen peroxide and is formed in

Appendix----. These determinations, however, were not effective in demonstrating any trends with depth. Even duplicate samples contained errors > 10%, so that these results should be taken only as an estimate of the trace element concentrations of the core as a whole.

X-Ray Diffraction

In this study X-ray diffraction is to be used to determine the identity and quantity of the soil components that play important roles in the adsorption of organics in soils.

X-ray diffraction is a very powerful, but easily performed tool for the determination of the lattice structure of crystalline compounds. It is not useful in the characterization of amorphous material. The pertinent information is obtained by bombarding a crystalline material with monochromatic x-rays, and observing the angles that these X-rays are diffracted from the sample. From these angles, and the intensities of the diffracted rays, information on the positions of the ions that make up the crystalline substance can be extracted. The position of each diffraction peak is dependent on the interatomic spacings whereas its intensity depends primarily on the type of atoms present.

Although the x-ray diffraction pattern cannot unequivocally identify each atom in a sample, each mineral configuration will produce a characteristic diffraction pattern. When a sample diffraction pattern is compared with a list of known diffraction patterns, the identity of the samples can be deduced.

An x-ray diffractometer is a device whereby a small crystalline sample which has been ground to a powder, is mounted in a sample container. The sample will contain tiny crystalline particles characteristic of the gross sample, ideally in a complete random orientation. The random orientation of the particles causes the incident x-ray beam to diffract in all the possible angles simultaneously. These diffracted beams are scanned by the instrument to produce the characteristic powder x-ray spectrum. The identity of the samples can be determined by comparing the diffraction pattern to the list of known diffraction patterns caralogued by the Joint Committee on Powder Diffraction Standards (JCPDS) which can be done by searching microfische files, or by comparison by computer.

Quantitative X-Ray Diffraction Analysis

Quantitative mineralogical analyses of x-ray diffraction was popularized by Alexander and Klug in 1948 (Hooton et. al., 1977). However, the need for a simple and direct determination of mineralogical content has prompted other researchers to derive techniques similar to Alexander and Klung's but more practical for everyday research.

Powder x-ray diffraction analysis is an excellent technique for crystalline-mixture analysis, since each component of the mixture produces a characteristic pattern independent of the other. More importantly the intensity of each component's pattern is proportional to the amount present, except for a correction factor due to absorption. Unfortunately these absorption effects prevent us from directly comparing line intensities of a component in a mixture, with the pattern of a pure component prepared under identical conditions. Furthermore if a mixture contains both a weak absorber and a strong absorber the signal due to the weak absorber will be alternated, while the peaks of the strong absorber will be even further enhanced over thoe of the pure unmixed samples, even if those are run under identical conditions. Luckily, the differential absorbtion is not random and calculations may be made which will predict characteristic absorption coefficients for separate components.

For this purpose, Hooton and Giorgetta (1977) modified the early calculations, formulated by Alexander and Klung (1948), into workable equations with easily obtainable unknowns, (see appendix for mathematical treatment) which make them useful for quantitative x-ray analyses.

Scanning Electron Microscopy --

To date, few researchers have studied soil organic matter-clay complexes in sediments (below the soil profile) using the scanning electron microscope (SEM). The SEM is used primarily to examine physical and structural properties of the samples being studied. For organizational purposes, this review has been divided into two main sections. The first section deals with the microstructure of relatively undisturbed soils, and the second section covers extracts of soil organic matter (SOM). To date, no research has been published in which soil organic matter was viewed in undisturbed soil samples using the SEM.

Soils and SEM -- Numerous researchers have studied various aspects of soil formation, micromorphology, and mineralogy using the SEM. Because much of this work does not concern itself with the examination of soil organic matter, a discussion of these papers will not be presented. However, a few authors have used innovative sample preparation techniques or examined micromorphilogical characteristics which may be relevant to subsurface characterization. Summaries of these papers are presented below.

Gilliott (1969) has examined the fabric of fine-grained clays using the SEM and discussed orientation of micaceous clay minerals relative to bedding structures. A section analyzing the relative merits of air-drying, freeze-drying, and critical-point-drying of clay soils was also presented in the paper. No comparisons were made of the prepared soil photomicrographs using each of the three methods. Gilliott concludes that a quick-freeze followed by a freeze-drying at less than -130 C is the most effective method for preserving the original soil structure without creating ice artifacts on the sample (this technique has been used extensively on biological specimens). The drawback to this technique is that it is a very slow process.

Eswaran (1971) has studied fracture surfaces of soil peds using SEM. The soil microstructure of cambic, oxic, argillic, and spodic horizons was examined with regard to physical and minerologic characteristics. Sample preparation consisted of cementing selected fragments directly to aluminum stubs. The standard technique of lightly coating the sample with a layer of gold to make the surface conductive was then employed before viewing. Eswaran comments that he feels the viewing of soil-thin sections would yield more useful information; however, the impregnating resin would render the surface to be scanned non-conductive.

Eswaran and DeConinck (1971) have studied clay mineral formation and transformation in basaltic soils. The SEM was used to study morphological changes which characterize some clay minerals. The results included evidence of alteration of feldspars to kaolinite and halloysite and the neoformation of amphorous iron oxides in the studied soils. Eswaran and DeConinck concluded that soil microenvironmental factors play a greater role in these processes than climatic factors, which function as rate modifiers of the transformations. Lynn and Grossman (1970) have examined general pedological features of two soil horizons and present micrographs of the fabric of a fragipan, a skeletan,m and an argillan. The authors observed particle coatings and the lack of them, interparticle bridging, and variable orientation of clay on structural surfaces. Magnifications of 3000X to 10,000X were employed. Samples were prepared by mounting freshly exposed surfaces on aluminum stubs and coating the samples with gold in the prescribed manner.

Van Ranst, etal (1980) have studied the accumulation of clay and organic material in various soil horizons which lead to the formation of argillians and organans (collodial-free grain coatings consisting of amphorous organic substances associated with aluminum and iron). SEM micrographs indicate that argillians are strongly layered coatings that are seldom cracked. The authors proposed that argillians are formed by the slow deposition of layer silicates out of a dispered phase. Organans were found to be not layered and appeared to be composed of discrete small bodies stacked at random. Also, organans exhibit a strong polygonal cracking pattern, leading to the conclusion that they were deposited as gel-like, organo-metallic compounds from which the solvation water gradually evaporated. The authors have concluded that organans are composed primarily of humic and fulvic acids due to their almost complete extractability in Na4P2O7, at pH 10. Organans are thought to have accumulated as organo-aluminum or organo-aluminum and iron complexes. No information is presented on sample preparation techniques.

Stoops (1970) has studied the micromorphological characteristics of a laterite using SEM. The paper focuses on a description of clay mineral structure and orientation within the soil. Small fragments were chosen for viewing after examination under a binocular microscope. The usual techniques for mounting and coating samples were used.

Chen, Banin, and Schnitzer (1976) studied subsamples of a sandy loam soil in which the exchangable sodium percent (ESP) values had been artificially altered to levels ranging from 1 to 20. When examined under the SEM, those soils at low ESP values showed clay particles aggregated between sand grains leading to the formation of large pore spaces. At higher ESP values the clay aggregates dispersed to form networks filling pore spaces between sand grains. Soil preparation for viewing under the SEM was accomplished by obtaining saturated "cores" of the artificially leached soil and freeze drying them. Small chunks were then scratched to expose a fresh surface, and then the samples were mounted using the standard techniques.

Soil Organic Matter and SEM -- Several researchers (Flarg and Beutelspacher, 1951; Vesser, 1963; Wersmuller, 1965; Khan, 1971; Orlov and Glebova, 1972) have used the SEM to observe the shape and dimensions of humic acids. In these studies, sample preparation was limited to air-drying of a solution spotted on a conducting surface. The resulting micrographs indicated no definite visible structure. Schnitzer and Kodama (1975) undertook the study of fulvic acid using a simular sample preparation procedure and found that the appearance varied somewhat with a change in pH. Spheroids, irregular shaped particles, and aggregates of these ,as well as amphorous material, were visible at different pH values. The authors concluded that fulvic acid has a relatively open structure in which the voids are of variable dimension.

Several workers have used the SEM for observation of humic and fulvic acid particles (Schnitzer and Kodama, 1975; Chen and schnitzer, 1976). They have found that the crystallinity, shape, dimensions and extent of aggregation of the particles is effected by pH. These structural phenomena can be readily observed at magnifications well within the range of the instrument. This study was the first in which the quick-freeze followed by freeze-drying method (described by Boyde and Wood, 1969, for biological specimens) of sample preparation was used to examine soil organic matter. Micrographs of fulvic acid solutions (pH 2, 4, and 6) not subjected to this preparation process all showed thick layers composed of fine particles having little apparent structure.

This data agrees with that of earlier studies.

Use of the quick-freeze-freeze-dry technique allowed ready observation of the organic molecules being studied. At low pH (2-3), fulvic acid occured as fibers and bundles of fibers, forming a relatively open structure. At pH 4-7, a finely woven network, having a sponge-like texture, was visible. At pH 8, a sheet-like structure was predominant, and fine, homogeneous grains became visible at pH 10. The effect of pH on humic acid's structure was similar although its limited solubility (pH > 6) caused the transitions to occur at higher values.

Chen and Schnitzer republished the study described above in 1976 along with results of additional research into the shapes and dimensins of fulvic acid-metal and fulvic acid-clay complexes. Solutions of known molar concentration were prepared in the laboratory and quick-freeze, freeze-dried for viewing under the SEM. Chen and Schnitzer found structural differences in each fulvic acid-metal complex examined, as well as variability in structure of any paticular complex at varied pH values.

The SOM clay complex that Chen and Schnitzer studied was sodium montmorillonite-fulvic acid. The acid's structure was also found to vary with a varying pH; clay flakes interconnected with fulvic acid fibers at pH 2.5 but apparently only adsorbed to fulvic acid surfaces at pH 5.0. The authors concluded that complexing with fulvic acid seemed to interfere with the natural orientation of the clay minerals toward sheet-like structures.

Chen, Senesi, and Schnitzer (1978) once again observed humic acid and fulvic acid at varied pH values to compare the results described above with those obtained when using soils of various composition from different regions. The authors found that the fibrous, spongy textures were present in all of the micrographs although the dimensions and extent of the aggregation of the fibers varied with each soil examined.

Much research has been done using scanning electron microscopy to examine clay structure and micromorphology of soils (Stoops, 1970; Eswaran, 1971; Van Ranst etal, 1980). The emphasis has been on the presence of particle coatings or the lack of them, interparticle bridging and orientation of clay on structural surfaces. Chen and Schnitzer (1976) have examined soil organic matter (SOM)-clay complexes using fulvic acid extracts in solution with sodium montmorillonite.

Current Work -- During this phase of the subsurface characterization study, we we have attempted to use the SEM for the following work:

1) Identification of humic materials in sediments from each study area utilizing extraction and purification techniques.
2) Identification of SOM-clay complexes by the addition of clays (also from each study area) to the solutions described above.
3) Examination of the interaction of these clays with humic acid and fulvic acid at varied pH values to determine the the type and extent of the complexing that could occur.
4) Development of a methodology by which these structures can be observed without treatment and disturbance of the natural sediment fabric.

Three modes of sample preparation are currently being considered and assessed as to their applicability for the above tasks.

1) In-situ impregnation of soils and sediments with epoxy resins followed by thin-sectioning. This method

preserves detailed soil structure and fabric.

2) Quick-freeze-freeze-dry as described by Boyde and Wood (1969). This technique has the advantage of allowing observation of the structure of the humic materials.
3) Critical-point drying, in which the water content of the specimen is successively replaced by ethanol, amyl acetate and liquid carbon dioxide. The sample is then heated to slightly above its critical point to allow release of the carbon dioxide without creating artifacts in the sample (Anderson, 1951).

Results

Experiment 1: Soil Standards

The object of the experiment was to determine how loose, dry soils could be prepared for viewing under the SEM. The problem was to find a means of affixing soil grains to aluminum stubs since silver paint alone was not a good adhesive. The technique chosen for the trial involved the coating of the grains with quick-drying epoxy resin.

Procedure

1) Epoxy mixed and dropped onto the aluminum foil is allowed to partially set.
2) Soil grains are poured over the epoxy and allowed to dry overnight.
3) The foil backing is removed from the hardened samples.
4) The samples are affixed to the aluminum stubs with silver paint and are then coated with a 200 angstrom layer of gold.

Results and discussion

Presence of the epoxy prevented a clear, sharp image from being obtained. In all four samples, the grains seemed to be floating in a gelatinous substance making clear resolutions of the grains impossible.

The method of resin impregnation has been used by numerous workers for studies of in-situ soils. If injected into an undisturbed sample, the resin helps to preserve physical and textural structures which would have otherwise been altered during transport. To facilitate viewing, the impregnated blocks are thin-sectioned so that fresh surfaces can be scanned. Attempting this procedure on the soil standards available to us would not yield much useful information because in-situ characteristics were lost when the samples were collected. This same limitation exists with all the samples collected during the summer of 1983. If undisturbed samples are to be used for SEM viewing, impregnation must be done during collection. The usefulness of this technique to subsurface characterization is also questionable. It is almost as impossible to obtain an undisturbed sample of aquifer sediments as it is to resin impregnated water saturated core.

Experiment 2: Great Soil Groups

The object of the experiment was to determine whether quick-freezing followed by lyophilization of soils would provide an adequate method of sample preparation for SEM viewing. Some workers who have used this technique claim that it perserves structural characteristics.

Procedure

1) One gram each of soils 3, 5b, 6, and 7a were chosen. These represent the great soil groups.
2) Each sample was placed in a glass beaker which was then immersed in liquid nitrogen for 15-20 seconds.
3) The beakers were then placed in a dessicator connected to a lyophilizer. The samples were allowed to dry overnight.
4) Control samples were air-dryed.
5) Both sets of samples were broken to expose a fresh surface for viewing.
6) After coating the samples with gold, they were viewed using the mini-SEM.

Results and discussion

There was no visible difference between those samples allowed to air-dry and those freeze-dried. We later learned that quick-freezing cannot be done directly in liquid N2 because the heat of the soil creates a film of gaseous nitrogen around the sample which insulates it from quick-freezing. The samples chosen were also relatively large (7.5 mm diam), so that while organic matter complexes and might prove just as useful with soil. The object of this type of procedure would be to try to identify soil organic matter (SOM) as it occurs in its natural state. However, the low percentage of SOM in most sediments and the highly controlled sample preparation conditions required for viewing SOM, might prevent this objective from being realized.

Experiment 3: Soil Organic Matter

Initially, standard humic acid, marketed by the Aldrich Chemical Company, was used in an attempt to duplicate the work done by Chen, Banin, and Schnitzer (1976), in which the shapes, dimensions, and extent of aggregation of humic and fulvic acids, extracted from various soils, were viewed under the SEM.

Procedure

1) A 1% solution was prepared using 1 gram of humic acid and 100 ml of distilled water. The natural pH of this solution was ~7.0. The solution was then divided into parts A and B.

2) The pH of part A was lowered with addition of hydrochloric acid (HCl) to ~2. Subsamples of the solution at pH 5,4,3, and 2 were collected and stored in test tubes.

3) The pH of part B was raised with addition of sodium hydroxide (NaOH) to ~10. Subsamples were collected at pH 9 and 10.

4) All subsamples were allowed to sit overnight in preparation for quick-freezing and freeze-drying.

5) All solutions were centrifuged at 3000 rpm for 20 minutes to see whether any fulvic acid would separate out. Only the sample at pH 2 showed a distinct separation.

6) Drops of the supernatant of pH 2 (fulvic acid?) and the solutions at pH 3 and 5 were spotted on glass slides.

7) The slides were placed in quartz crucibles which were dipped in liquid nitrogen to quick-freeze the samples

8) Quick-freezing was repeated on all samples using liquid freon immersed in liquid nitrogen. The original N2 frozen sample were discarded.

9) The slides were then transfered to a dessicator and lyophilized overnight.

10) All three slides retained residue which was coated with gold and viewed under the SEM.

Results and discussion

No structure similar to that reported by Cheng et al. was visible on our samples. The residue appeared sheet-like with only a few "grains" visible. It was determined that these grains were sodium chloride crystals occuring as an impurity in the soil organic matter.

The standard humic acid should not have been used because its origin and purity were questionable. A decision was made to extract the organic matter from some of our own samples to try and obtain better results. We also realized that in Schnitzer's experiments, a low temperature (-70 C) freeze-drying process was used; whereas, we had access solely to a standard lyophilizer.

Experiment 4: Soil Organic Matter Extracts

Soil organic matter (SOM) was extracted from soils 5b (histosol), 7a (spodosol), J1 (Johnson Ranch), and J10 (Johnson Ranch) according to the procedure described below. The purpose of these extractions was twofold: first, the extractions were an attempt to duplicate thew experiments of Schnitzer in which the structure of humic and fulvic acid was found to vary with pH, and second, the extractions were an attempt to reassociate the clay fraction of each soil with its organic matter counterpart and view any complexes that may have been formed. Due to the lack of proper equipment, the goals of the experiment were never realized. The following is asummary of the extraction procedure we used with annotations where we encountered problems.

Procedure

1) A total of 100 grams of each sample was ground until it could pass through a 100-mesh sieve.
   (ten 10-gram subsamples were prepared for each sample because of the container volume limitations. The following steps were performed on each 10-gram sample)
2) The sample was treated with 40 ml of 0.1 normal hydrochloric acid in a mechanical shaker for 10 minutes
3) The sample was then centrifuged at 4500 rpm for 6

minutes followed by the decantation of the supernatant.

4) After the we decanted the supernatant, we repeated the hydrochloric acid treatment.
5) The sample was then treated with 50 ml of 0.5 normal sodium hydroxide and shaken overnight on a mechnical shaker.
6) Afterwards, the sample was centrifuged at 6000 rpm for half an hour.
7) The supernatant (the organic matter in solution) was then decanted and saved.
8) The remaining residue was placed in jars and stored.
9) The supernatant was then acidified to pH 1 to separate the fulvic and humic acid fractions.
10) We then centrifuged the supernatant at 6000 rpm for half an hour.
11) Then, the supernatant (liquid) fulvic (?) fraction and the residue (solid) humic fraction were separated and stored.
12) The humic fraction was allowed to air-dry. (because of the addition of hydrochloric acid and sodium hydroxide, the liquid (fulvic) acid portion contained a considerable portion of sodium chloride.

It was necessary to remove these ions to purify the fulvic acid.

13) Dialysis tubs were set up into which the extract was placed for up to 4 days (deionized water changed twice per day). Dialyzing was considered complete when the surrounding solution tested negative for chloride ions.

14) The sample volumes then had to be reduced before freeze-drying could take place. A rotary evaporator was used for this purpose. Because of equipment failure, only 5b and 7a were evaporated sufficiently. As the volume of the sample reduced, a precipitate formed in both samples.

15) These precipitates were then millipored, and the liquid and solid fractions saved. The solid fraction would not redissolve in distilled water. Samples of this material were run on the FTIR.

Results and discussion

At this time in the experimental procedure, our access to a lyophilizer was cut off and the experiments terminated. The extracts have been stored for future study.

One technique of sample preparation which may help in the elucidation of soil organic matter - clay complexes is quick-freeze freeze drying. Discussed by Boyde and Wood, 1969 for the preparation of biologic specimens, its main advantages are the prevention of the growth of ice-crystal artifacts and lack of alteration of surface detail on the sample. The procedure, as described in their article is summarized below.

1. Initially a vacuum chamber containing a cold stage must be pumped down at least 10 minutes priorto sample loading to achieve a temperature of -60 C to -80 C on the cold stage.

2. During this time, the samples must be quick frozen in an appropriate quenchant; liquid freon is reccomended. Subsequently, temporary storage can be provided by immersing each sample in a shallow layer of liquid nitrogen in a flat bottomed metal boat.

3. The specimen and metal boat may then be transferred directly to the cold stage, or if the samples are to be loaded directly liquid freon must be poured over them at no greater than 10 second intervals.

4. The time required for freeze-drying is dependent upon the mass of the sample and the capacity of the instrument being used. However, the cold stage must be maintained at -80 C overnight.

5. The sample is then warmed to room temperature while still

under vacuum. It is then coated with gold-palladium or carbon as rapidly as possible after removal from the vacuum chamber.

This technique has been used by Chen, Banin and Schnitzer, 1976 on soils in which the Exchangeable Sodium Percent had been artificially altered. The resulting scanning electron micrographs showed structural variations between sand grains and clay particles at different ESP values.

If the work with soil organic matter (SOM) extracts is to be continued, certain equipment must be procured. This equipment includes the following:

1) A centrifuge that will operate at 6000 rpm.
2) A rotary evaporator.
3) A lyophilizer for intial freeze-drying of the extracts.
4) A freeze dryer with a cold stage for final freeze-drying of the organic matter before viewing.

It is questionable whether a continuation of these experiments is warrented at this time. Since the primary goal of the subsurface characterization program is to examine soil organic matter in its naturally occuring state, the viewing of the extracts may not yield much useful information.

FOURIER TRANSFORM INFRARED SPECTROMETRY - FTIR

Whereas X-ray diffraction is a result of the total crystal structure, infrared spectroscopy looks at individual bonds, making it one of the few tools available for characterizing amorphous constituents such as natural organic matter, amorphous hydroxides and synthetic organic pollutants.

A recent development of infrared spectroscopy is the availability of Fourier Transform Infrared Spectroscopy (FTIR) which has higher sensitivity than the older wavelength instruments as well as having computerized data manipulation capabilities including spectral stripping. The latter is essentially the non-chemical separation of mixtures using difference or subtraction spectroscopy. This capability is essential if colloidal interactions are to be identified. A major problem in using this technique is the requirement of having available pure reference standards. Obtaining uncontaminated reference standards of crystalline phases is a considerable challenge, but obtainiong uncontaminated reference samples of amorphous phases is a major undertaking. This is one problem being addressed in our current research program.

Common FTIR instrumental configurations are simple specular reflectance, attenuated total reflectance (Harrick, 1981), photo-accoustics (Rockley, 1980, Rockley et. al. 1981, and Krishnan, 1981), and diffuse reflectance.

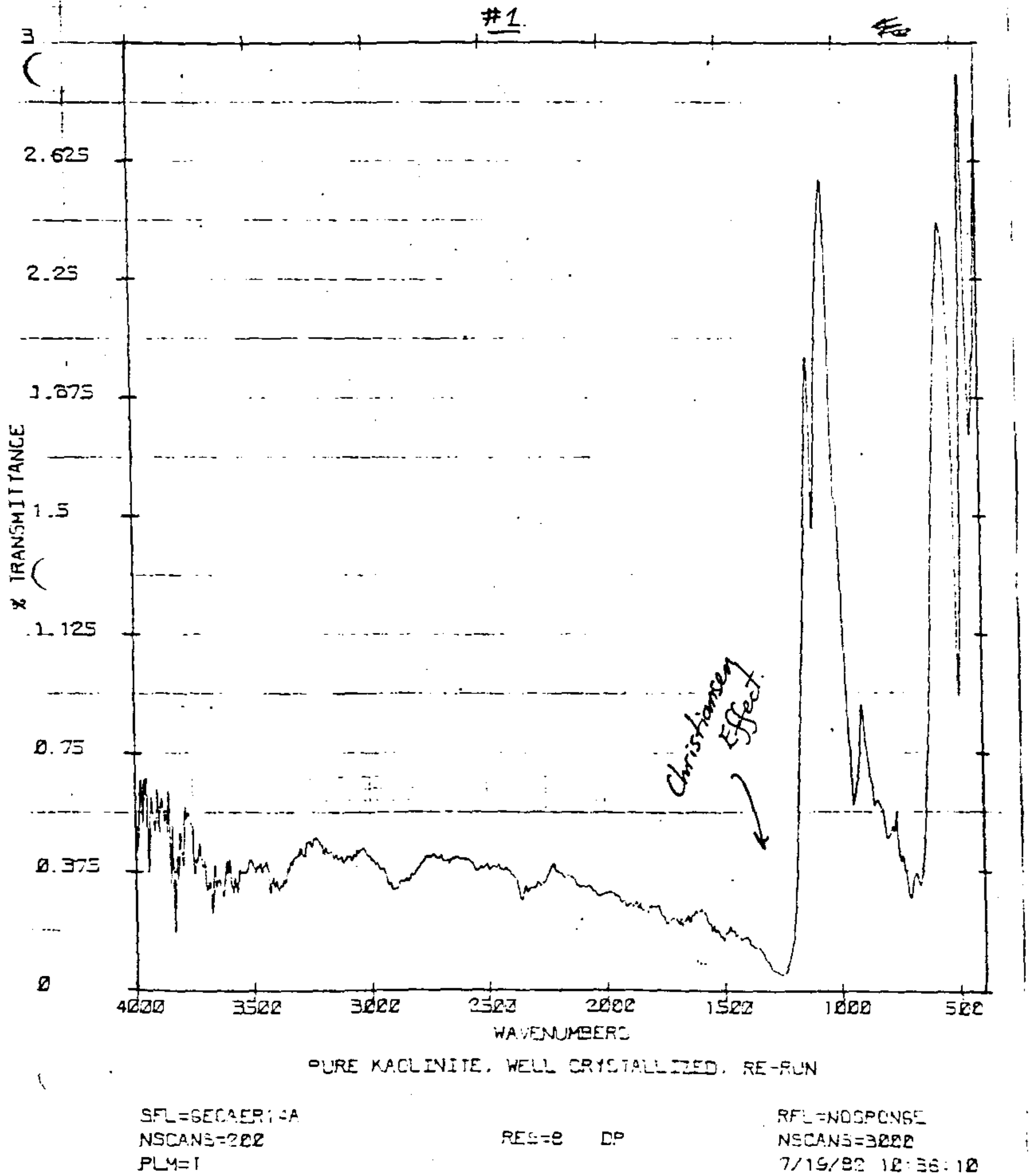
Infrared spectroscopy (IR) has provided much information about the structural chemistry, nature, and origin of humic and fulvic acids. The major application of IR spectroscpy to humic substances up to this time has been the identification of their functional groups from soil, peat, and coal (Ceh and Hadzi, 1956; Moschopedis, 1962; Wagner and Stevenson, 1965; Stevenson and Goh, 1971; Theng etal., 1967). These investigators however depended for their success on the examination of a "pure" concentrate of humic or fulvic acid obtained by a long and tedious extraction procedure from either soil or water samples. An idea of the difficulty involved can be gleaned from the fact that a standard humic acid sample obtained using these proceedures is being sold for $10 per milligram (about 1000 times the cost of gold).

Experimental Results

Following the experimental plan established one year ago, we have examined a wide range of experimental Fourier Transform Infrared Spectrometer (FTIR) spectroscopic techniques in search of a method for examining solid particulates , primarily amorphous organic matter and clay minerals, which are relatively free of spectroscopic artifacts and which is also very sensitive. These techniques are specular reflectance, FTIR-photoacoustic spectroscopy, FTIR diffuse reflectance and KBr pellet techniques. Conclusions pertaining to each technique follow.

The specular reflectance is a very fast analysis procedure which can give semiquantitative information about what components are present in the solid matrix, and which lends itself to convenient sample preparation because the samples may be studied in-situ on such media as polycarbonate filters and glass substrates. Specular reflectance has one major disadvantage which occurs when there is an intense absorption in the system, such as the Si-O stretch at about 1000 cm-1. Accompanying the absorption is a dispersion effect known as the Christiansen effect which produces a negative feature on the blue side of the band. As a result, intense features take on a second-derivative type appearance, band intensities are incorrect, and in some cases the spectrum may cease to be readily identifiable. An example of this spectral artifact can be observed in figure 18. Furthermore, note that in this spectrum of kaolinite, the hydroxyl feature at ca. 3500 cm-1 is absent. This absence is probably due to a chemically induced change in the structure of the kaolinite and needs to be further investigated. Because the problems outweigh the advantages of this technique, it was considered to be unsuitable for our present purpose.

FTIR-Photoacoustic spectroscopy (FTIR-PAS) was found to be useful in the measurment of the solid spectra without any sample preparation. The band intensities were reproducible, enabling spectral subtraction to be performed with accuracy to at least the 1% contaminant level. However, the maintanance of this low contamination level is difficult without the use of a purged sample chamber to remove water vapor as a contaminant in the sample (and spectra). Since the rotational vapor bands of water lie in the same region as ketone, lactone, and organic acid absorption in the mid-infrared, this interference can be very annoying. Subsequently, the FTIR-PAS is found to be unsatisfactory at least at this stage of development of the technique because it takes typically 30 minutes to measure 1



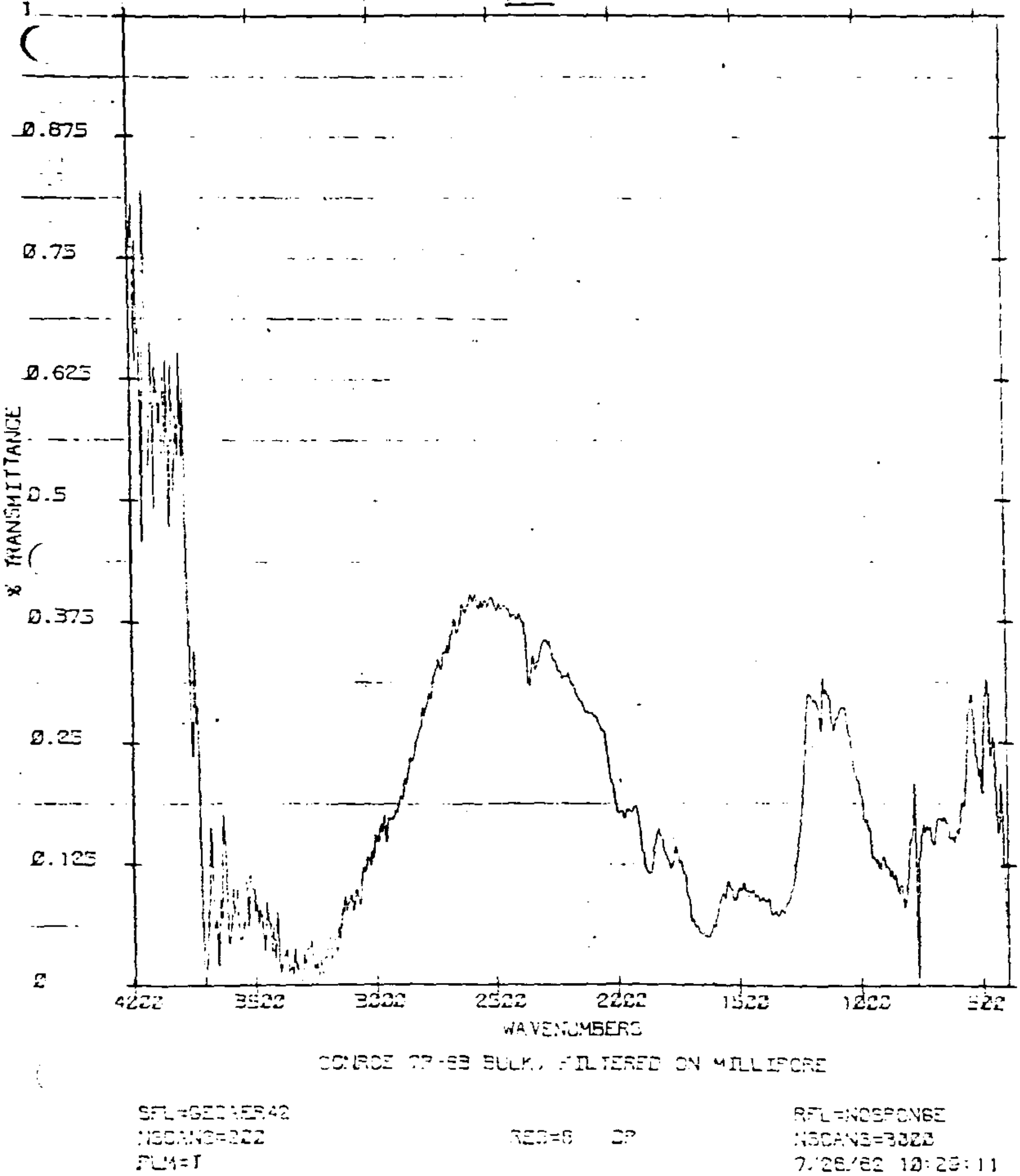
Example of Christiansen effect on FTIR scan of kaolinite.
Figure 18

spectrum with a signal to noise ratio high enough to make reliable observations at the 1% by weight contaminant level. This technique should be re-examined when the inherent sensitivity of the FTIR-PAS detector has been substantially improved. Nevertheless, the advantage of FTIR-PAS over specular reflectance can be seen through the example spectra in figure 19 and 20 (is by specular reflectance and is by FTIR-PAS of the same sample--the sample is clearly assigned as being a mixture of montmorillonite, quartz, and liquid water with traces of organic contaminants present). Although promising, this technique lacks the sensitivity that we require.

Diffuse reflectance (DRIFT) was used successfully to examine a wide variety of samples. The resulting spectra were easily assigned and were representative of the true spectra of the samples with one exception. For the more intense bands, the absolute intensity would vary from sample to sample (relative to less intense features) by as much as 10% of the peak intensity. Whereas the method is rapid by comparison with FTIR-PAS, it is not satisfactory for the examination of mineral samples where any sort of quantitative information is going to be required or where a contaminant at less than 1% needs to be studied in the presence

7a.

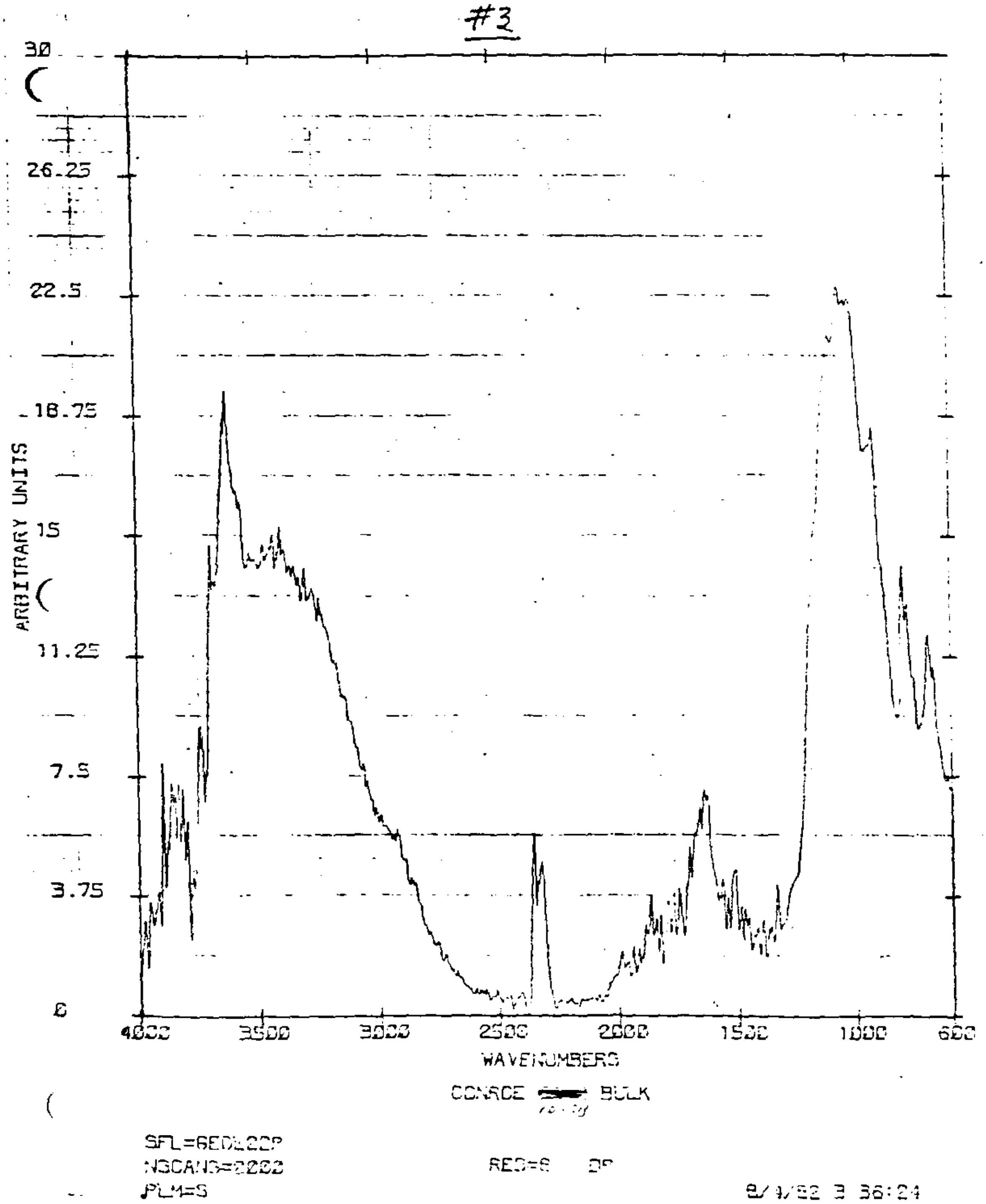
#2



FTIR-PAS spectra of Conroe Bulk sample

Figure 19

7a.

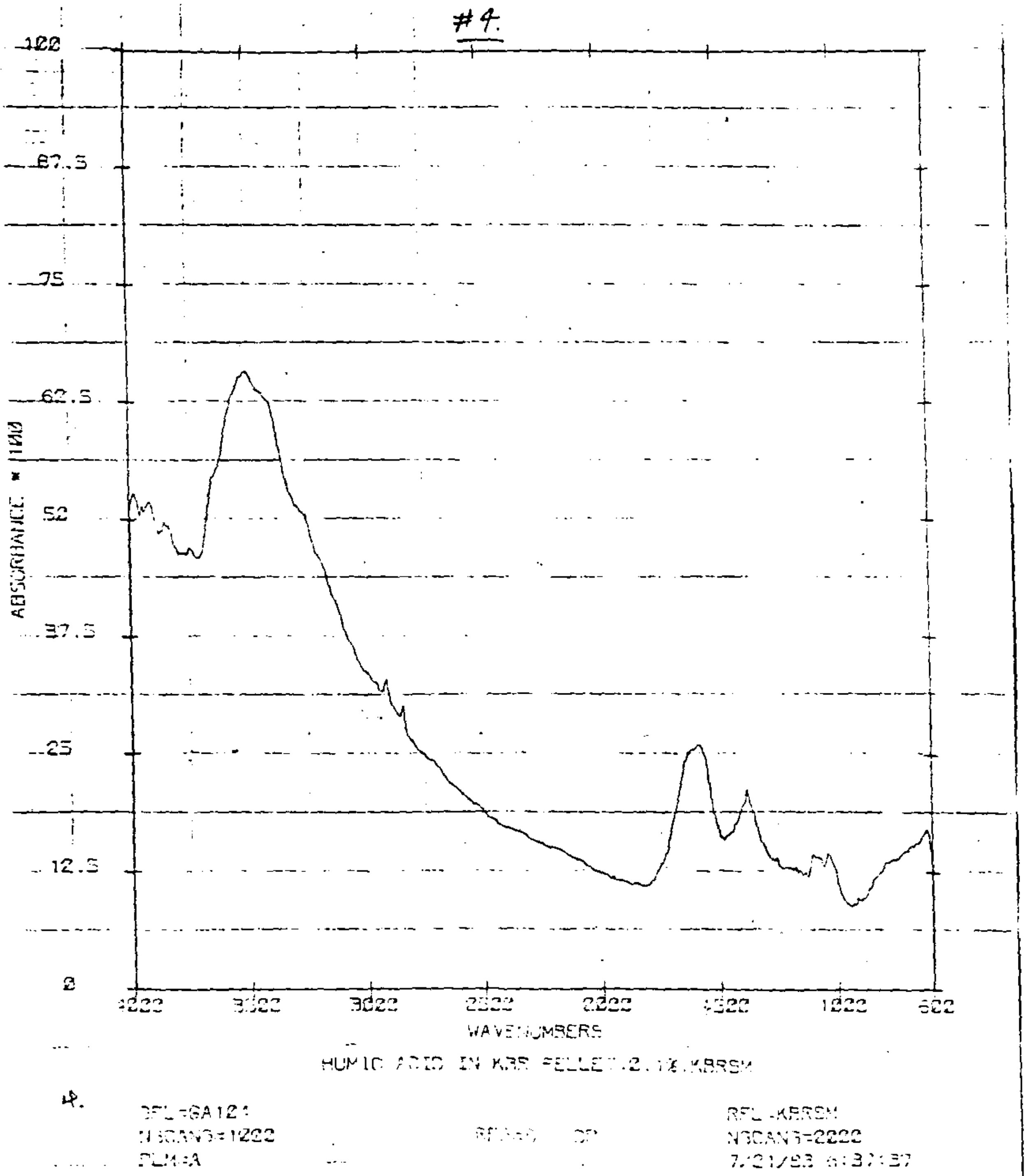


FTIR-PAS reflectance of Conroe Bulk sample.

Figure 20

of a strongly absorbing contaminant making up the bulk of the rest of the sample. Furthermore, for accurate measuremnets and calculation of the spectra, the total sample must be powdered to a reproducible mesh (true also with FTIR-PAS) and be diluted into KCl powder to a final sample level of not more than 1% by weight (a requirement of the Kubelka-Munk diffusely reflecting correction of the measured spectrum). Therefore, the gains in speed of analysis by comparison with FTIR-PAS, for example, are severely reduced. Because the requirements of this project were to accumulate accurate measurments of what might be trace level contaminants, DRIFT was pursued only as a tool for qualitative evaluation of samples. Several reference spectra of clays were measured using the technique.

Standard transmission FTIR techniques using pellets made by pressing carefully ground samples into pure KBr powder (0.025% by weight) and subjecting the system to high pressure were examined. These systems produced high quality spectra in a time primarily determined by the sample preparation time (which could be as short as 15 minutes per sample in batch). Provided that the samples were ground to an appropriate mesh, quantitative analysis could be performed on the samples. Figure 21 is the pellet



FTIR spectra of pellitized humic acid

Figure 21

spectrum of a commercially available sample of humic acid. Figure 22 is the result of subtraction from the spectrum of 95% quartz sand and 5% humic acid of varying amounts of the pure quartz sand's spectrum. Clearly, the resultant is identifiable as humic acid, indicating the feasibility of spectral subtraction at least down to the level of 1% by weight contaminant in paticular sample. Given all the previous considerations, this measurement technique is probably the optimum choice.

At this stage, it should be mentioned that since variations in component spectra can be considerable and because of linearity problems whenever one is examining a weak absorber in the presence of a strong absorber, it is not feasible to obtain quantitative accuracy in the measurments of trace contaminants at concentrations less than 1 part per thousand without prior concentration. This inaccuracy also holds true for RAMAN or NMR techniques, although RAMAN measurments may be able to accomplish the same effect as preconcentration if the beam is focused onto a sample region known to be high (perhaps artificially so) in the contaminant. A conclusion is that preconcentration must be an essential first step towards an effective examination of the chemical bonds formed between adsorbed material and substrate.

As part of an effort to examine ways favorable to

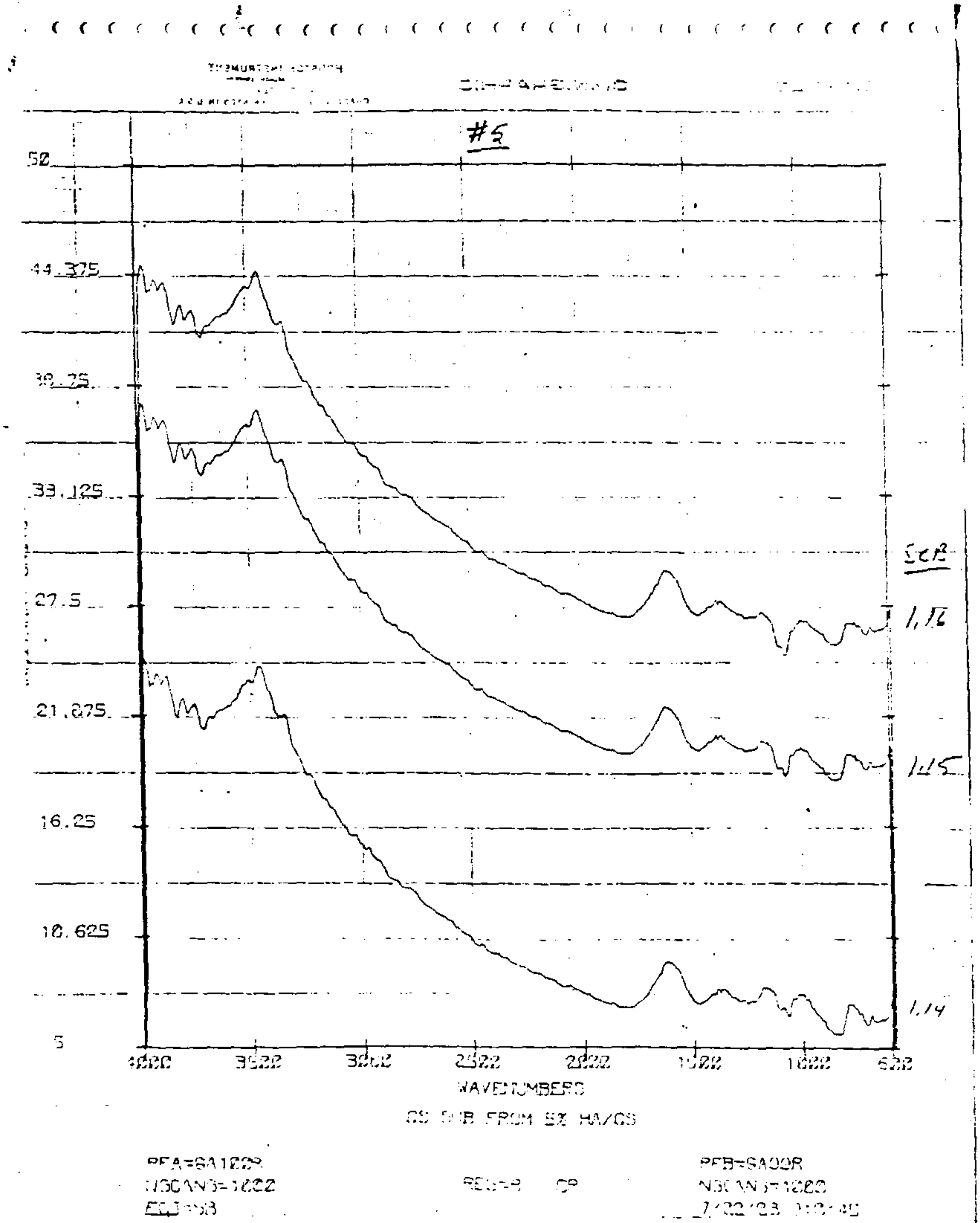
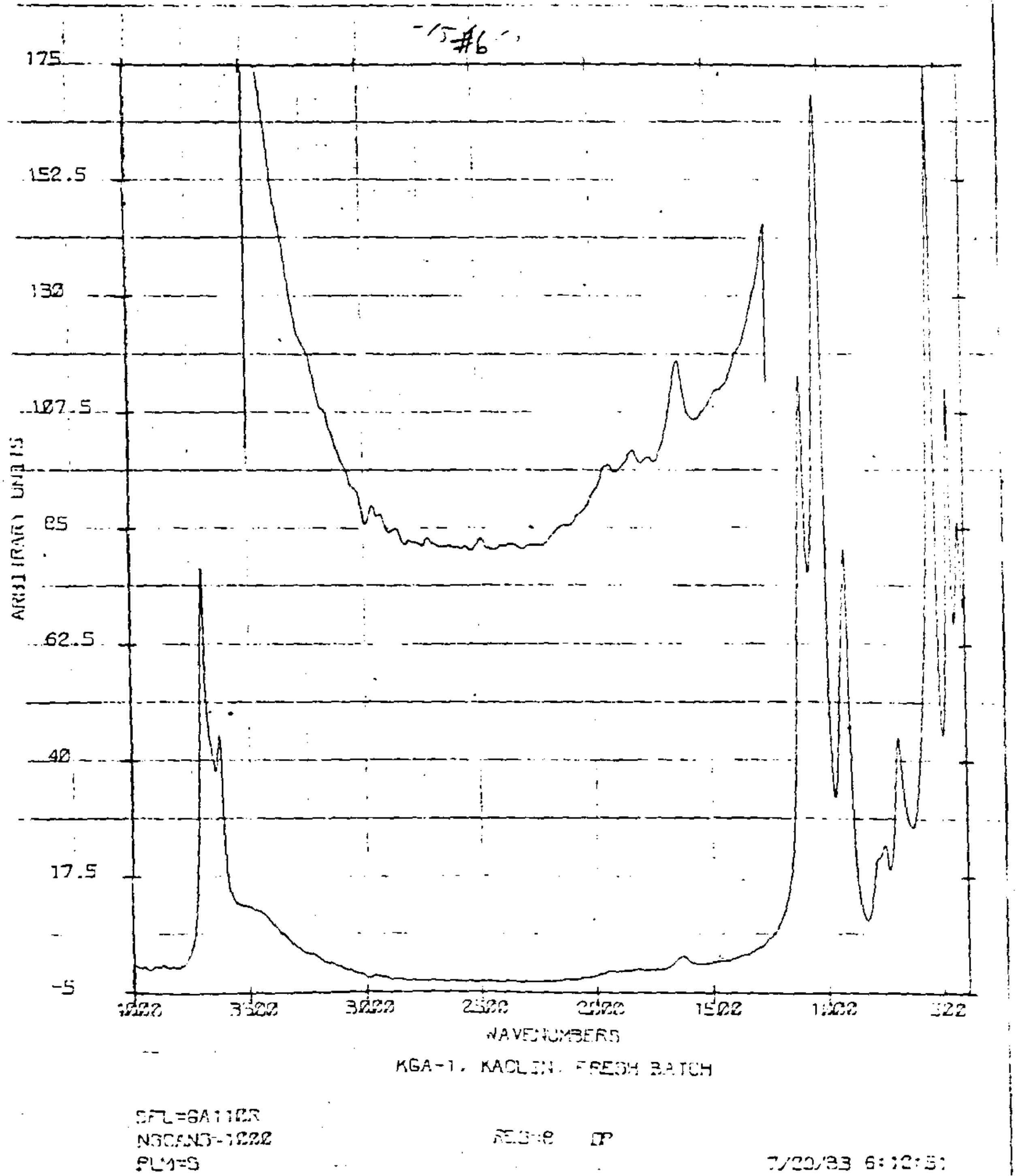


Illustration of spectral subtraction technique.

Figure 22

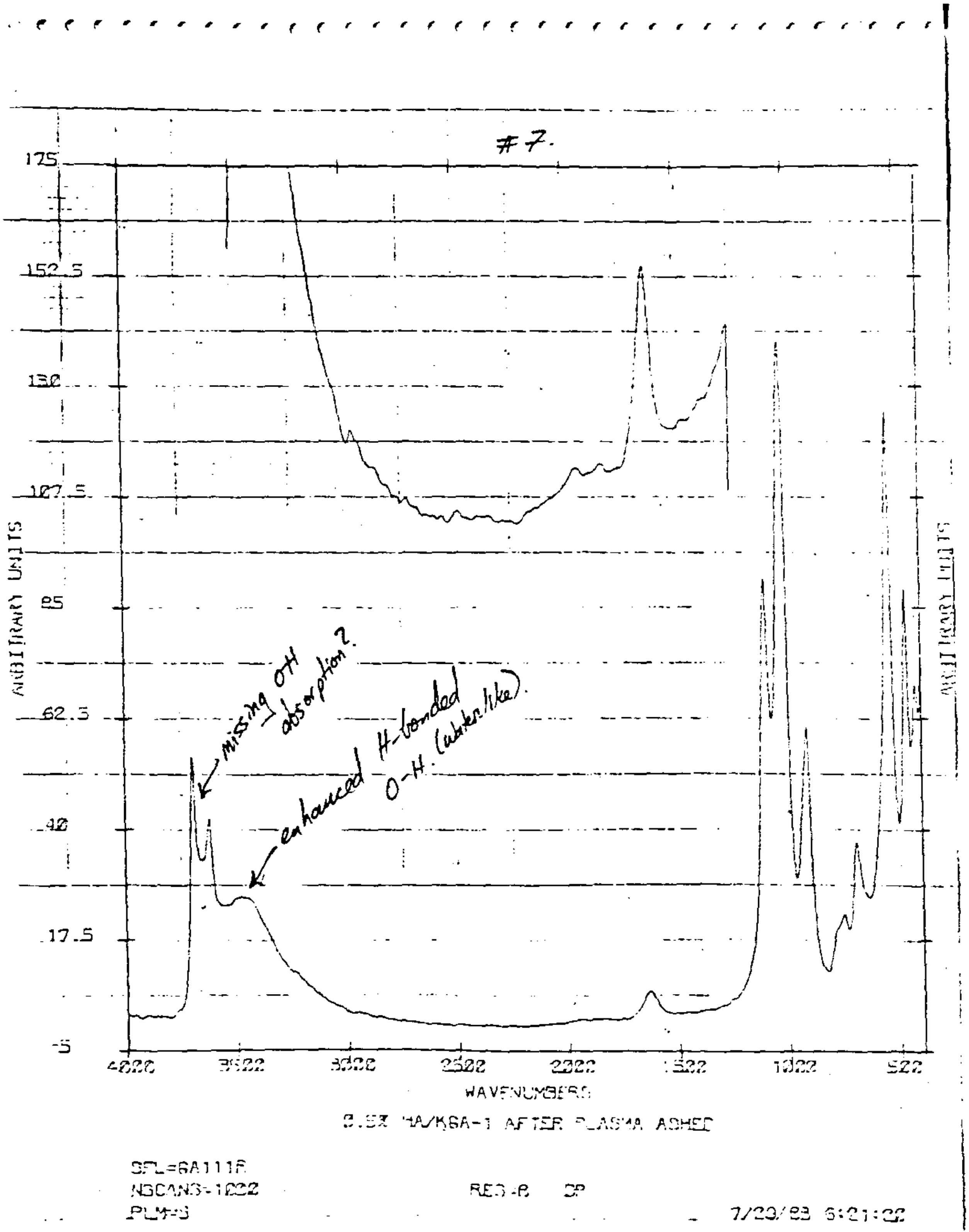
concentration, we thought that the measurement of a sample before and after low temperature plasma ashing would by difference leave the spectrum of the residual soil organic matter (SOM). In theory, this hypothesis is reasonable. In practice, we have noticed that at least in Kaolinite (see figure 23 before ashing versus figure 24 after ashing) a substantial difference in the hydroxyl region occurs with one adsorption appearing to disappear and the total amount of liquid water or lattice bound water appearing to increase. This observation has been made only once and obviously should be repeated in a more thorough series of experiments. However, the experiment does show that plasma ashing alters the structures of clays. This phenomenon should also be clarified. The experiment furthermore brings into doubt the ability to do the before versus after ashing analysis to infer the residual component spectrum, especially if there were alterations in the spectra of various mineral components in the fingerprint region of the mid-IR spectrum as a result of the plasma ashing process. The method should be examined prior to making a positive decision for or against the procedure as a whole.

An interesting observation was made with the plasma ashing



FTIR spectra of sample KGA-1 before ashing.

Figure 23



missing OH absorption?

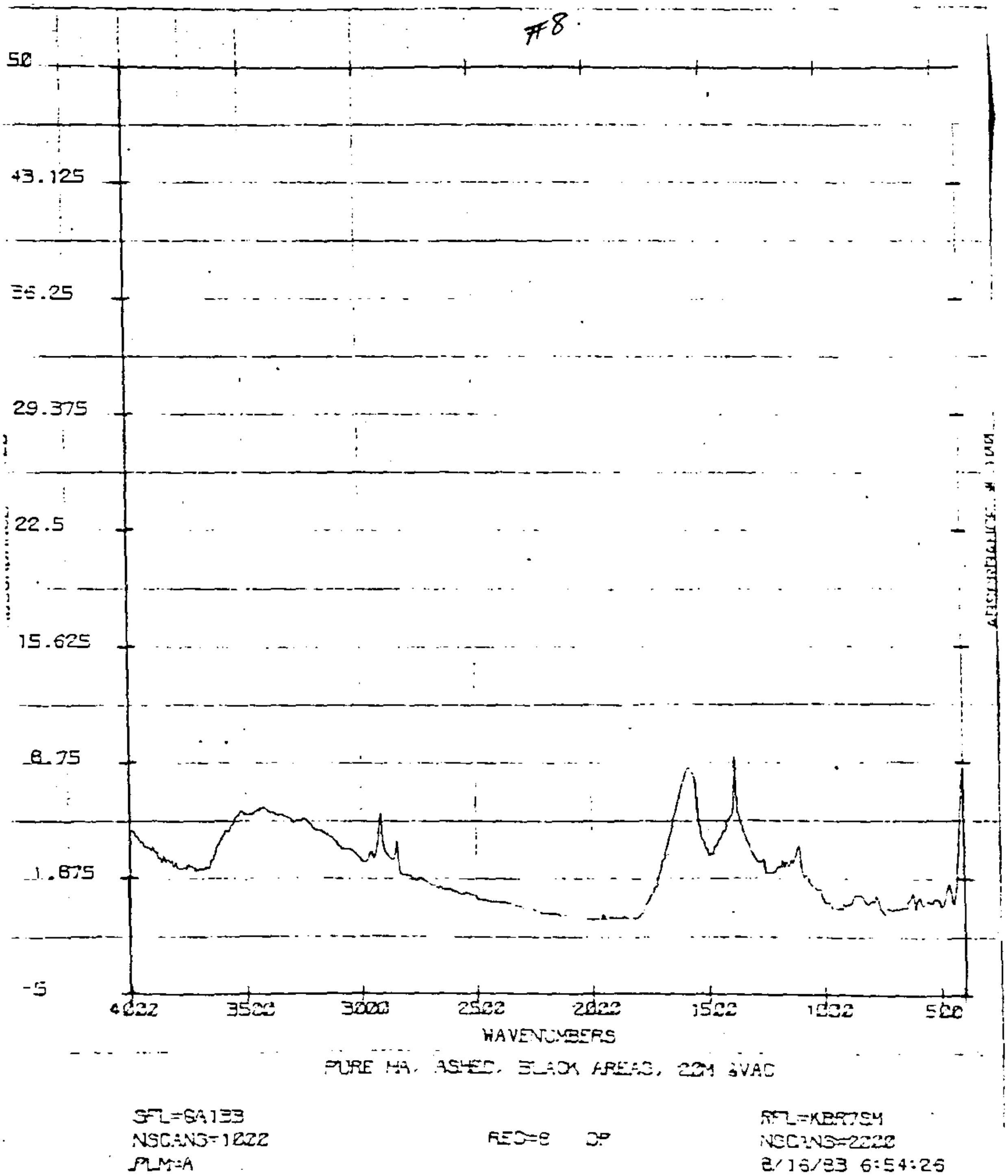
enhanced H-bonded O-H. (waterlike).

FTIR spectra of sample KGA-1 after ashing

Figure 24

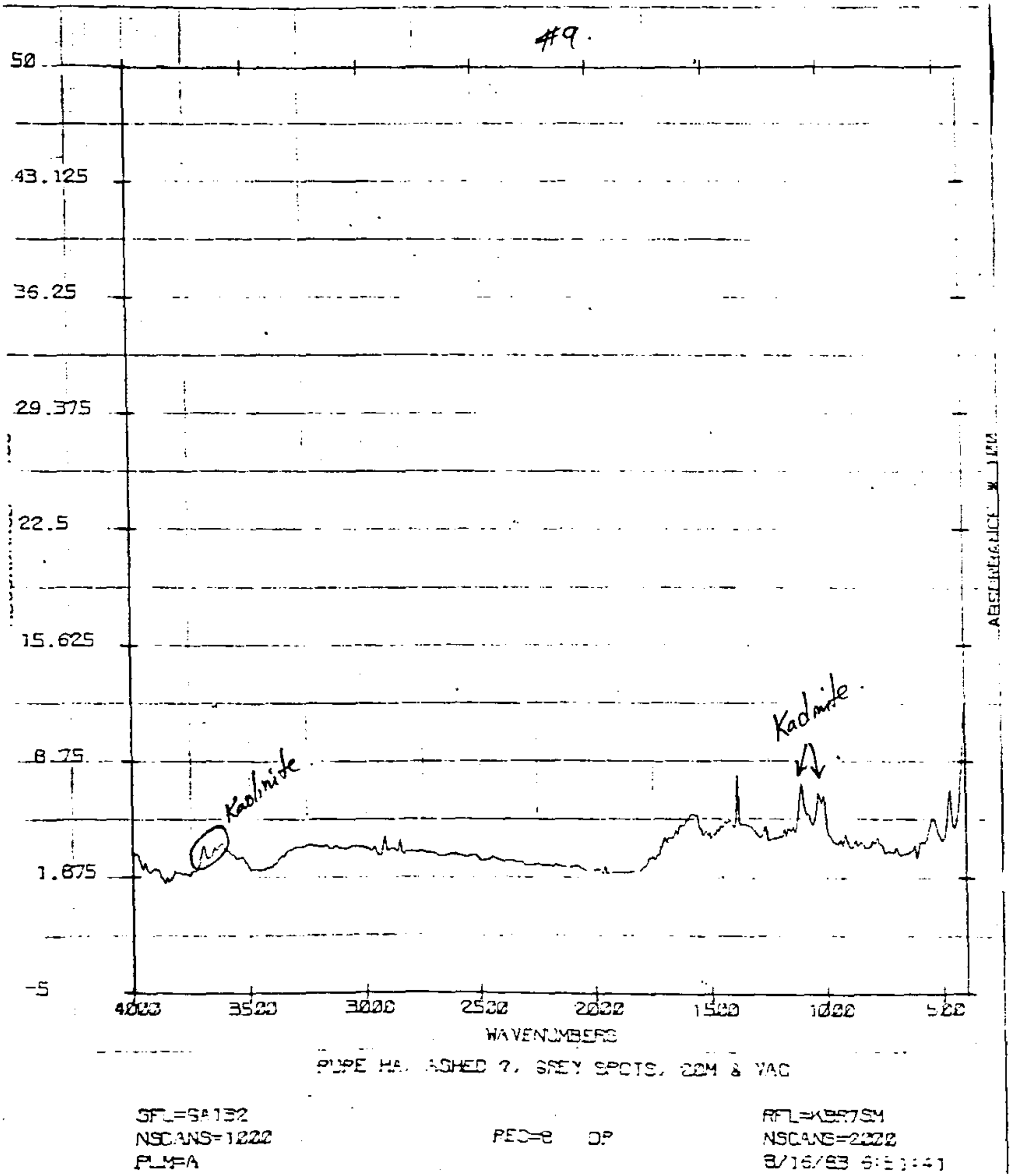
system. Commercial preparations of humic acid were subjected to 24 hours of ashing. While almost no weight changes were registered (ca. 1%), several black grey specks appeared after the ashing. Figure 25 shows the black crystals of humic after the ashing while figure 26 shows the spectrum of the grey specks. Clearly, these grey specks are associated with the clay contaminant present and that the commercial samples contain a significant percentage of kaolinite and perhaps other minerals.

Figures 27-29 are various pellet and FTIR-PAS spectra of fulvic acid, humic acid, and humin which give an idea of the spectral complexity of the problem. While a commercial sample of humic acid will generate spectra which are always identical, as soon as the source of the humic or fulvic acid is varied, the spectrum also varies. This spectral variation indicates that the compound is not pure. Rather, these acids and residues may be more correctly described as homogeneous mixtures of coelluting fractions. Spectra 30 and 31 show that the extraction is sucessful in removing various minerals, such as carbonate, present in the samples, but there is no guarantee that the simple extraction techniques currently used in the field are anywhere near adequate enough for the generation of single components.



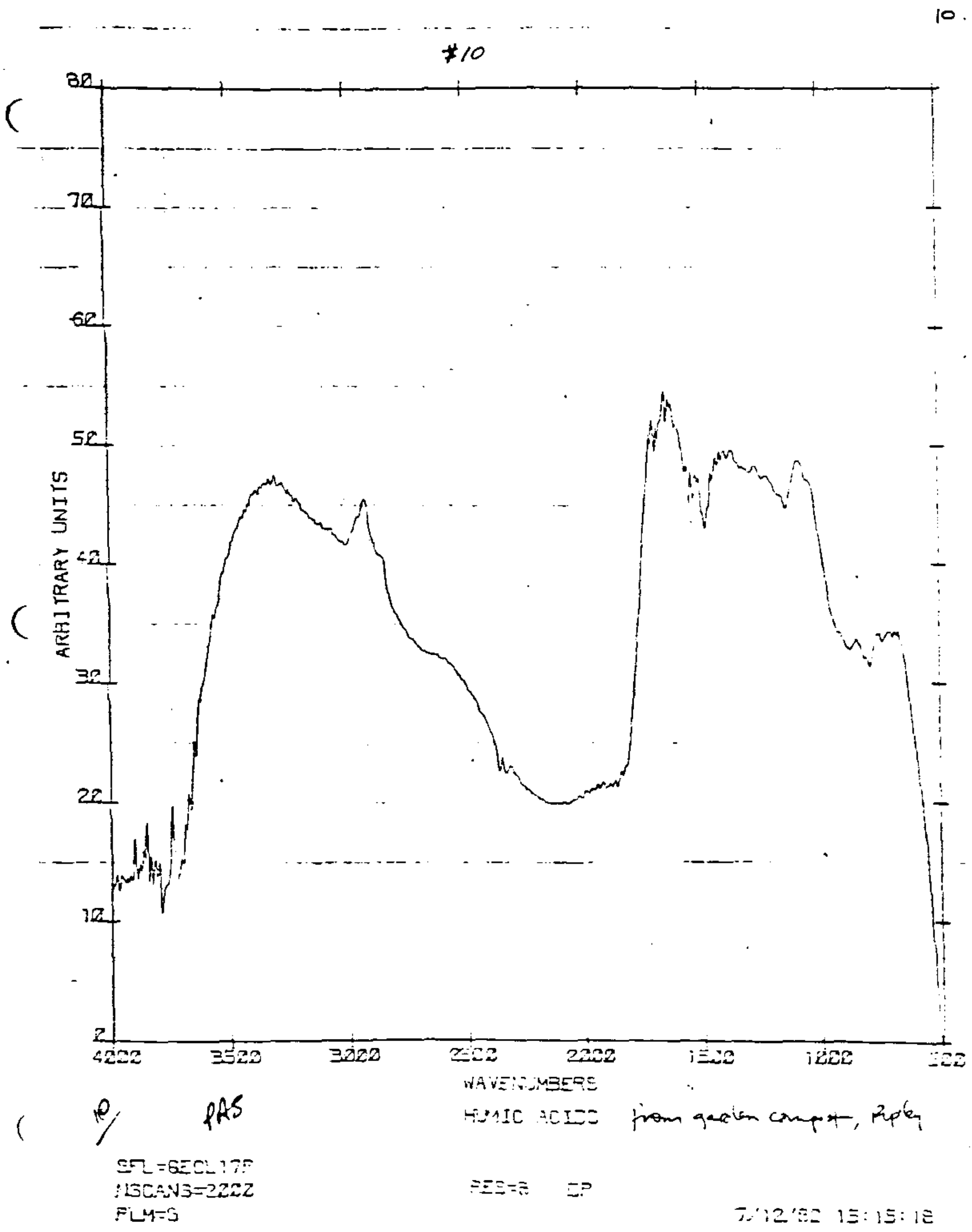
FTIR spectra of black crystals after ashing

Figure 25



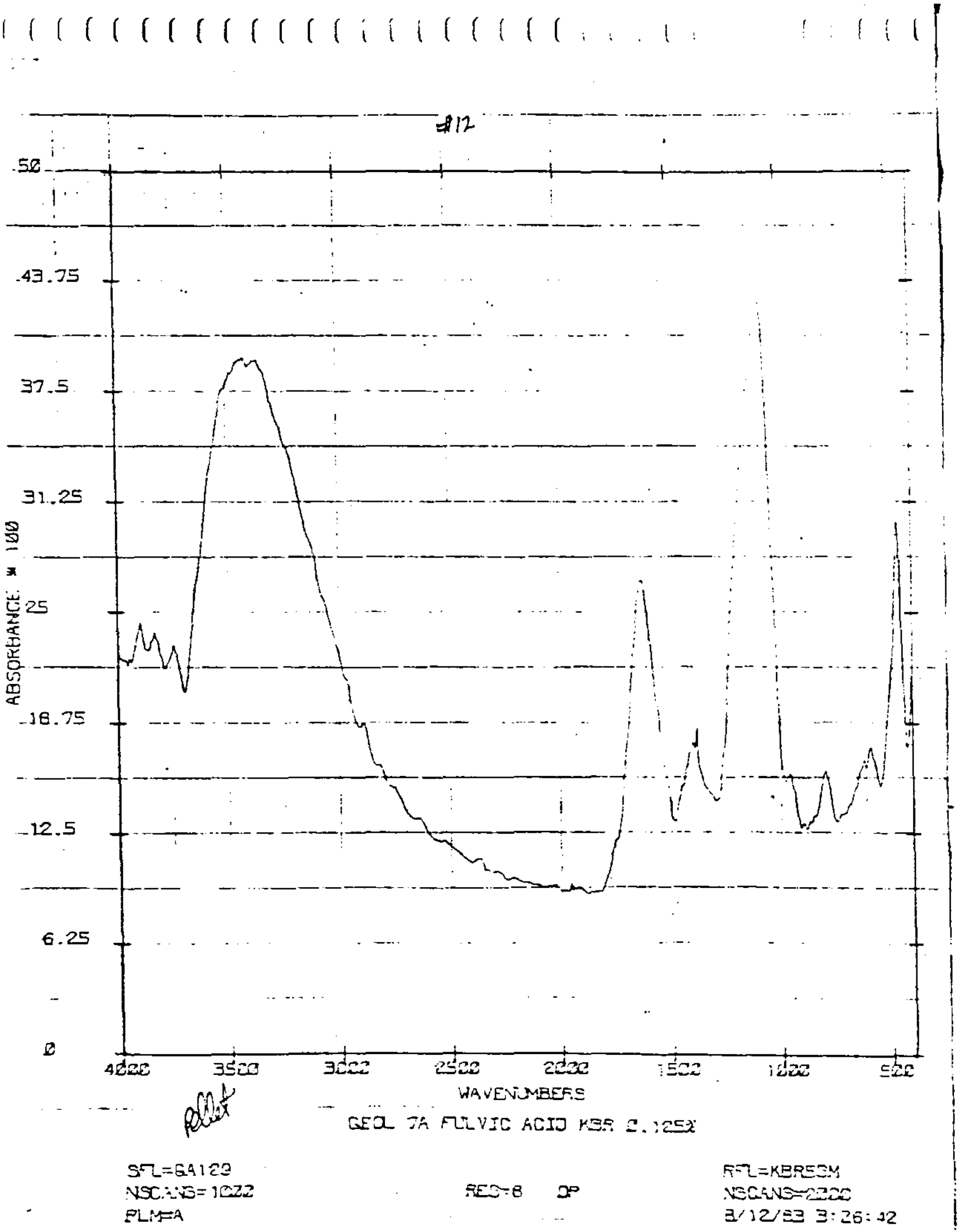
FTIR spectra of grey specks after ashing.

Figure 26



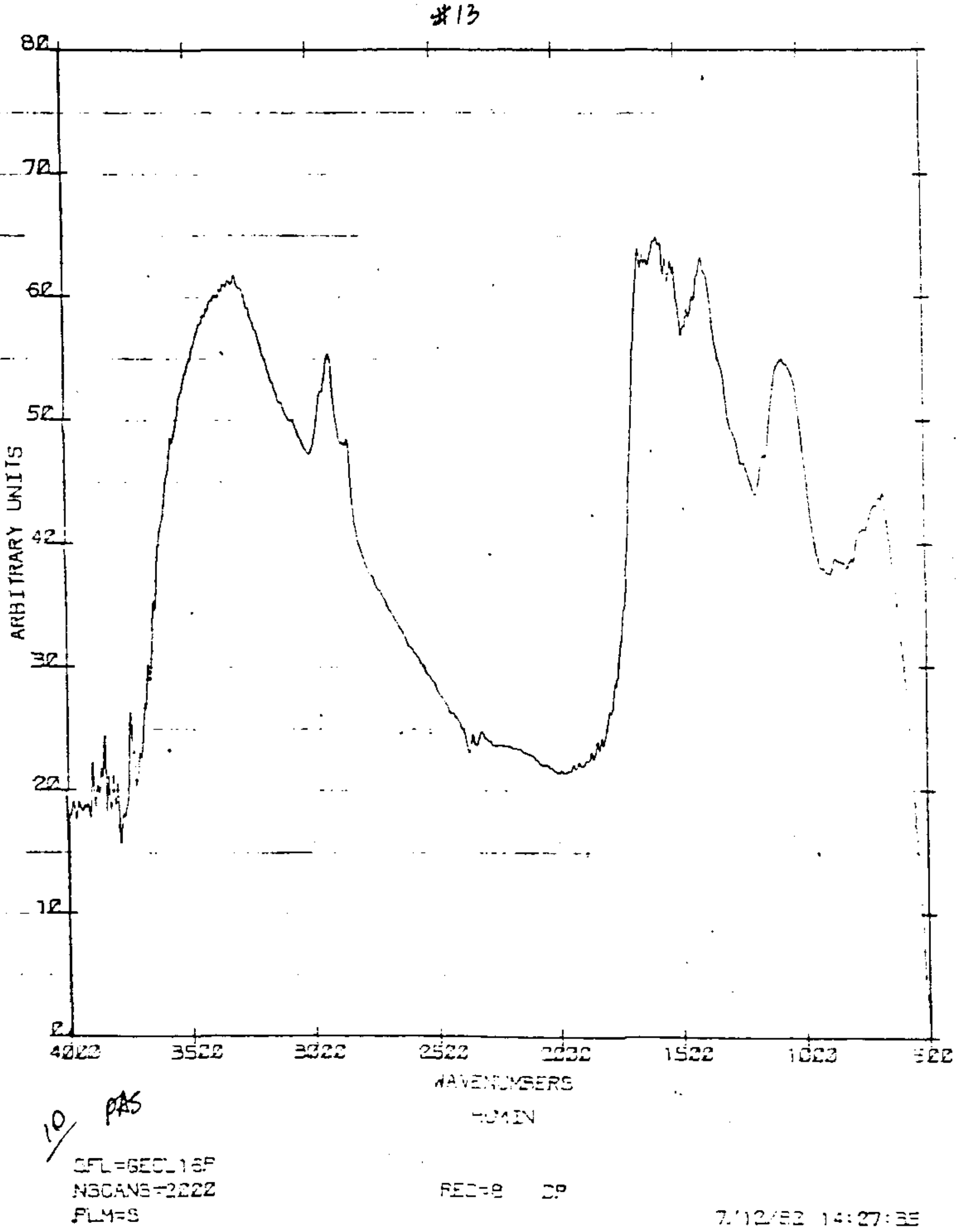
FTIR spectra of humic acids.

Figure 27



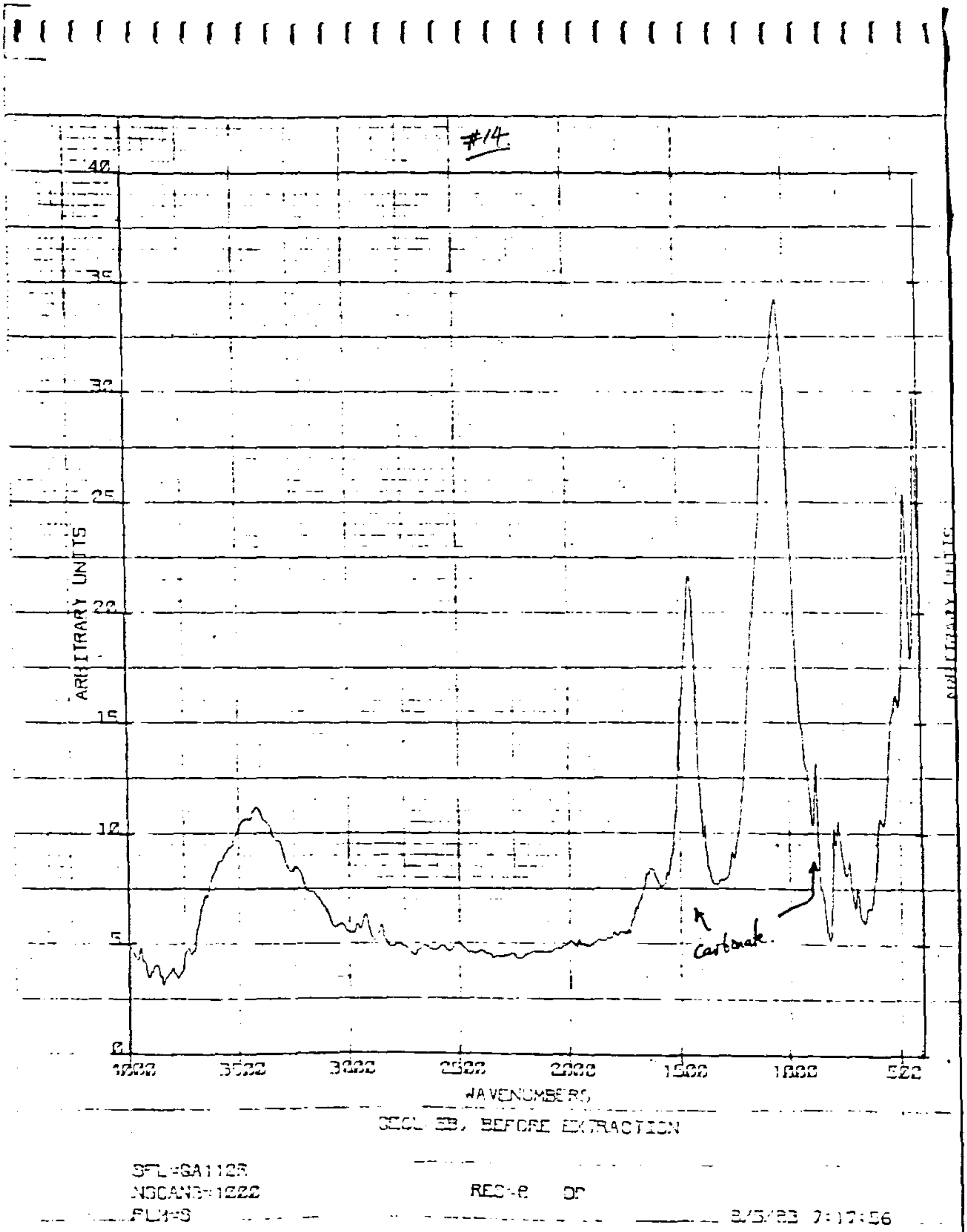
FTIR spectra of fulvic acids.

Figure 28



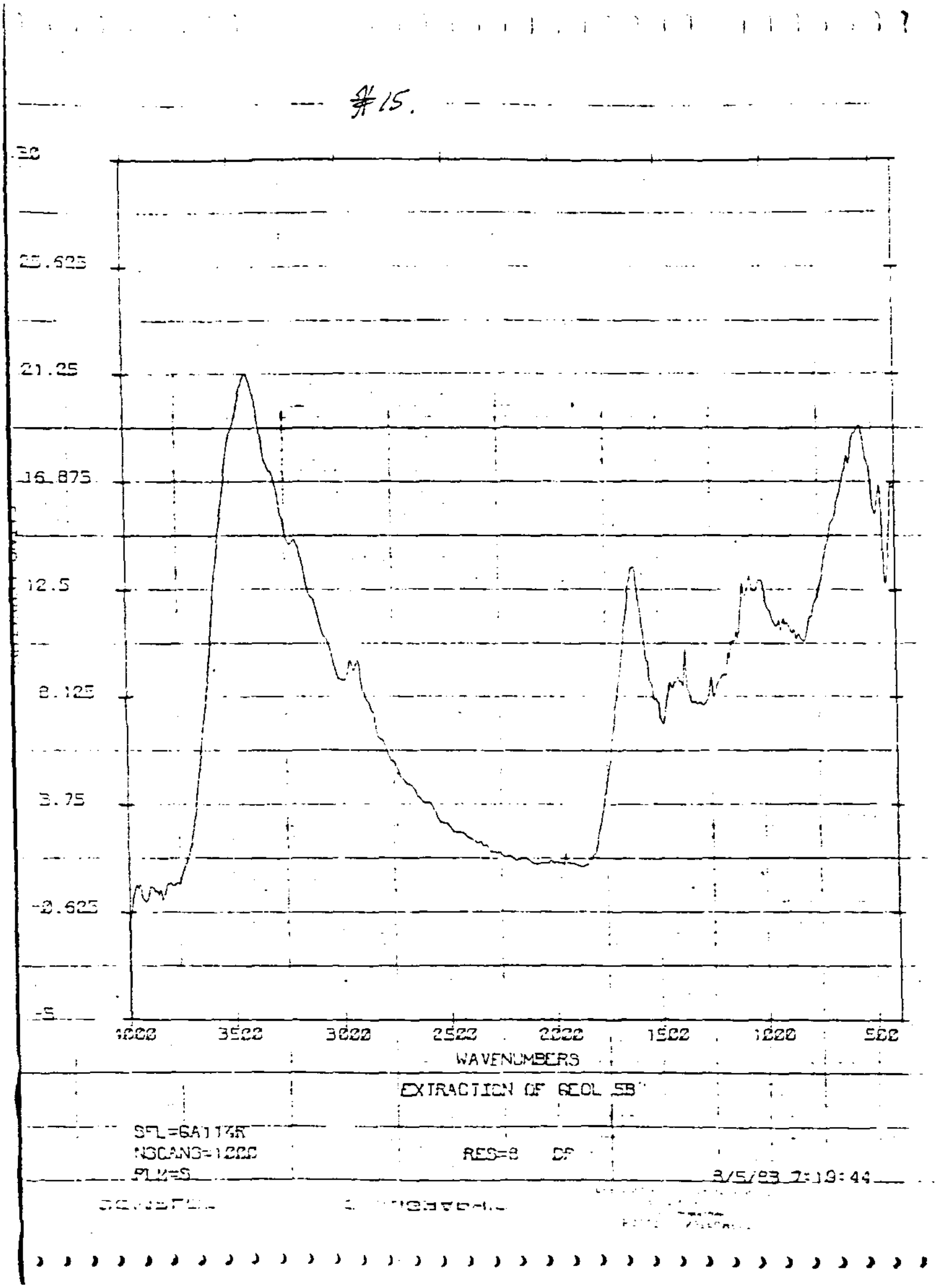
FTIR spectra of humin.

Figure 29



FTIR spectra before extraction.

Figure 30



FTIR spectra after extraction.

Figure 31

The conclusion is that the examination of clay-SOM-organic-pollutant complexes will require the thorough purification and characterization of various humic and fulvic acids and that the spectroscopic measurement of chemical bonds formed between pollutants and the substrate--what ever these bonds are--will be mandated to define the mechanism for chemical adsorption from ground waters. This research will be a tedious and difficult with a low probability of success. At this instant in time further persuit of FTIR techniques is not recommended.

LASER RAMAN MICROPROBE

The most recent addition to the study is the Raman Laser Microprobe, which is ideally suited to the examination of soil organic material and some of the other soil inorganic components.

The development of Raman spectroscopy has been a major advancement in the field of instrumental analysis because the Raman spectroscopy method provides information that has, in the past, been unattainable with other microanalytic techniques. One of the first of two Raman microprobes was developed at the U. S. National Bureau of Standards, was built primarily for experiments involving particle analysis. The second Raman, developed at the

Centre National De La Recherche Scientifique (Cnrs, Lille-France), served as the prototype for the now commercially offered Raman Laser Microprobe which is available from Instruments SA, Inc., J-Y Optical Systems Division. This latter is the instrument that we aquired. Raman microprobe spectroscopy is based on the excitation and detection of the spontaneous Raman effect. This effect is caused by the interaction of a laser (monochromatic light) with molecules of the sample, resulting in inelastic scattering. The appearance of scattered light at altered frequencies is the frequency shift (displacement of the Raman spectral lines from the excitation line) and is identical to the frequencies of molecular vibrations of the sample. Raman spectra thus provide the identity of the molecules which scatter the light. Solid samples also provide information on the nature and extent of crystallinity.

When incident light strikes sample molecules, it is scattered elastically (Rayleigh) and inelastically (Raman). In Raman scattering, the photons colliding with the sample molecules may either lose energy (Stokes shift) or gain energy (anti-Stokes' shift). The Stokes lines are generally studied because they are of greater intensities than the anti-Stokes lines. The Raman effect is very weak as evidenced by a scatter by solids which is typically less than 10E-7 of the incident radiation.

The incident light energy for the Raman effect is less than the energies of excited electronic states. However, if these excited states occur,, then other inelastic scattering processes such as flourescence occurs over a wide portion of the Stokes region of the Raman spectrum, which could pose a serious interference problem.

The ISA microprobe couples a research microscope, a state-of-the-art Raman specrometer and a powerful argon ion laser. The laser is focused through the objective of the microscope, onto whatever part of the sample the operator desires, with a beam diameter or sampling area of about 1 square micrometer. The scattered light is collected back through the microscope objective and directed into the monochromator of the spectrophotometer to be detected by a sensitive, cooled photomultiplier tube. The instrument is interfaced to a Columbia microcomputer by which the instrument is controlled. The microcomputer also provides spectral averaging of multiple scans, as well as other spectral manipulations making this instrument an extemely powerful tool for the microscopic examination of small particles such as are characteristic of soil.

Major Advantages of the Raman Method

1. Raman microprobe techniques are nondestructive and require little sample preparation time.
2. Sample may be analyzed in situ.
3. Molecular specificity--the frequency shifts are equal to the vibrational frequencies of the sample molecules. These frequencies are different for different molecules and change with the environment of the molecules, making the identification of each component of a Raman spectrum possible.
4. Samples may include all states of matter. Any type of molecule organic, inorganic, or biological may be identified by the Raman microprobe.
5. Ambient laboratory conditions may be used during the analytical procedure. Other microprobe techniques require use of a vacuum for sample placement.
6. The mapping of the surface of the sample is possible, allowing for identification of the different components of a heterogeneous sample.
7. Because the vibrational bands of most molecules are well separated, interference is kept to a minimum.

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8. The detection limits range from approximately 10 pictograms to 100 pictograms because of a good signal-to-noise ratio. This limit may be lowered one or two orders of magnitude for samples that can tolerate greater levels of irradiation.
10. Because water exhibits only a very small Raman signal, it does not matter if the sample contains or is examined in water. Water as discussed earlier is a major limitation of Infrared techniques.

Major Limitations of the Raman Method

1. The inherent weakness of the Raman effect is its low light level event. The weak signals are difficult to detect and place strenuous requirements on the spectrometer.
2. At this time, quantitation of sample components is not possible due to the lack of adequately developed theory of Raman and flourescence scattering from microparticles.
3. Local heating effects caused by a buildup of heat in the sample from the laser radiation may exist. Since many compounds absorb over a wide spectral range, using a

different excitation frequency may not eliminate the problem.

4. The weak Raman signal may be difficult to detect when the sample also emits flourescence. Using a red line excitation source or quenching techniques may eliminate the problem.
5. Some solid compounds are unstable under high intensity laser radiation, inducing photolytic reactions which can lead to optical breakdown.
6. Lack of standard reference spectra because of the newness of the analytical technique makes identification of unknowns more time consuming.

The Laser Raman Microprobe has been in use only a limited time and we have not as yet been able to carry out many of the investigations we hope to do. At this point we have made an effort to characterize some of the standard clays, including montmorillonite and several Kaolinites. In time, we hope to be able to identify an adsorbed organic pollutant and to determine whether its substrate is an organic or inorganic fraction of the soil. Our immediate objective is to the mode of distribution of the natural organic matter in the various soil types.

Raman microprobe techniques can yield information about material characterization that has been incompletely provided by conventional techniques. Entirely new information may be obtained from sampling microscopic regions approximately one micrometer in dimension. Information on the molecular nature of the components of a sample, the distribution in the sample, and the chemical and physical character of the matrix are the characteristics that may be explored.

The ultimate limits of detection, quantitation of individual species present, sample size, sample heating and fluorescence, and the compositional complexity of sample are questions whose answers must wait for increased understanding that will come from future studies.

MACROPORE EXAMINATION

To distinguish "macro" pores from smaller "micro" pores the property of permeability will be utilized. The distribution of "macro" pores throughout a given volume may be classified with respect to the soil moisture content.

The soil moisture content is measured directly by neutron scattering. Use of this method requires that a calibration curve be prepared which describes the relation between neutron counts per minute and the soil moisture percentage. A computer program "NUTPROB" calculates the water contact values from the field data using the equation.

$0 = A + B * R$

0 = water content

A + B Calibration curve constants

R - ratio of measured count over standard count

The number of counts per minute, corresponding to a certain soil moisture content, are affected by the soil type. The bulk density and chemical composition affect the count rate. High count rates are obtained in fine textured soils as a result of hydrogen in the lattice structure of the clay minerals, and also in soils with high organic matter contents.

Another method to be employed for characterizing the soil water movement will be a resistivity survey. The plots will be ponded with a saline solution. The potential at each depth will be measured. Integrating the potentials over all depths will record the soil water movement and its distribution with time.

Procedure:

The site was cleared of all vegetation on a fairly level square area 20 ft by 20, and subdivided into sixteen 4 ft by 4 ft squares. Within each square the abundance (density), diameter, vertical depths, and length or continuity of the macropores were measured and photographed over time. The site contains 8 access tubes for recording soil moisture contents and 1 centrally located piezometer for obtaining water quality data. A hand auger was used for construction of the monitoring holes. Along the edge of the site a wooden border was constructed to a depth of 2 inches below the soil surface and 4 inches above. The inside border was lined with bentonite to form a relatively impermeable barrier so water could be ponded over the surface.

The site was ponded with water until a 4" depth was reached. Water was pumped from Lake Carl Blackwell and sprinkled onto the site area. Water samples for the lake and the site area were taken for analyses and compared. Soil moisture contents were measured on a weekly basis several months prior to the infiltration experiment, during the infiltration experiment, and for a period of 48 hours after infiltration. Water samples were also taken before and after infiltration to detect any changes in quality.

Future Work

The experimental site will be monitored continuously throughout the winter and spring to observe the effects of precipitation and temperature on the development of macropores. As the mean temperature gradually rises with the arrival of summer the formation of macropores will be slow. As the temperature increases and mean precipitation decreases macropore development will reach a peak, usually by late summer or early fall. Prior to this period an additional site shall be constructed in an analogous manner. Infiltration experiments will be conducted at each site prior to macropore development (early summer), during macropore development (mid-summer), and at the peak of macropore development (late summer). Resistivity surveys shall also be conducted at each site for determining water contents throughout the plot over time.

Additionally, the soil morphology at each site will be characterized extensively as to the particle size distribution and mineralogic content. For each mineralogically distinct horizon a grain size distribution will be determined via sieve analysis. The mineralogic content will be determined via X-ray diffraction. The water quality before and after infiltration and throughout the year shall be analyzed via atomic absorption analysis.

SECTION 5

SITE CHARACTERIZATION

To date four sites in various parts of the Continental United States have been chosen as study areas. These are: the former creosote waste disposal lagoon in Conroe, Texas, the D'Imperio Dump in Atlantic County, New Jersey, the Apple Creek drainage basin in Burleigh County, North Dakota, and north central Payne County, Oklahoma.

Various aspects of subsurface characterization are being considered in each area. The first two sites represent point-source ground water pollution problems where in-depth studies over restricted areas will be undertaken. The third site represents a region, where subsurface conditions on a greater areal scale will be examined. At the fourth site, a study of macropores and their effect on the transmission of surface recharge to a ground water system is being conducted.

D'IMPERIO DUMP, ATLANTIC COUNTY, NEW JERSEY

The D'Imperio site was chosen for study for several reasons. The nature of the contaminants (organic solvents) renders the problem directly applicable to our research. The site is located in a relatively undeveloped area where water quality would not be affected by other contaminant sources. The geologic and hydrologic settings are relatively simplistic and, therefore, would serve as adequate controls for the study of minor constituents (i.e. clays, oxides, hydroxides) in the sediments and their effect on the movement of pollutants.

An unknown number of years ago, many 55 gallon capacity drums of chemical waste were dumped into the pit. The site was subsequently covered with native soil to conceal any signs of waste disposal. In recent years, rusting drums have begun to appear at the surface.

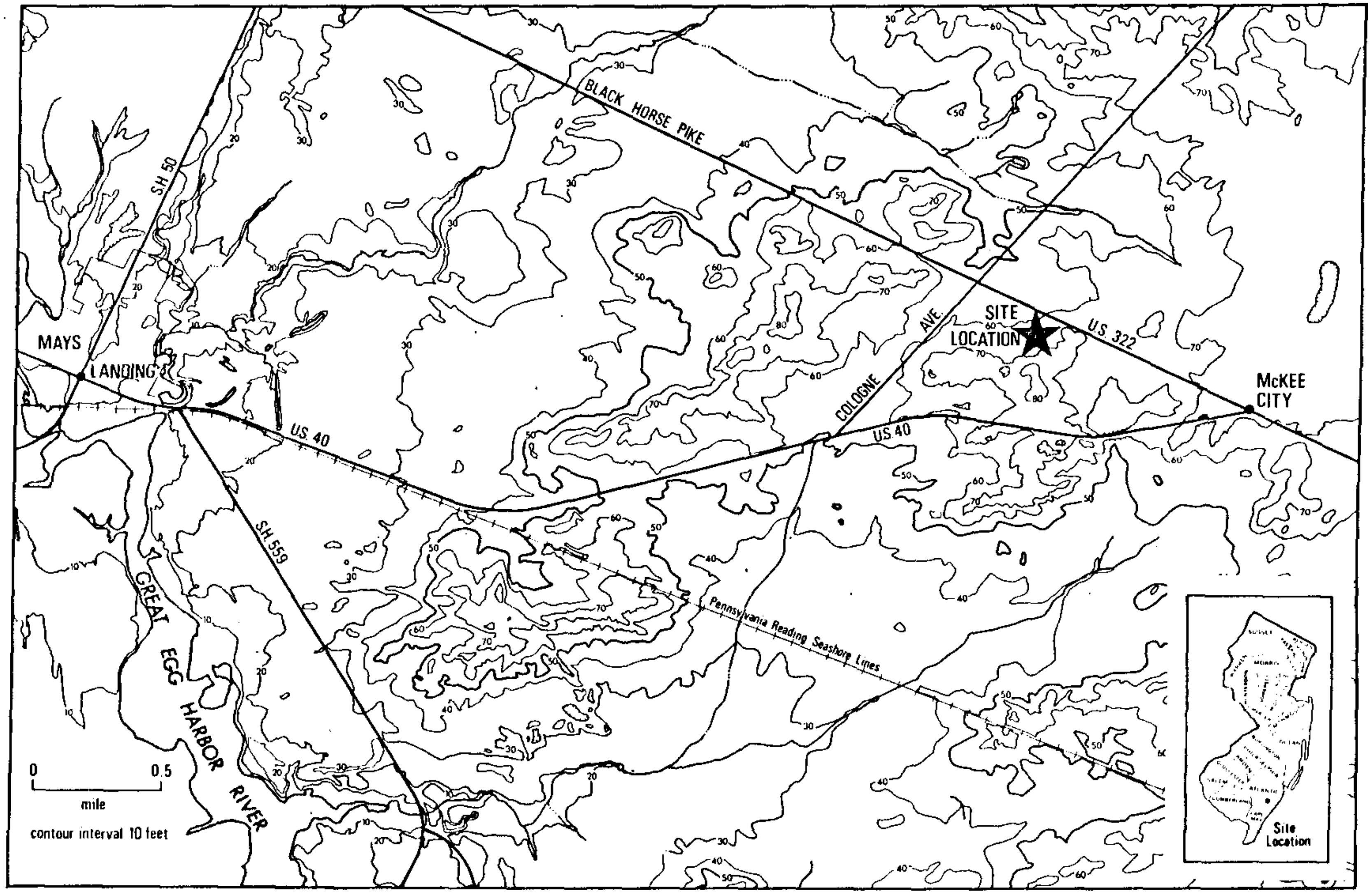
The property owner has applied for and received aid from the federal government in the form of Superfund Monies to delineate and remediate environmental hazards posed by the site. Work done previously by private consultants has demonstrated that significant ground water contamination has occurred. At least one plume of both organic and inorganic pollutants has migrated ~ 1000 feet off-site. Several potable wells are located within 1/2 mile of the site.

Geography

The D'Imperio Dump site is situated in a rural, wooded area of Atlantic County, New Jersey approximately 7 miles west of Atlantic City between State Route 40 and County Route 322. It consists of a 1/2-acre abandoned gravel pit (Figure 32a).

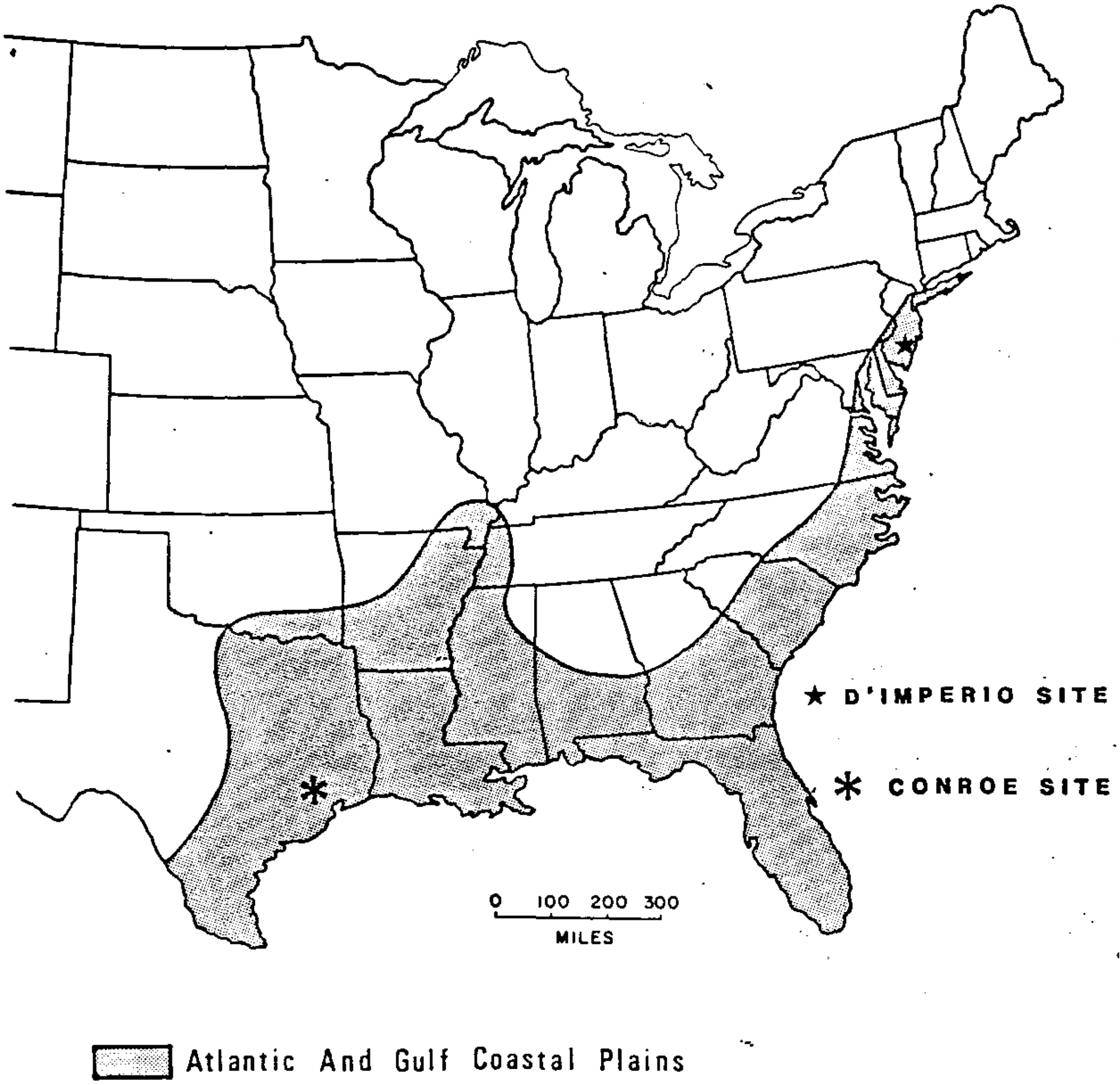
Physiography and Topography--

The Dump site is located in the Atlantic coastal plain physiographic province (Figure 33). The coastal plain in New Jersey is a region of low relief having a gentle slope to the east and southeast, toward the Atlantic Ocean. It is characterized by flat to gently undulating uplands and wide flat-bottomed valleys containing shallow streams. Small hills and hummocks commonly rise above the larger flat and undulating surfaces. Many of the smaller geomorphic features closely resemble those of shore, beach and coastal environments. They are thought to be relics of former high-level Pliocene-Pleistocene sea sands (Gill et al., 1963). Surface gradients on the gently sloping plain average 3-10 ft/mile. Primary surface drainage occurs along the Mullica, Great Egg Harbor, and Maurice rivers and associated tributaries. These rivers all flow east-



Location of the D'Imperio Dump Site in Atlantic County, New Jersey
(After U.S.G.S.)

Figure 32



Atlantic and Gulf Coastal Plain
(After Deussen, 1914)

Figure 33

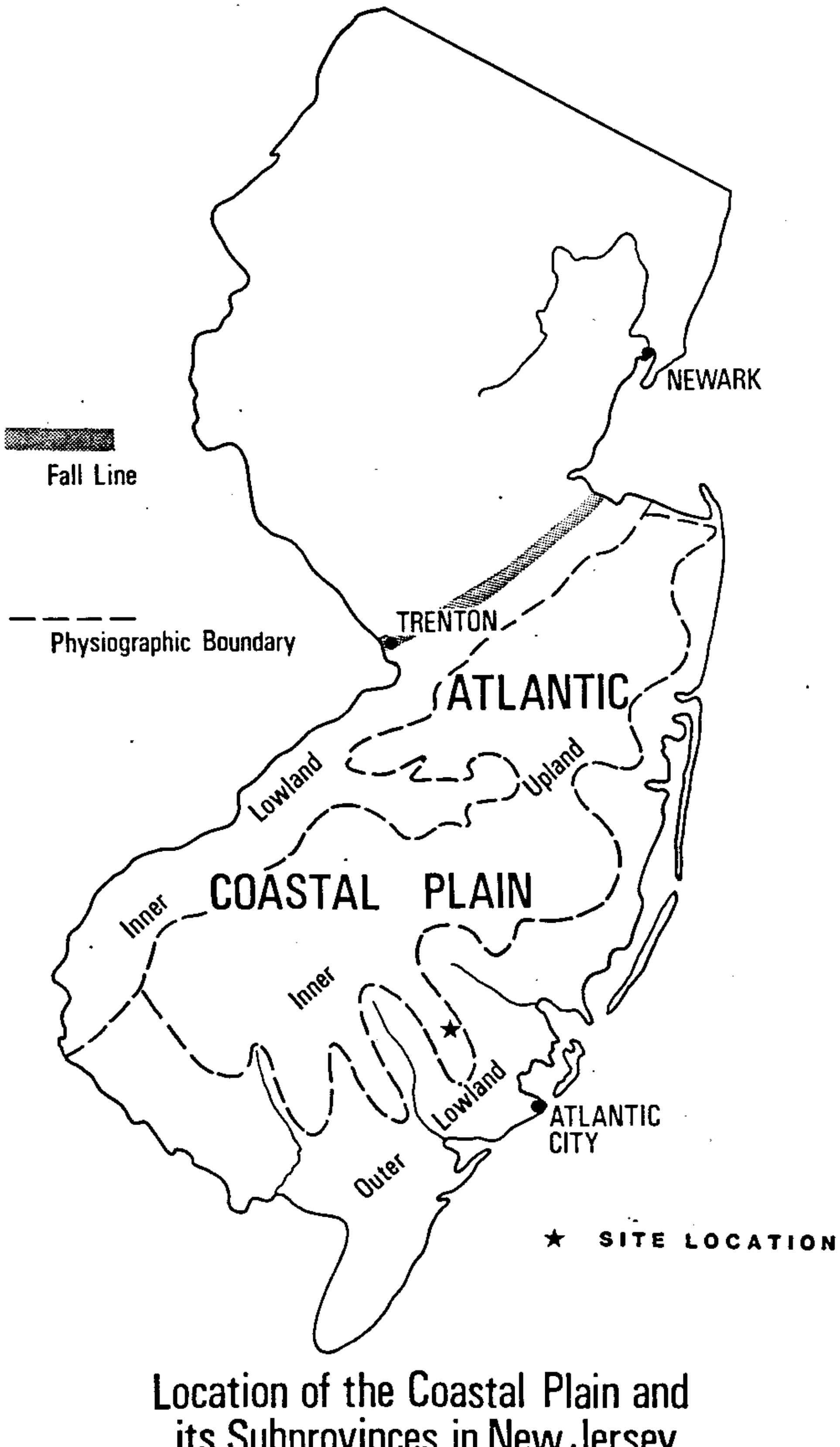
southeast to south and drain into the Atlantic Ocean.

The coastal plain has been subdivided by Owens and Minard (1960) into three physiographic sub-provinces (Figure 34); an Outer Lowland along the coast where the elevations rarely exceed 50 feet above sea level, a broad Inner Upland with elevations as great as 300 feet, and a narrow Inner Lowland along the Delaware River having elevations of 50-100 feet. The dump site is located near the eastern margin of the Inner Upland sub-province.

Soils--

In the coastal plain region, soils often control the rate and amount of infiltration, the amount of recharge to aquifers, and the chemical quality of ground water (Rhodehamel, 1973). This situation exists because of the relatively flat topography and highly permeable nature of the sandy sediments. In general, the soils present are characteristic of podzolic soil development in humid and temperate climates having mixed conifer and hardwood forests. Free drainage, characteristic of podzols, causes the upland soils to become dry soon after rainfall (Rogers, 1955).

Soils of the basin are variable despite a rather uniform gray, sandy appearance at the surface. Although the dominant



Location of the Coastal Plain and its Subprovinces in New Jersey

(After Gill, 1963)

Figure 34

grain size is sand, soils range from fine to coarse, free-draining sand and gravel through silt and clay (Rhodehamel, 1973). Fine textured soils are more common in the southern and western parts of the study area; the average clay content of most associations ranges from 10 to 30 percent. The dominant clay mineral present is Kaolinite, though illite sometimes occurs (Dalton, personal communication). Clay particles originally present at the surface are rapidly leached from the A horizon during soil development and commonly occur as coatings on larger particles, or as an interstitial matrix in the B horizon below (Rogers, 1955). Calcium carbonate is virtually nonexistent in the soils present in the study area.

Hydraulically, the soils of the coastal plain can store and transmit large quantities of water. Infiltration rates in the dominantly mineral soil horizons range from 0.6 to 9.0 inches/hr (Rogers, 1955). Even in the less permeable soils, the water storage capacity in the layer above the often present poorly drained zone is great enough to permit infiltration of most rainfall. Markley (1962) has determined cation exchange capacities for several common soils under both forest and cultivated conditions. These data indicate that the cation exchange capacity of most coastal plain soils is low as a result of rapid free drainage, single-grained soil structure, and stability of the quartz parent material. In addition, podzolic soils are acidic, with the pH of horizons ranging from 3.7 to 6.5 (more commonly 4.0-5.0)(Rhodehamel, 1973). Cation exchange capacity generally decreases with increased hydrogen ion concentration, therefore, it would be expected that minimal exchange would occur in these acid soils.

The soil survey of Atlantic County, New Jersey maps the soil present at the D'Imperio site as Matawan Sandy Loam (Mta). According to the current soil classification system, this soil belongs to the fine-loamy, siliceous, mesic family of the Typic Hapludult Subgroup, Order Ultisols (Table 2).

In a representative profile from a boring taken approximately 100 feet east of the dump, the surface layer is dark grayish-brown sandy loam 6" thick. The subsurface layer is 10" of rust colored sandy loam which grades into 11" of rust colored gravelly loam. The subsoil consists of 23" of brownish pink clay loam. The substratum, to a depth of seven feet, consists of pinkish brown fine sand with little clay.

Surface and subsurface soil layers are extremely acid (pH 4.5-5.8) and have a low organic matter content. Matawan sandy loam is considered moderately well to well drained. The dense

Depth from surface (inches)	USDA texture	Classification		Liquid Limit	Plasticity index	Permeability (inches per hour)
		Unified	AASHTO			
0-40	Sandy loam	SM, SC	A-2, A-4	15-25	4-8	0.6-6.0
24-60	Clay loam, sandy loam, clay loam	SC, CL, ML, SM	A-2, A-4, A-6	15-45	5-15	0.2-0.6

Depth from surface (inches)	Percentages less than 3 inches passing sieve—				Available water capacity (inches per hour)	Reaction pH	Shrink-well potential
	No. 4 (4.7 mm)	No. 10 (2.0 mm)	No. 40 (0.42 mm)	No. 200 (0.074 mm)			
0-40	95-100	90-100	50-90	20-40	0.10-0.18	3.6-5.0	Low
24-60	95-100	95-100	55-100	30-60	0.14-0.18	4.5-5.0	Moderate

Depth to seasonal high water table: $1\frac{1}{2}$-3 ft.

TABLE 2 SOIL PROPERTIES OF MATAWAN SANDY LOAM clay loam layer at 2-2.5′ can function as a semi-permeable barrier to downward percolation of water during winter and spring months, producing a seasonally perched water table condition at this depth.

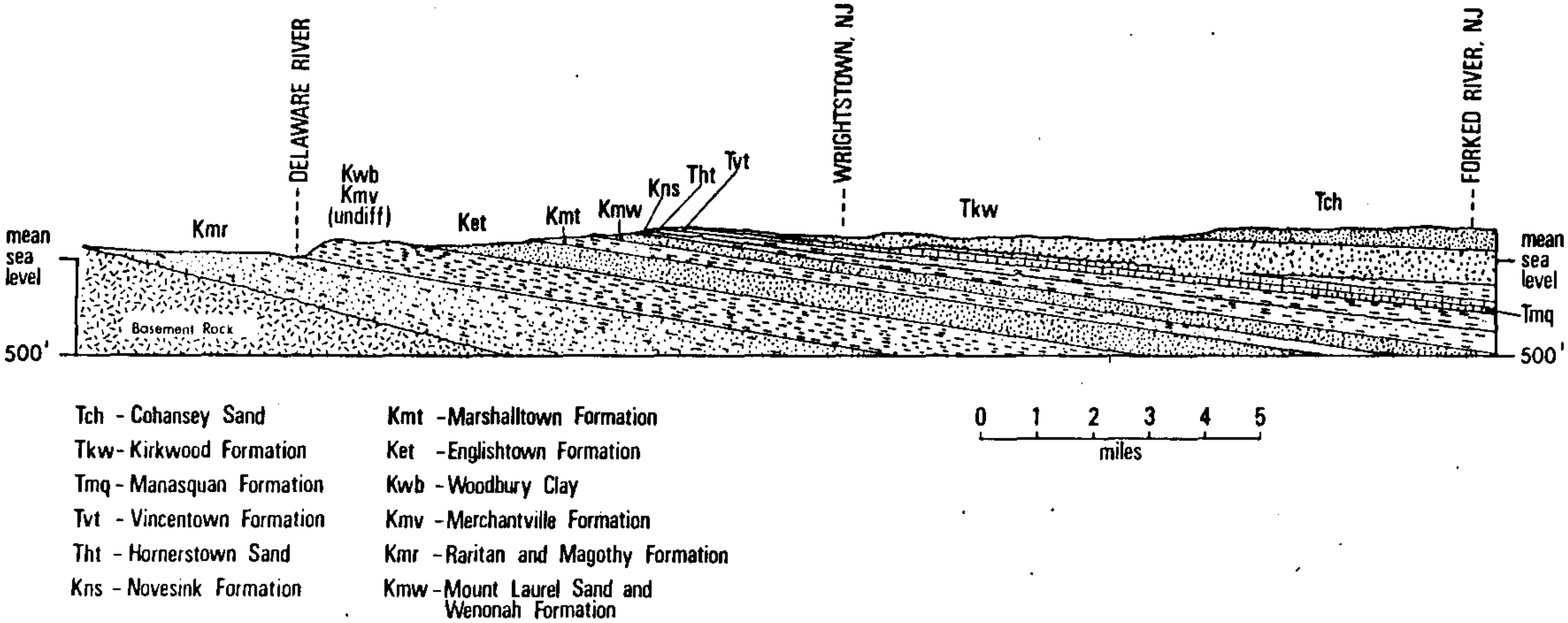
Vegetation--

This part of the state consists primarily of farmlands and forested areas. The main agricultural crops are blueberries, cranberries, and strawberries, which are well suited to acidic sandy soils. The forest vegetation consists of oak-pine and pine-oak upland tree communities that are also well adapted to droughty soils. The forest is an "open-type", where tree crowns do not form a solid canopy. Beneath this forest cover, woody shrub and scrub oak communities are widespread (Rhodehamel, 1973).

Geology

The formations exposed in the Atlantic Coastal Plain of New Jersey are of late Cretaceous, Tertiary, and Quaternary age. They consist of unconsolidated to semiconsolidated deposits of sand, silt, and clay, with minor quantities of gravel. The Cretaceous and Tertiary sediments form a wedge-shaped prism that lies unconformably upon Precambrian, Paleozoic and Triassic rocks of the Peidmont province (Figure 35). In their outcrop areas, the Cretaceous and Tertiary formations range from 500-800 feet in total thickness. These sediments thicken downdip (southeastward) and are believed to be in excess of 10,000 feet at the extreme southern tip of New Jersey (Gill, 1963). Deposits of Quaternary age, present in large areas of the coastal plain, are of variable thickness and extent.

The entire coastal plain sequence indicates several transgressions and regressions of the sea during the period of deposition. The sediments were deposited under relatively stable shelf conditions and were laid down in continental, transitional, and marine environments. The materials comprising these sediments were derived primarily from highlands north and west of the present fall line (Figure 34). In general, coarser sands occur in the outcrop areas of each formation and represent continental, transitional, and shallow water or near-shore depositional environments. Southeastward near the Atlantic coast, the Cretaceous and Tertiary near-shore deposits grade into offshore marine deposits composed of calcareous clays, silts, and



CROSS SECTION THROUGH THE ATLANTIC COASTAL PLAIN IN SOUTHERN NEW JERSEY

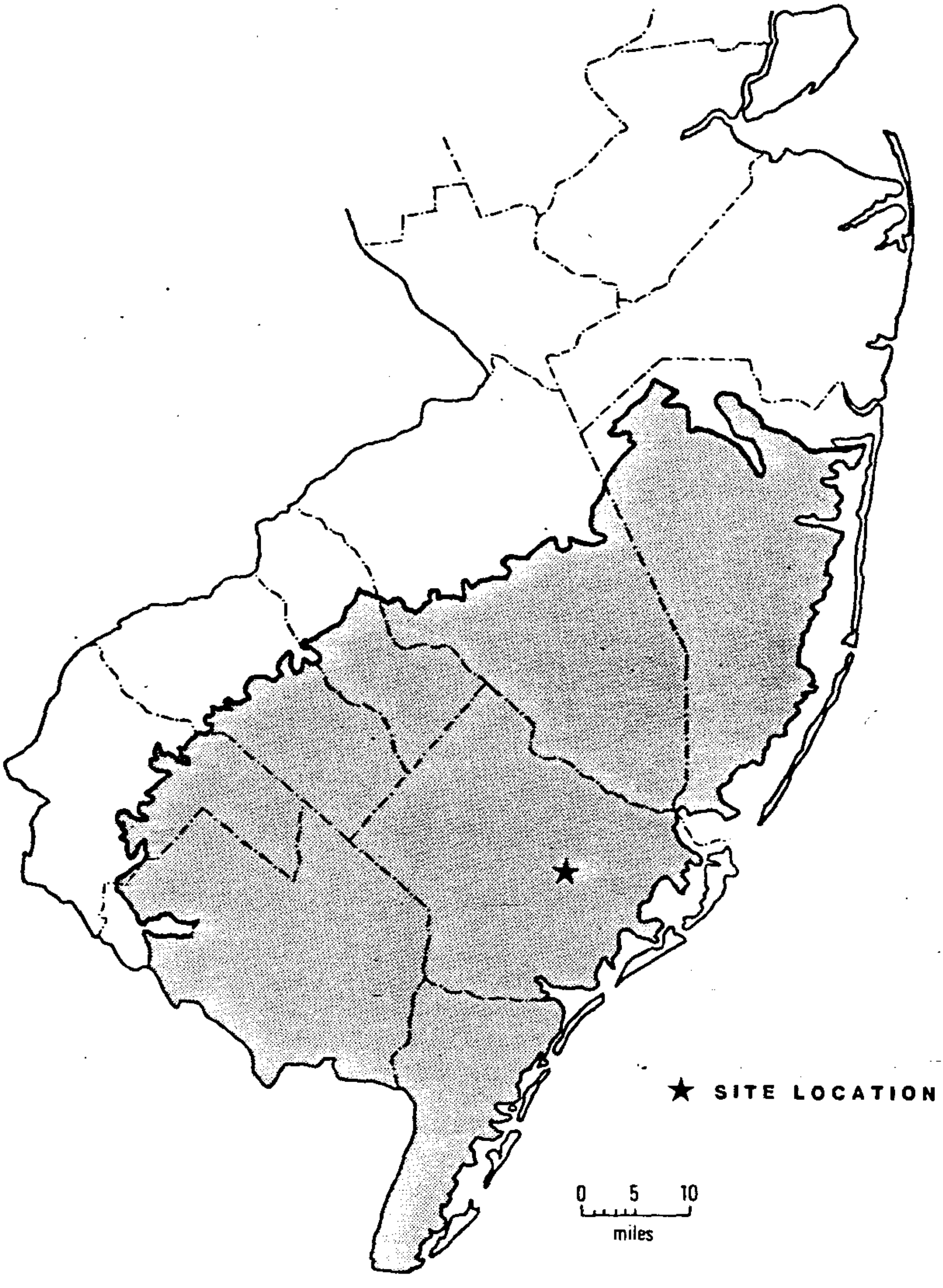
Figure 35

(Gill, 1963)

glauconite sands. Quartz sand decreases as thickness and percent of glauconitic sand increase seaward.

The Cohansey Formation, a thick, areally extensive wedge of sandy strata of Late Tertiary age is the geologic unit present in the shallow subsurface at the D'Imperio Site. It outcrops over an area of approximately 2,350 square miles in southeastern New Jersey and is mantled in places by thin deposits of Quaternary age. Its thickness ranges from 0 to greater than 250 feet as one progresses in an east-southeasterly direction toward the Atlantic Ocean (Figure 36).

The lithology of the Cohansey Sand is variable. It is dominantly a yellow (limonitic) quartz sand containing pebbly sand, fine to coarse sand, silty and clayey sand, and interbedded clay. It contains small amounts of weathered feldspar, chert, vein quartz and ironstone pebbles, and lenses or fragments of carbonaceous material within beds of kaolinite clay (Kummel, 1940). Sand units range from massive beds to thin seams intercalated with clay units. Gravel beds are generally less than 1 foot thick, but may attain thicknesses of several feet in some areas. Carbonaceous clays range in thickness from stringers to massive beds upwards of 20 feet thick, which can be continuous over extended areas (Gill, 1963).



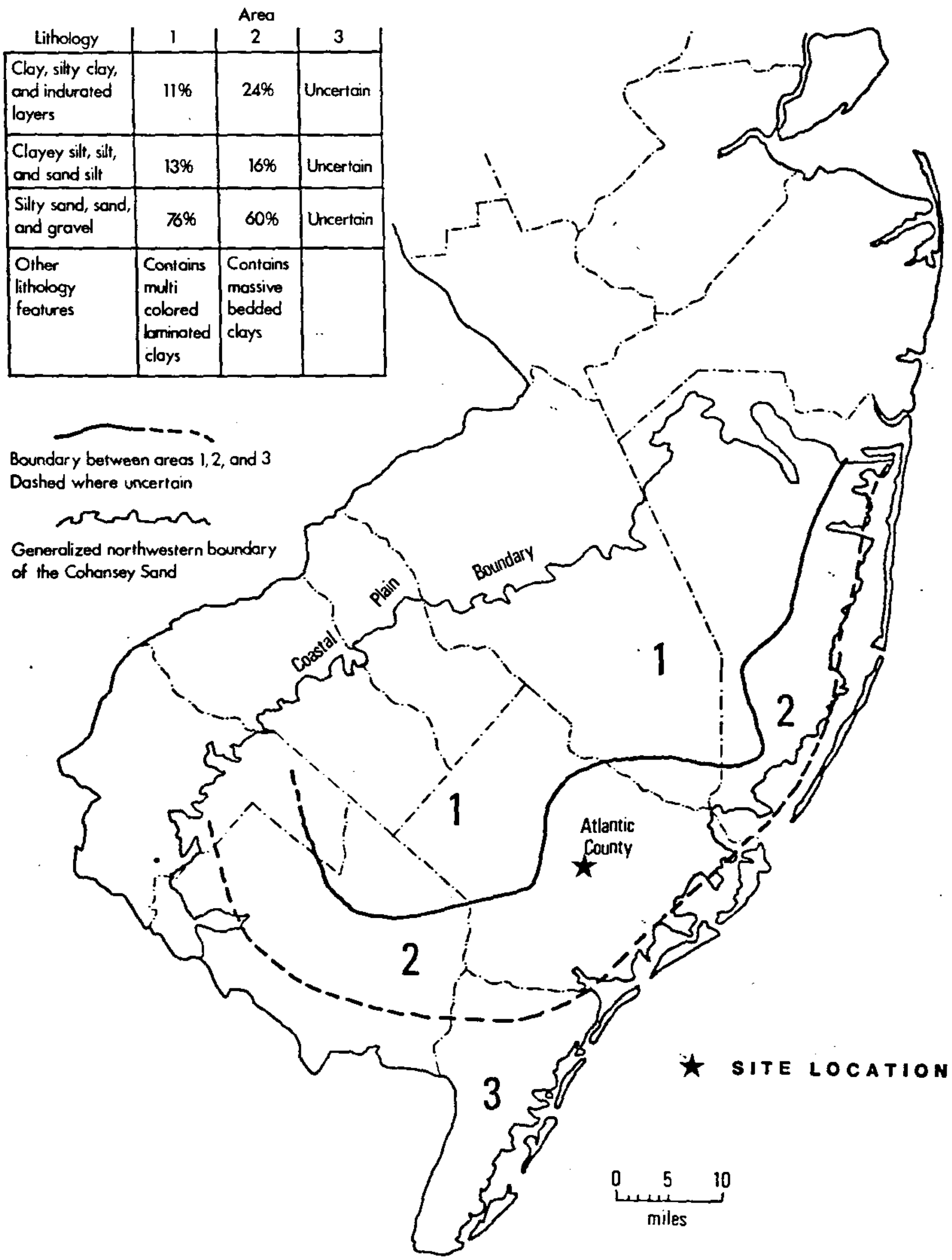
Outcrop Area of the Cohansey Sand
(base map after Rhodehamel, 1973)

Figure 36

Areal variations in textural content of the Cohansey can be seen on Figure 37. Area 1 contains thick sand beds interpreted as fluvial and delta front deposits containing relatively thin discontinuous sections of laminated clay. A thicker sequence of more massive bedded clays generally occurs in Area 2 (Rhodehamel, 1973). The relative textural composition of the sediments in Area 3 has not been documented, although well logs from Cape May County indicate a greater proportion of sand than in Area 2 (Dalton, personal communication).

The Cohansey Sand has been identified as consisting of stream, fluvial plain, deltaic, estuarine, lagoonal, beach and other nearshore-marine deposits in different areas and by various authors. In general, the Cohansey can be interpreted as a mixed or transitional unit that, overall, consists of a partly dissected ancient subdeltaic plain. The origin of the sediments comprising the formation has also been interpreted in a number of ways. Rhodehamel (1973) believes that because the fluvial Cohansey materials are composed primarily of quartz sand, kaolinitic clay, and chert, the sediments have undergone multicyclic erosion and redeposition and are the product of subaerial erosion of older coastal plain deposits.

The sediments at the dump site just at and below the water



Lithology	Area 1	2	3
Clay, silty clay, and indurated layers	11%	24%	Uncertain
Clayey silt, silt, and sand silt	13%	16%	Uncertain
Silty sand, sand, and gravel	76%	60%	Uncertain
Other lithology features	Contains multi colored laminated clays	Contains massive bedded clays	

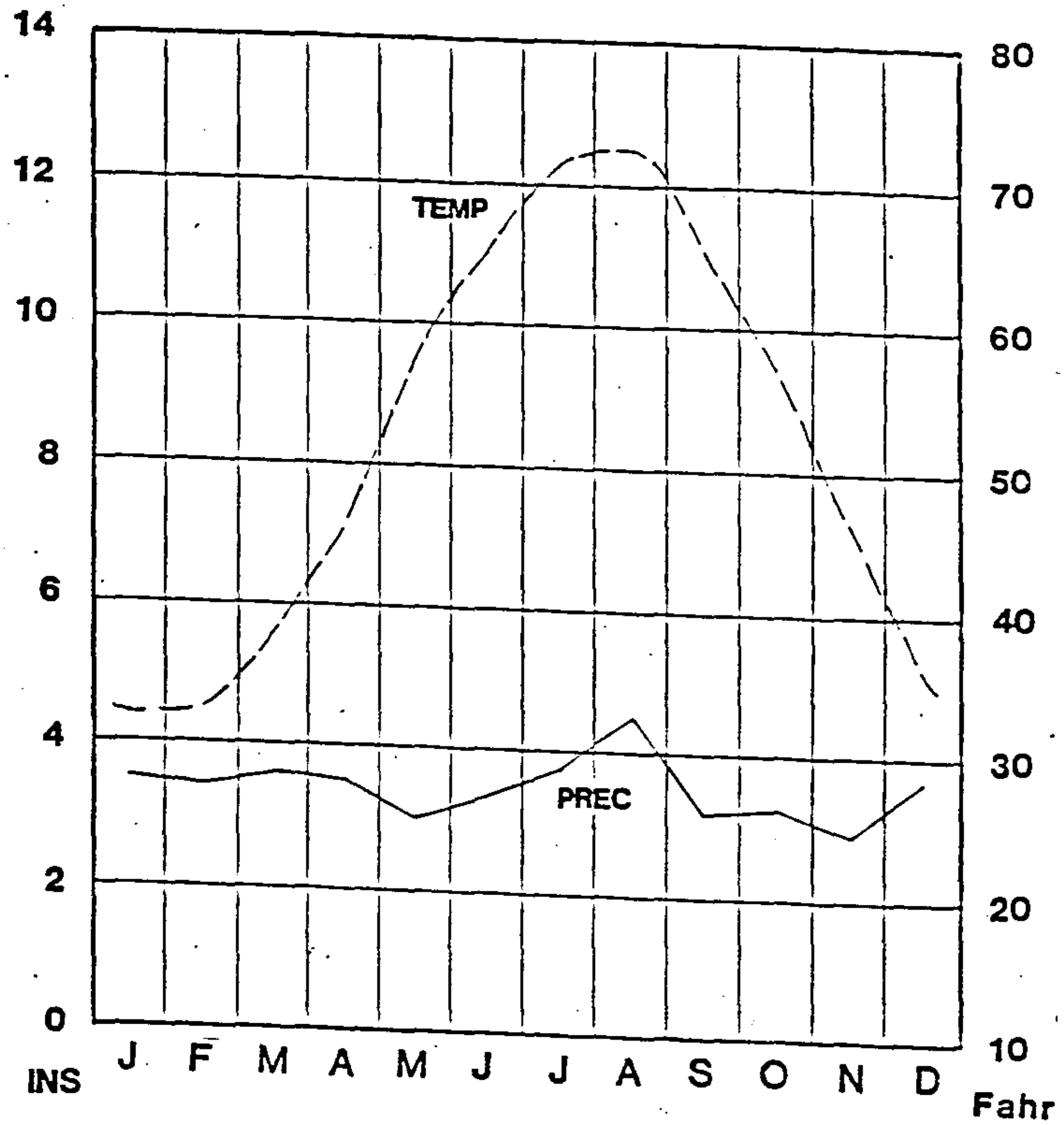
Areal Variations in Selected Lithologic and Hydrologic Parameters of the Cohansey Sand
(after Rhodehamel, 1973)

Figure 37

table consist of light colored (white-pink-tan) fine sand with a trace of silt. These grade into tan, dense, medium to fine sand at a depth of 15-20 feet. A white-gray coarse to fine sandy zone underlies the site approximately 20 feet below the surface. The logs indicate that this unit may be up to 20 feet thick, and contains in places stiff, gray to pink and yellow clay stringers and lenses. One borehole on site was advanced to a depth of 55 feet; the log indicates a 10' thick clay layer at a depth of between 40' and 50'. It has not yet been determined whether this confining zone is present over the entire site.

Hydrogeology

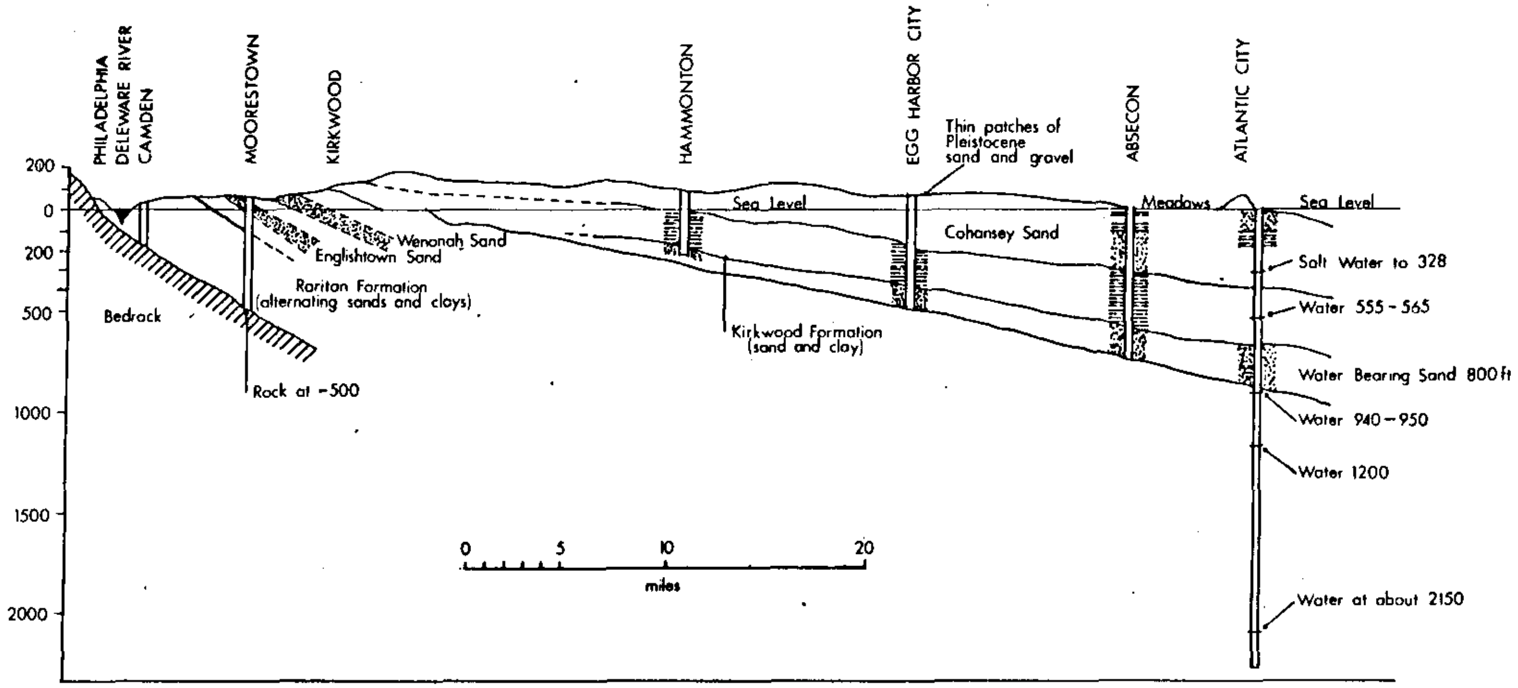
The coastal plain of New Jersey experiences a temperate, humid climate and is considered to be within the humid continental or intermediate climate zone. Climatic conditions are characterized by temperatures ranging from 0 to 100o F, and annual precipitation of 40 to 60 inches. Average monthly precipitation is relatively uniform, with slightly higher values occurring during summer months due to convective thunderstorms. Average temperatures exhibit a range of 40o to 55oF, with an annual mean of approximately 50oF (Figure 38). Barksdale (1943)



Average Monthly Temperatures and Precipitation

in Atlantic City, New Jersey

Figure 38



CROSS SECTION THROUGH THE NEW JERSEY COASTAL PLAIN SHOWING PRINCIPAL WATER-BEARING HORIZONS

Figure 38

(Thompson, 1932)

concludes that although pan evaporation exceeds precipitation during summer months, this relationship is reversed when correction factors are applied. During the remainder of the year, precipitation exceeds evaporation (quantitative data not available) as a result of the humid, temperate climate (Rogers, 1955, and Barksdale, 1943).

Surface Water--

Two large river systems dominate the outer coastal plain in New Jersey. The southernmost system is composed of the Great Egg Harbor River and associated tributaries, while the northern system includes streams in the Mullica River drainage basin. Both the Mullica and Great Egg Harbor Rivers can be considered steady streams, as ground water contribution to their baseflow is high (Means et al., 1981). However, discharges of the rivers vary significantly during the year, with periods of lowest flow during late summer. Average annual surface runoff in the Pine Barrens region is estimated to be 6% (Rhodehamel,1970), yet river response to precipitation is rapid. This is a result of the relatively flat topography and permeable nature of the coastal plain sediments.

Average chemical composition of river water for the outer part of the New Jersey coastal plain is shown below (all values in mg/l; data from Means et al.,1981):

Ca	1.05	Cl	4.72
Mg	0.57	SO4	6.16
Na	2.58	PO4	0.04
K	0.63	SiO2	4.32

pH = 4.51

TDS = 20.07

The total dissolved solids content of 20 mg/l is substantially less than that of the world average for rivers of 105 mg/l (Livingstone,1963). This is due to the high percentage of quartz in the sediments as well as the lack of pollution from man's activities. The very low pH of these coastal plain waters is due to the presence of organic acids which are produced in abundance during decay of Pine Barrens vegetation.

Groundwater--

Several of the Coastal Plain formations contain aquifers capable of yielding moderate (50-200 gpm) to large (>200 gpm) quantities of water (Figure 39). From oldest to youngest (outcropping from northwest to southwest) these are; the permeable zones of the Raritan and Magothy Formations, the Englishtown Formation, the Wenonah Formation and Mount Laurel Sand, the Vincentown Formation, the Kirkwood Formation, and the Cohansey Sand (Gill, 1963). An overlying discontinuous veneer of Quaternary sands and gravels can recharge these formations, but it is rarely thick enough to yield a usable quantity of water.

The Magothy-Raritan, Kirkwood and Cohansey aquifers are the principal sources of water supply in the Coastal Plain. The Magothy-Raritan has been developed extensively near its outcrop area due to high demand in this populated region. It has also been tapped along the coast where it occurs at a depth of 1,700 to 3,800 ft. The Kirkwood-Cohansey aquifers are virtually undeveloped and have the potential for providing a great amount of water.

Based upon its storage capacity, hydraulic conductivity and availability for direct recharge, the Cohansey is the most important aquifer in the New Jersey coastal plain. The unit is essentially a water table aquifer but low pressure artesian conditions exist over large areas near the base of the formation.

The source of virtually all of the water contained in the aquifer is precipitation that falls onto the coastal plain. Discharge is not restricted to one area but occurs to surface waterways throughout the region. The amount of water in storage, though fluctuating seasonally, has remained essentially constant over the period of record (Gill, 1953).

Logs of borings done on-site indicate that the water table occurs at an average of eleven feet below surface. Abbreviated aquifer testing using monitoring wells drilled in 1980 indicates the hydraulic conductivity of the water table aquifer to be in the range of 10-3 to 10-2 cm/sec.

Additional monitoring wells will be drilled this fall to delineate more accurately the shape and direction of movement of the contaminant plume. Following this phase of the site investigation effort, geophysical studies and aquifer tests will be performed to aid in the design of a decontamination system.

Water quality of the coastal plain formations is quite variable areally and with depth; a detailed discussion of these variations is not within the scope of this paper. However, certain generalizations can be made and are reported as an overall statement on coastal plain water quality. A more detailed discussion of water quality in the Cohansey Sand is presented as it forms the background and basis for future studies at the D'Imperio Site.

Water quality in the Magothy-Raritan aquifers is generally good to moderate, having low dissolved solids (<250 mg/l) content. However, high concentrations of iron and sodium and chloride ions (>1000 mg/l near the coast) are common in some areas and render the water unsuitable for drinking purposes. Water from Aquifers in the Rancocas Group and Kirkwood Formation is soft low in chloride and dissolved solids content. Rancocas water has been classified as a sodium-bicarbonate type and Kirkwood water at calcium-bicarbonate type.

Water quality in the Cohansey is considered to be very good for most uses, except where high iron concentrations and low pH make pretreatment a necessity. Ground water in the formation is derived from precipitation that has infiltrated through surface debris to the relatively chemically inert aquifer below (Rhodehamel, 1973). The water is low in dissolved solids which generally range from 25 to 50 mg/l. Because of its acidic character, the water readily dissolves iron from organic matter and iron-bearing minerals in the soil. Water quality in the aquifer is controlled to some degree by kaolinite lenses and calcareous material present in the sediments. However, the clay content rarely exceeds 20 percent and calcareous material comprises 10 percent of the formation (Kummel, 1940).

Forty-two analyses of ground water from the Cohansey Sand aquifer (well depths 25-200 ft) were examined in an effort to determine the weathering characteristics of the formation. Of these, 32 had a dissolved solids content of less than 50 mg/l. Eighteen had a dissolved solids content of less than 25 mg/l. These low values were present in wells up to 200 feet deep.

In general, it appears that an increase in sodium content in the water can sometimes be correlated with increased sulfate and decreased bicarbonate percentages, although this was not true for all samples. A second characteristic of water from the Cohansey is that calcium and magnesium ions rarely exceed 15 percent of the total dissolved material. Back (1966) indicates that water from this aquifer is primarily chloride-sulfate-bicarbonate type. Using the analyses provided by Back in conjunction with others from two additional sources, it is concluded that water from the Cohansey is not readily classified.

The variability in water quality at low TDS values is caused by a number of factors. Initially, water percolates through the rapidly drained, coarse textured soils present over much of the recharge area. Because of the high percentage of quartz present in the sediment, the soils do not contribute a significant quantity of dissolved material to infiltrating water. As described earlier, iron and bicarbonate ions are most likely dissolved at this point. Variability in vegetative cover and microbial activity could affect the quantities of these ions entering the water. After passing through the soil column, water is stored in the predominantly quartz sand aquifer. Multicyclic erosion and deposition of the sediments comprising the aquifer has weathered out most of the soluble material originally present. The result is ground water that appears to have the characteristics of local rainfall (which is often acidic) coupled with the addition of ions from minor quantities of residual feldspar, clay, or calcareous material. It is possible that TDS values would be higher if leakage were induced from some of the less permeable strata present in the formation,. Two wells completed near the top of the underlying confining bed seem to confirm this idea.

Approximately twenty organic chemicals have been detected in the water table aquifer beneath the site. 1,2 Dichloroethane, 1,1 Dichloroethane, carbon tetrachloride and toluene have each been found to be present in concentrations of greater than 100 mg/l down-gradient of the dump. Other contaminants are present at depths of up to 50 feet at a distance of 1000 feet from the landfill area. The surface water discharge point of the plume is suspected to be a swampy area approximately 1 mile to the southeast although it is possible that a northwestward flow component also exists.

CREOSOTE DUMP, CONROE, TEXAS

An abandoned creosote facility in the town of Conroe, Texas has been selected for this contamination site study for two main reasons. The first reason is that previous work on this site is relatively extensive. Bedient (1982) completed a study on contaminant identification and defined the limits of plume migration. The geology of the region is described in detail by Doering (1935). Deussen (1914) and Popkin (1971) have interpreted the hydrogeology of the area. Excellent soil descriptions were found in McClinttock et al. (1972). The second reason is that access to the site for sample collection and permission to drill was granted by the owner to the Texas Department of Water Resources (TDWR) and the United States

Environmental Protection Agency (EPA).

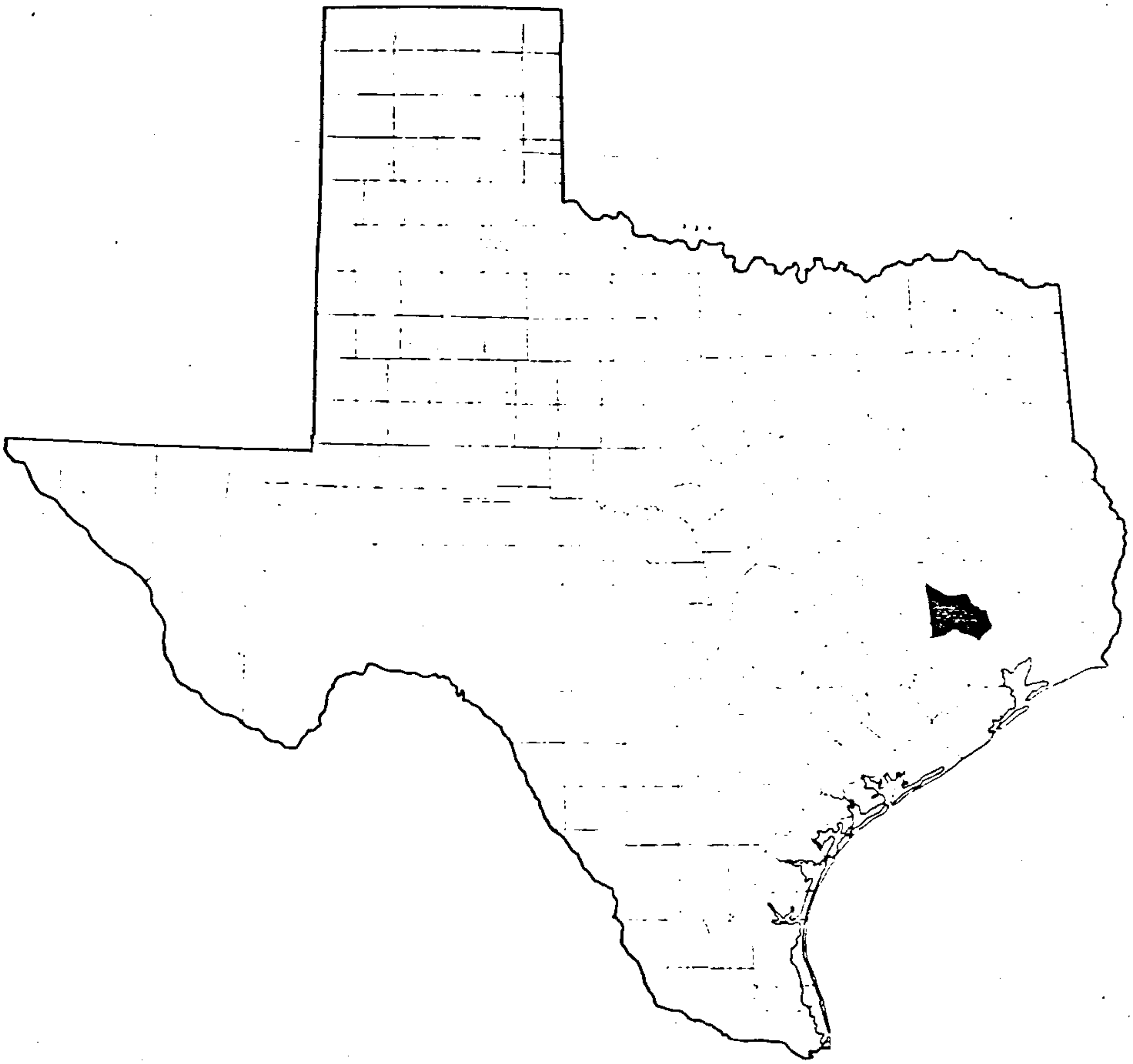
Geography

The town of Conroe lies in Montgomery County, Texas and is located 75 miles north of Houston (Figure 39). The cresote dump itself lies at about 30o 20′ north latitude and 96o 25′ west longitude, (Figure 40).

Physiography and Topography--

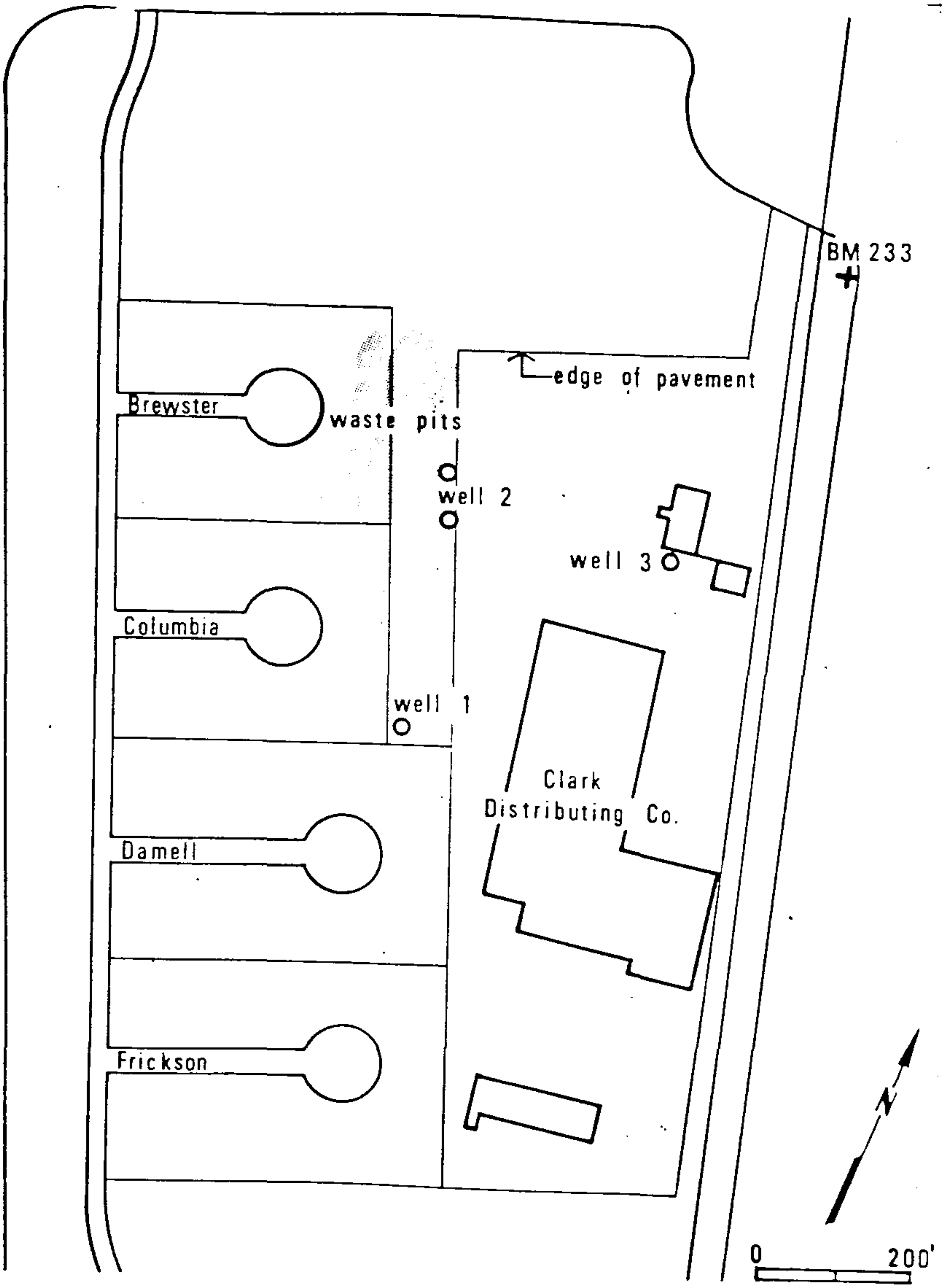
Montgomery County is located in the West Gulf Coastal Plain physiographic province. This area is the western continuation of a similar plain that borders the Atlantic. The Gulf Coastal Plain is a broad region which extends up to 500 miles inland from the coast and slopes gently toward the Gulf of Mexico from an interior highland region. The topography of the coastal margins is relatively flat, but it yields to an undulating and broadly dissected plain landward (Deussen,1914).

The subdivisions of the Gulf Coastal Plain Province generally parallel the coastline (Figure 41). The creosote-contaminated site lies in the second district in from the Gulf,



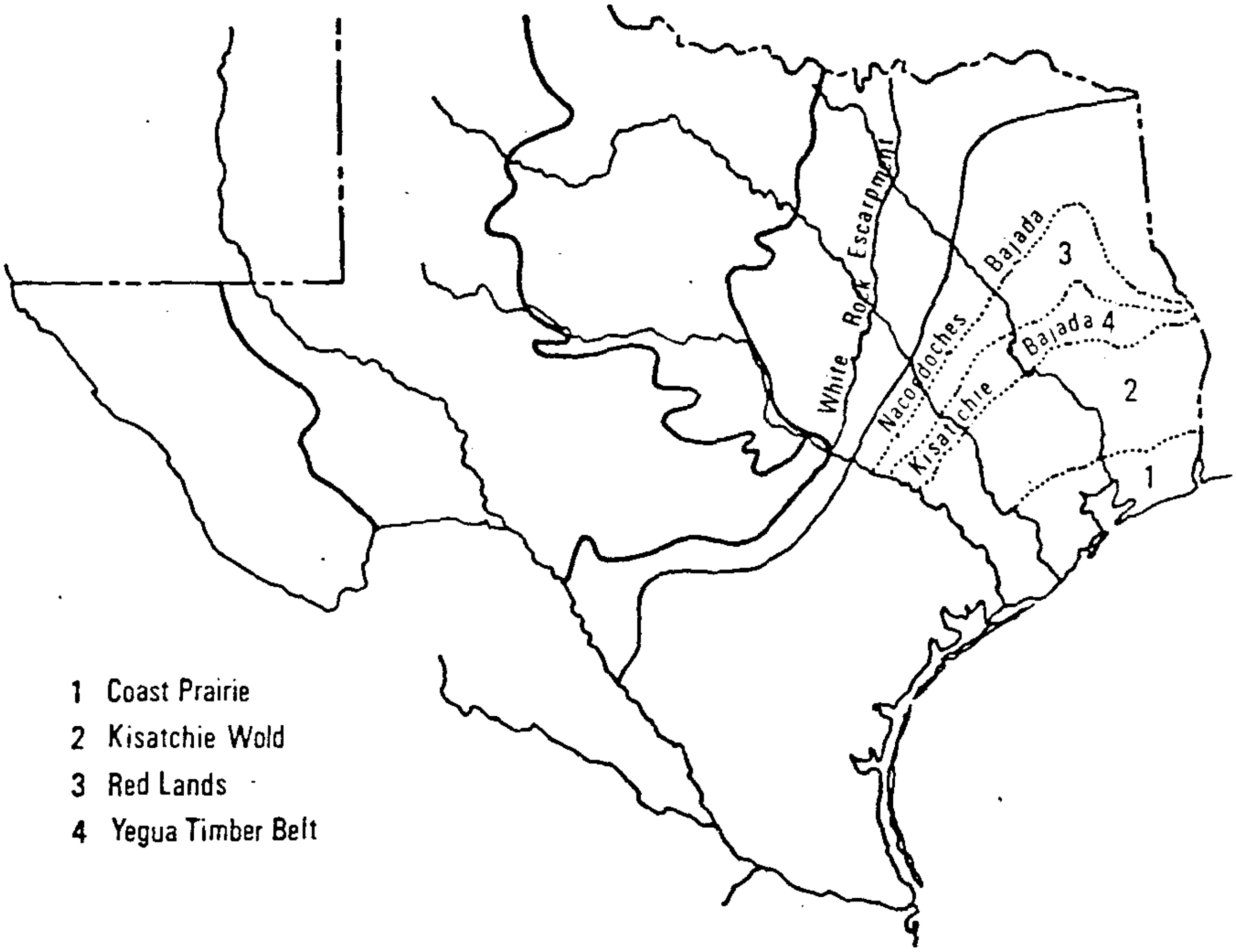
Location of Montgomery County

Figure 39



United Creosoting Company Hazardous Waste Site
Conroe, Texas
(After Bediant et al., 1972)

Figure 40



Physiographic Regions of Texas
(After Deussen, 1914)

Figure 41

namely the Kisatchie Wold. This subdivision is characterized by a transition from a southeasterly dipping plain in the southeast to gently rolling hills in the northwest (Deussen,1914).

Soils--

The two primary soil associations (Figure 42) in Montgomery County are the Conroe and the Splendora-Boy-Segno. Together these cover nearly 50 percent of the land surface in the county (McClinttock et al., 1972).

The Conroe association consists of deep sandy soils with lower clay layers. They exist primarily on rolling terrain and steep sides of ridges. These soils are well drained and possess a mild acid pH (McClinttock et al.,1972). This association covers the area of the creosote dump.

Loamy and sandy soils with loamy sub-horizons are characteristic of the Splendora-Boy-Segno association. These soils cover the lowlands where the topography is nearly level to gently sloping. Drainage within the association is variable, ranging from poorly to well drained, and the pH is mildly acidic (McClinttock et al.,1972). This association surrounds the Conroe site though it does not actually cover it.

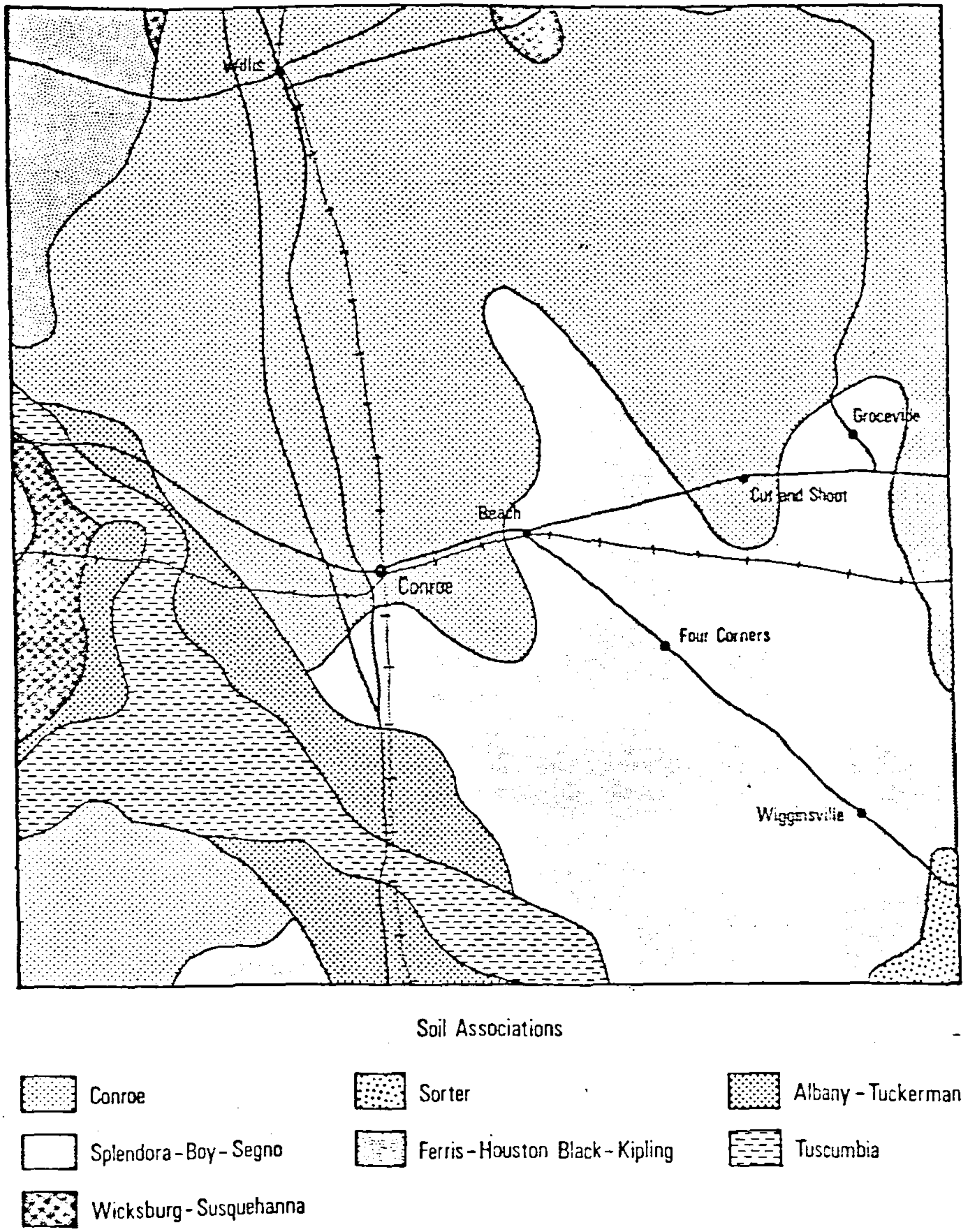
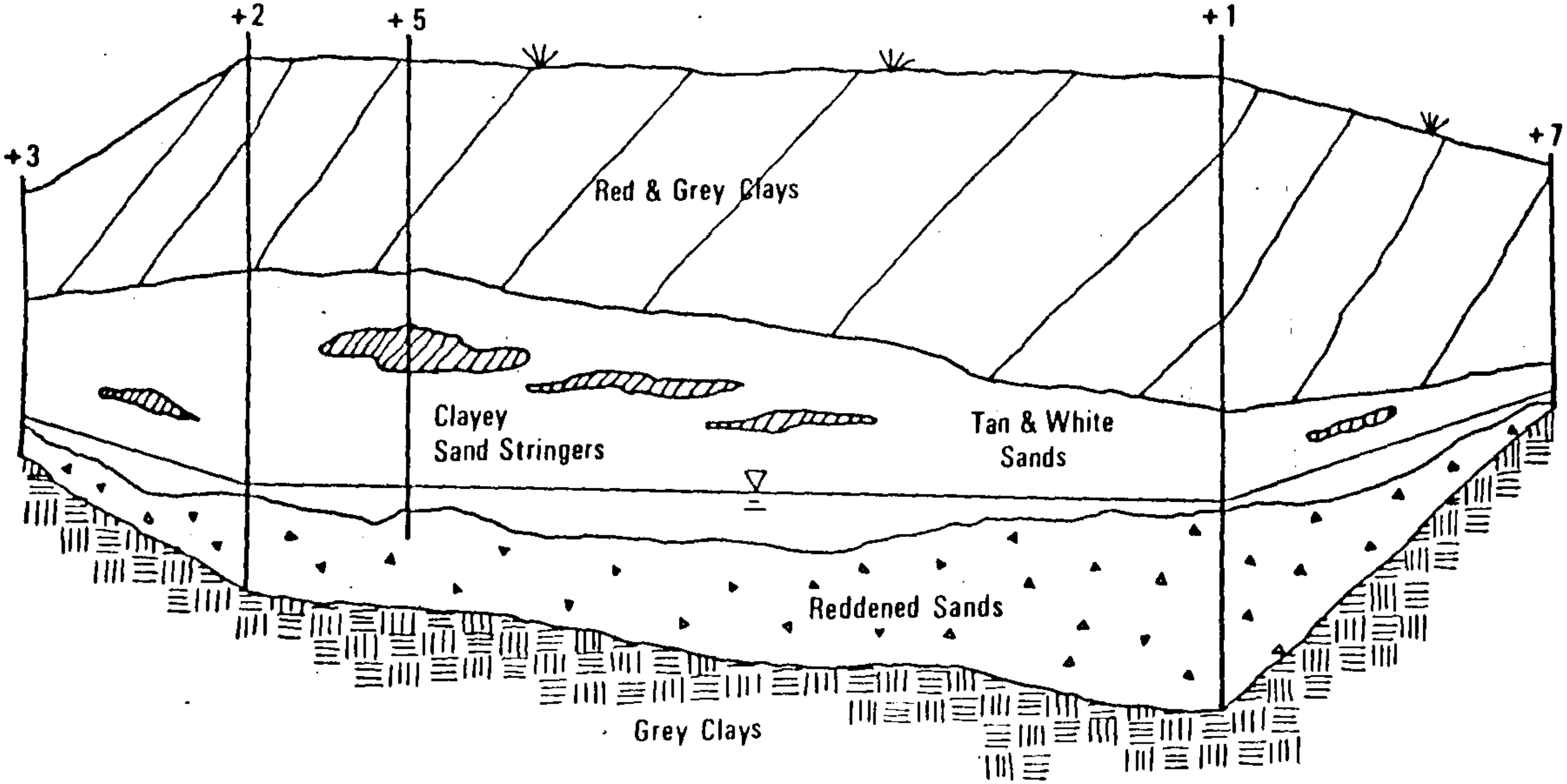

Willis
Grocevi le
Cut and Shoot
Beach
Conroe
Four Corners
Wiggensville
Soil Associations
Conroe
Sorter
Albany - Tuckerman
Splendora - Boy - Segno
Ferris - Houston Black - Kipling
Tuscumbia
Wicksburg - Susquehanna

Figure 42



Soil Profile

(After Bediant et al., 1972)

Figure 43

The soil profile (Figure 43) at the Conroe waste pit is the mapping unit Conroe gravelly loamy fine sand, 0 to 5 percent slopes. The upper layer is about 25 inches deep and is a grayish-brown, very friable, gravelly loamy fine sand. Ironstone concretions are prevalent and comprise nearly 30 percent of this surficial horizon. Below this layer lies a horizon of yellowish-brown, friable, sandy clay loam. Red mottling occurs, implying the existance of ferruginous material. A sandy clay forms the sub-horizon. It is brownish-yellow and light gray in color, and it is coarse, friable, reticulated, and mottled red (McClinttock et al., 1972).

The following is a representative soil profile from the Conroe waste site obtained through driller's logs.

0 to 60"	Light brown, fine sand with clay seams; gravel and abundant iron nodules present
60 to 84"	Red, sandy clay with tan, sand and gravel seams
84 to 120"	Gray, mottled, sandy clay with iron stains
120 to 180"	Gray, mottled, sandy to silty clay with iron stringers
180 to 216"	Moist, medium-grained, tan, clayey sand with white and red clay nodules

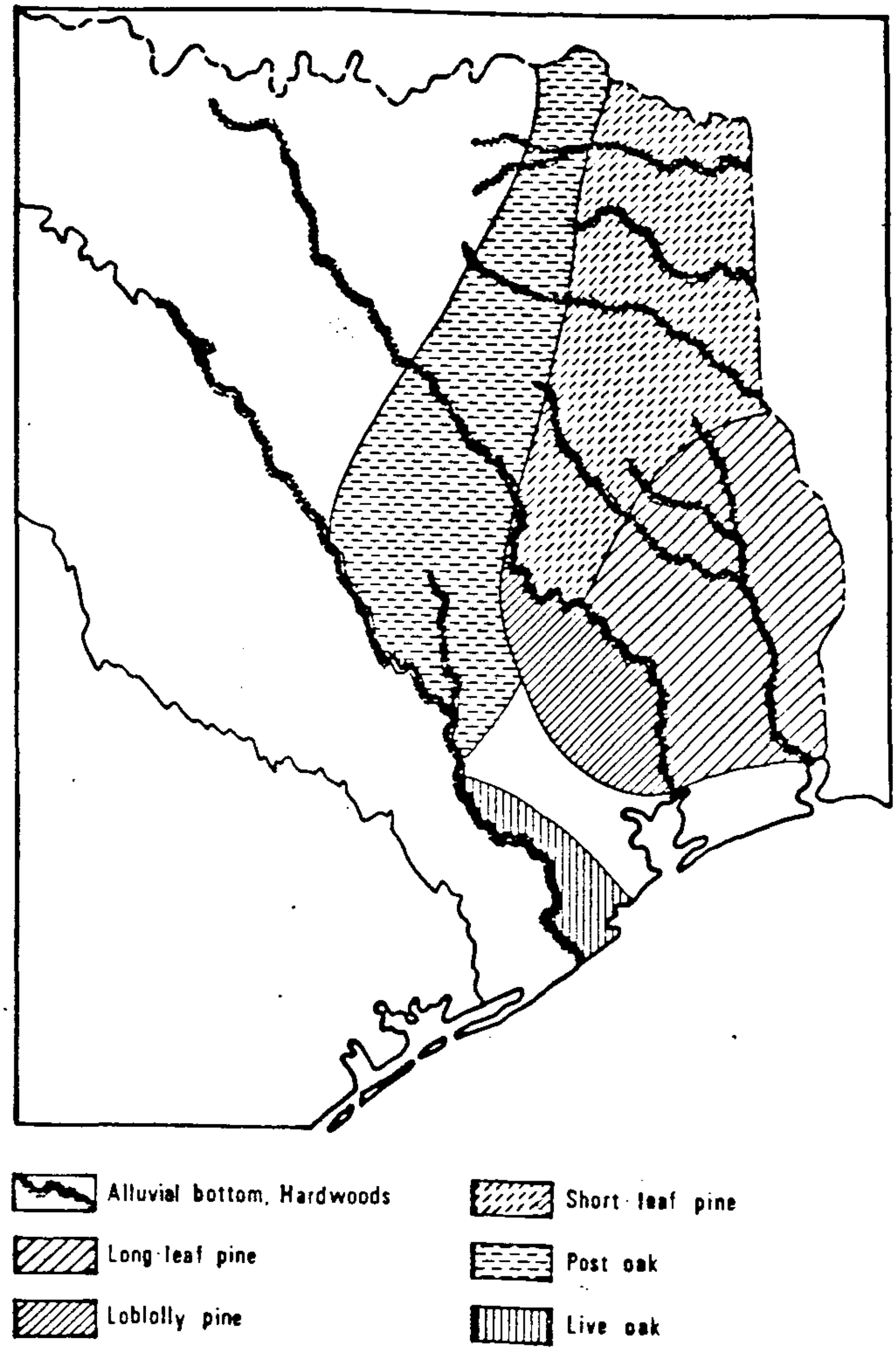
216 to 336"	Moist, medium-grained, tan, silty sand with iron stains
336 to 480"	Red, medium-grained, sand with gravel and clay stringers
480 to 528"	Gray clay with tan mottling; organic material present

Vegetation--

Conroe lies in a timber belt (Figure 44) which is bounded by the Coast Prairie on the east and the Eastern Marginal Prairie on the west (Deussen,1914). Hardwood forests predominate in the lowlands. Species present are Cow Oak, Overcup Oak, Common White Oak, Red Oak, Texas Oak, Willow Oak, Water Oak, White Ash, Green Ash, Sweet Pecan, Gitter Pecan, Shagburk, White Hickory, Sweet Gum, Black Gum, Tupelo, Cottonwood, Sycamore, Elm, and others. In the highlands pine forests flourish with such varieties as Shert Leaf, Loblolly, and Long Leaf (Deussen,1914).

Geology

The rocks exposed on the Gulf Coastal Plain of Texas are



Distribution of Timber on the Eastern Third of the Texas Coastal Plain

(After Deussen, 1914)

Figure 44

formations of a sedimentary sequence whose age ranges from late Tertiary through Recent. The period is marked by erosional and depositional episodes. Originally this sedimentary series was deposited horizontally, but active tectonics has uplifted and slightly tilted the beds towards the Gulf. The youngest rocks are found closer to the Gulf coast while older formations only crop out inland. This is due to a greater rate of erosion inland. Weathering of topographic highs to fairly uniform levels has created a surface approaching a plain (Metcalf,1940). The bedrock beneath the Conroe creosote dump consists of the Deweyville Formation. The Willis, Bently, Montgomery and Beaumont Formations will also be discussed, however, because they comprise the Chicot aquifer which has become contaminated by the dumping of creosote.

The Pleistocene age Willis Formation is predominantly a red sand though gravelly sand is also present. The formation is named after the town of Willis, 10 miles north of Conroe, in Montgomery County, Texas. It is bounded above and below by unconformable contacts. The basal unit of the formation is the Willis Gravelly Sand Member. It is composed of less than 5 percent gravel, 5 percent disseminated clay, and greater than 90 percent sand. The coarse sand fraction is very friable and bentonite, alone, acts as a binder. The Willis Ferruginous Sand Member overlies the Gravelly Sand Member. The gravel fraction is absent in this unit and limonite is the cementing agent. Clay lenses are in greater abundance at the base of this member and grade out at the top. The Hockley Mound Sand Member is the uppermost unit of the Willis Formation and is composed of light colored, friable sand (Doering,1935).

The Bentley and Montgomery Formations of Pleistocene age have very similar depositional histories and will therefore be described together. A continued gradual subsidence of the coastal area occured throughout the deposition of these formations and continues to the present time. Much of the material deposited at this time was ferruginous, consisting of concretionary nodules and cement. During the second phase of this depositional cycle, streams eroded and transported much of the previously deposited Bentley sand towards the coast. During this period of entrenchment of major streams and erosional-depositional sequences, a very flat alluvial plain was built near the coast. The deposits forming the plain were predominantly well sorted sand. Much of the material derived from the Bentley now comprises the Montgomery Formation (Metcalf,1940).

The depositional history of the Beaumont Formation of

Pleistocene age is closely related to that of the Bentley and Montgomery Formations. The stratigraphic division between the Bentley and Montgomery formations is based on a change in grain size. Subsequent to the cessation of the rapid eroding process responsible for the deposition of the Bentley and Montgomery, much of the load carried by streams was derived from further inland as the headwaters migrated upstream. These Beaumont sediments were finer and more calcareous than those previously deposited (Metcalf,1940).

Beaumont deposition may be divided into two periods. In the initial stage, the streams migrated back and forth across their zone of influence, building up channel deposits and producing distributaries. The second stage involved a steepening of the gradient caused by coastward tilting which resulted in channel degradation (Metcalf,1940).

The Beaumont is characterized by a high clay content with some silt and sand. Concretions of calcium carbonate, iron oxide, and iron-manganese oxides are present in the zone of weathering (Doering,1935).

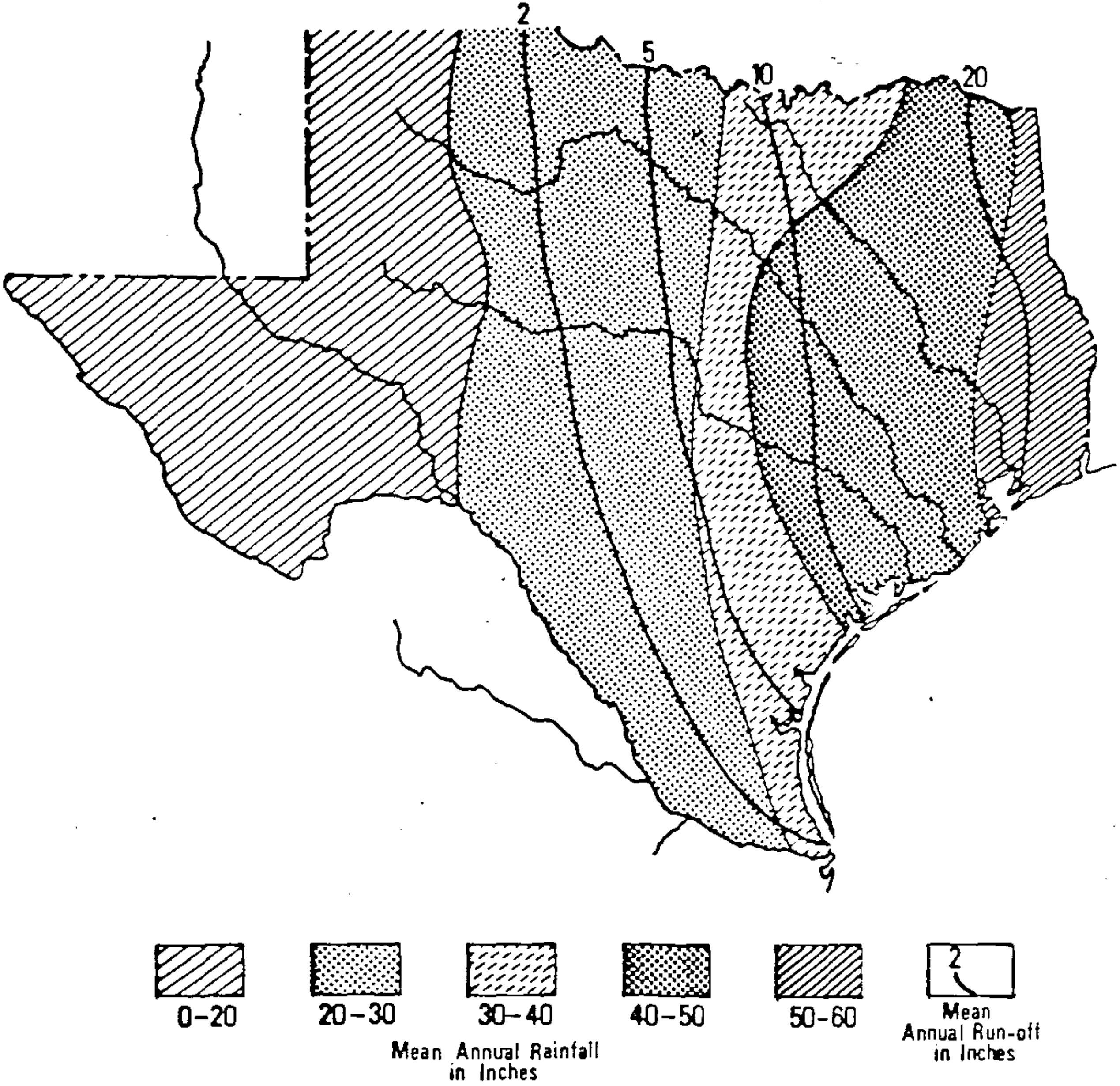
The Deweyville of Recent age is composed largely of reworked sediments from the Beaumont. It consists of sand, silt, clay, and some gravel. Depositional features present include point bar, natural levee, stream channel, and backswamp deposits (Doering,1935).

Hydrogeology

Montgomery County has a warm humid climate. Precipitation averages about 47 inches annually (Figures 45 and 46). Droughts seldom occur and generally are short lived. The average annual lake surface evaporation rate from 1940 through 1965 was 49.5 inches. The average annual temperature at Conroe is about 20 degrees celcius (68 degrees fahrenheit). Temperatures below freezing occur on the average of 22 days per year; temperatures greater than 38oC (100oF) are unusual (Popkin,1971). The mean date for the first frost is November 30; the mean date for the last frost is March 7. The county has a growing season of about 268 days (Taylor, 1907).

Surface Water--

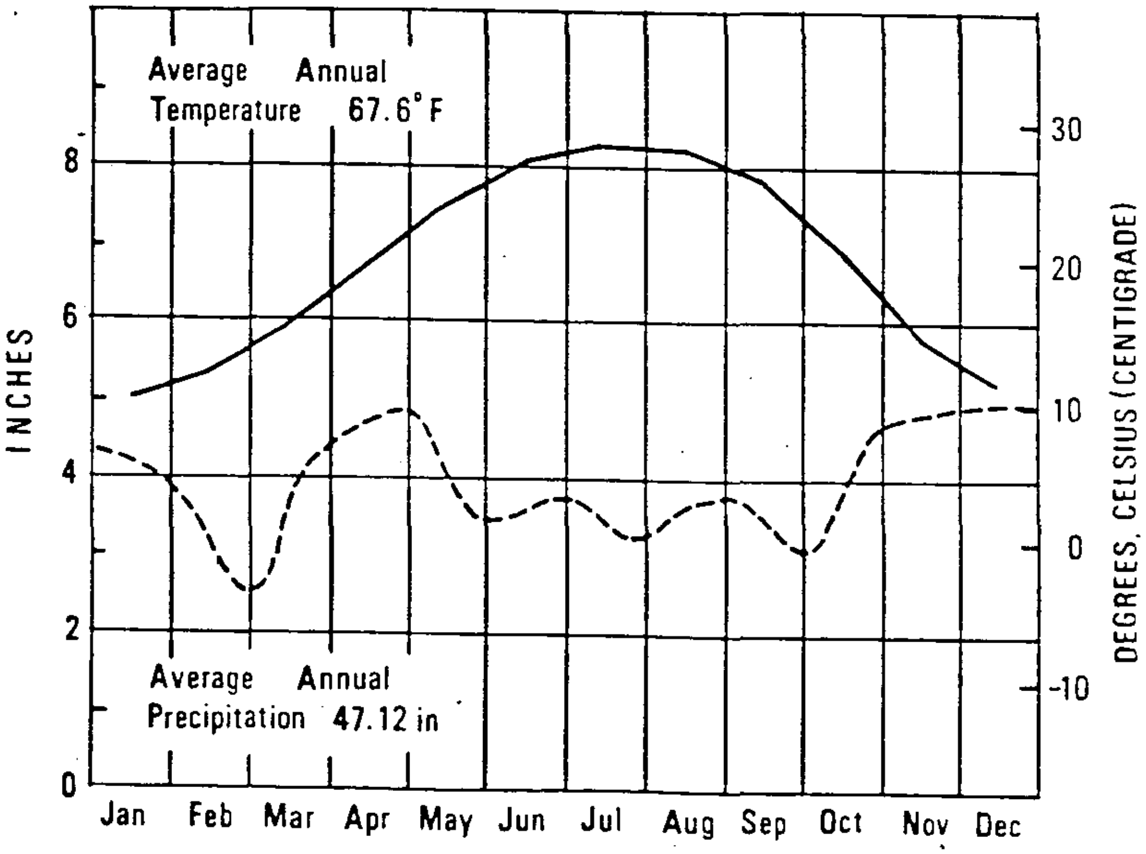
Two major types of streams prevail in the area (Figure 47); antecedent and consequent. The Brazos and Trinity rivers are antecedent streams which were formed before the formation of the



Mean Annual Rainfall and Run-off

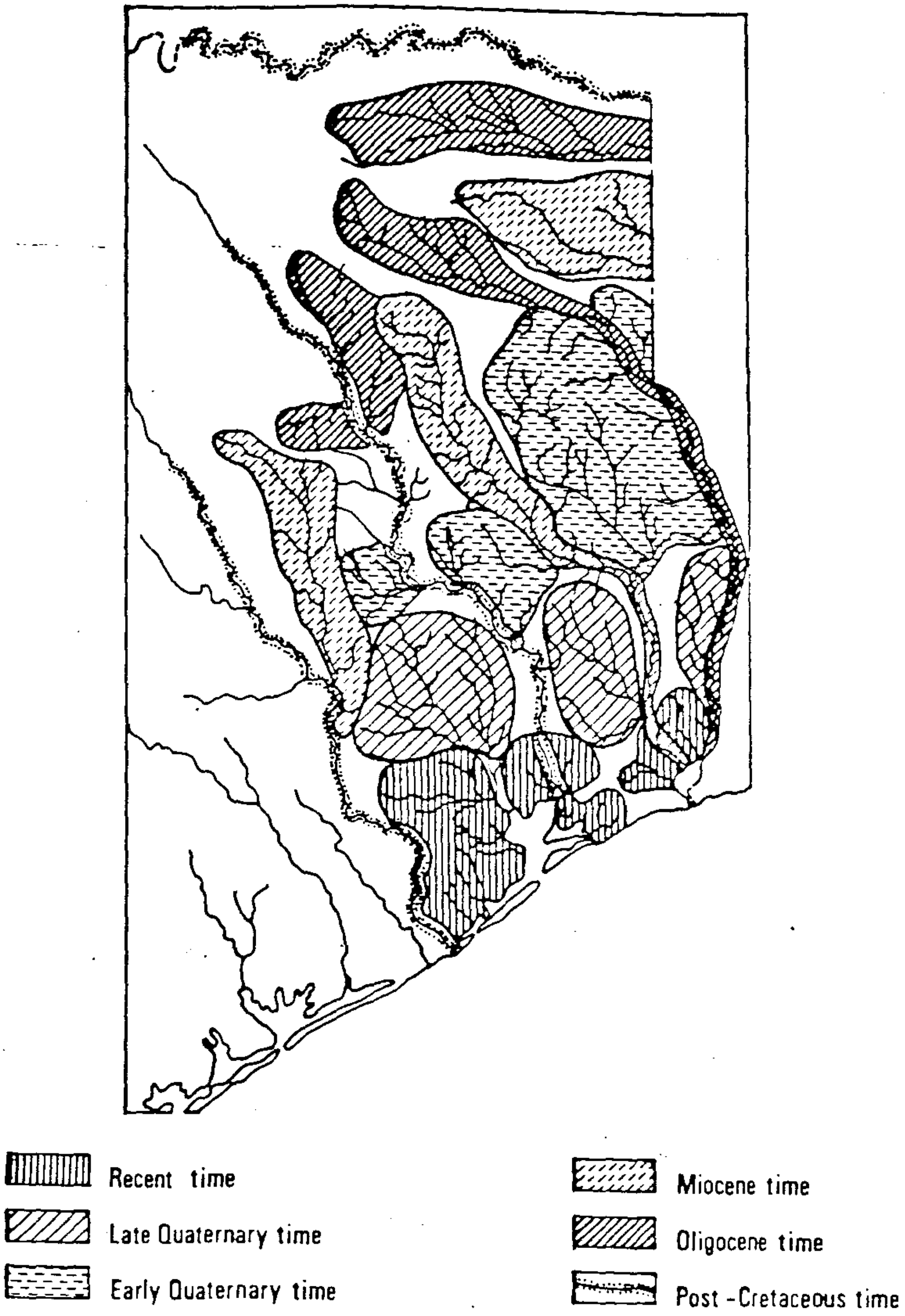
(After Deussen, 1914)

Figure 45



Average Monthly Precipitation
and Temperature at Conroe, 1931-66
(After Popkin, 1971)

Figure 46



Chronology of the Development of Drainage in East Texas

(After Deussen, 1914)

Figure 47

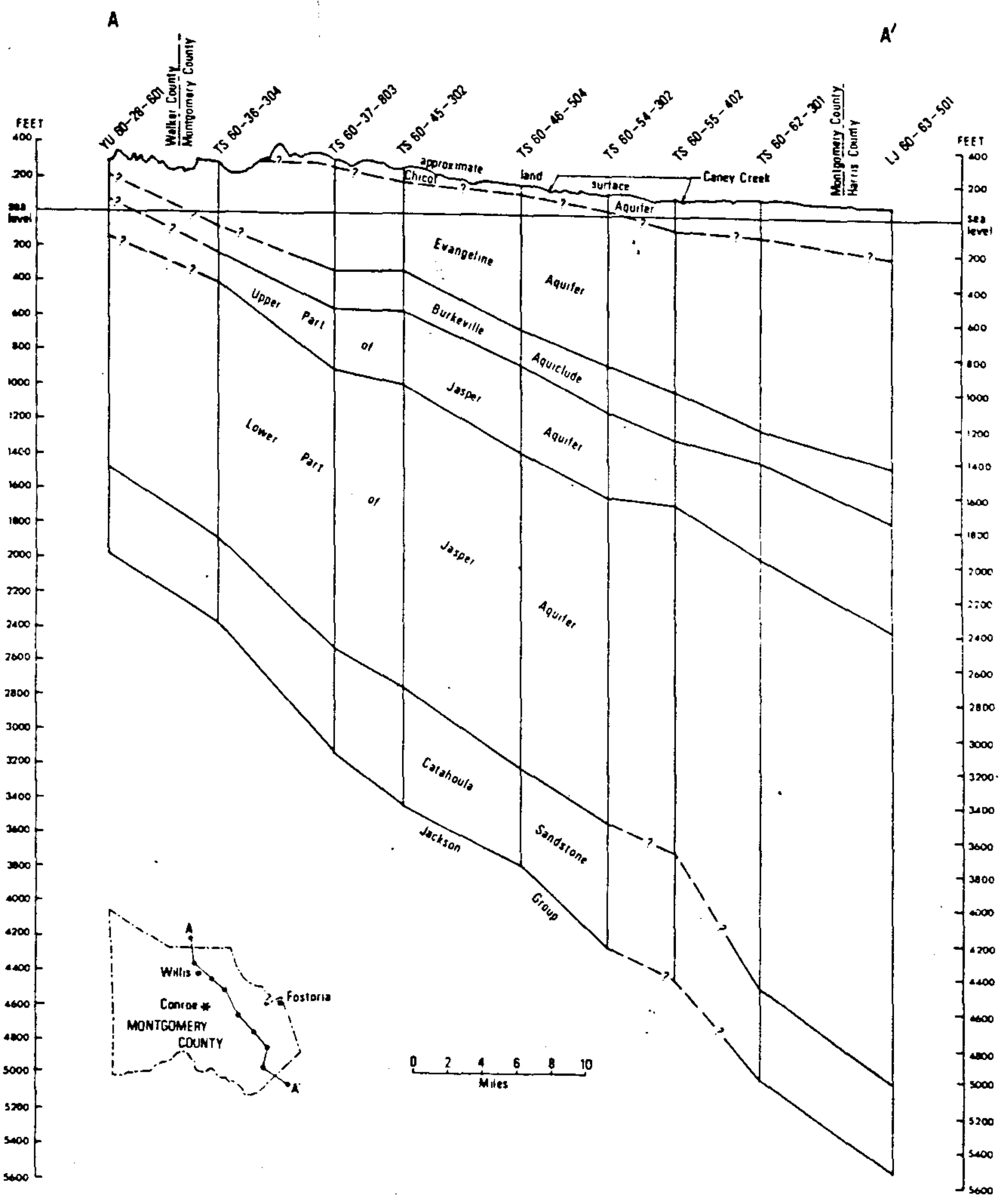
Tertiary plain, having been in existance on the Cretaceous plain when the shoreline of the gulf was far north of its present position. Smaller streams in the immediate area of Conroe (i.e. Stewarts and Little Caney) are predominantly consequent streams which developed after the formation of the Tertiary plain and occupy the territory between the extended or antecedent drainage (Deussen,1914).

The contamination site is bordered to the west by a small intermittent creek.

The surface water quality is relatively uniform, high concentrations of sodium and chloride predominate (probably due to oil field brine contamination) while variable amounts of calcium and sulfate are present (Deussen,1914).

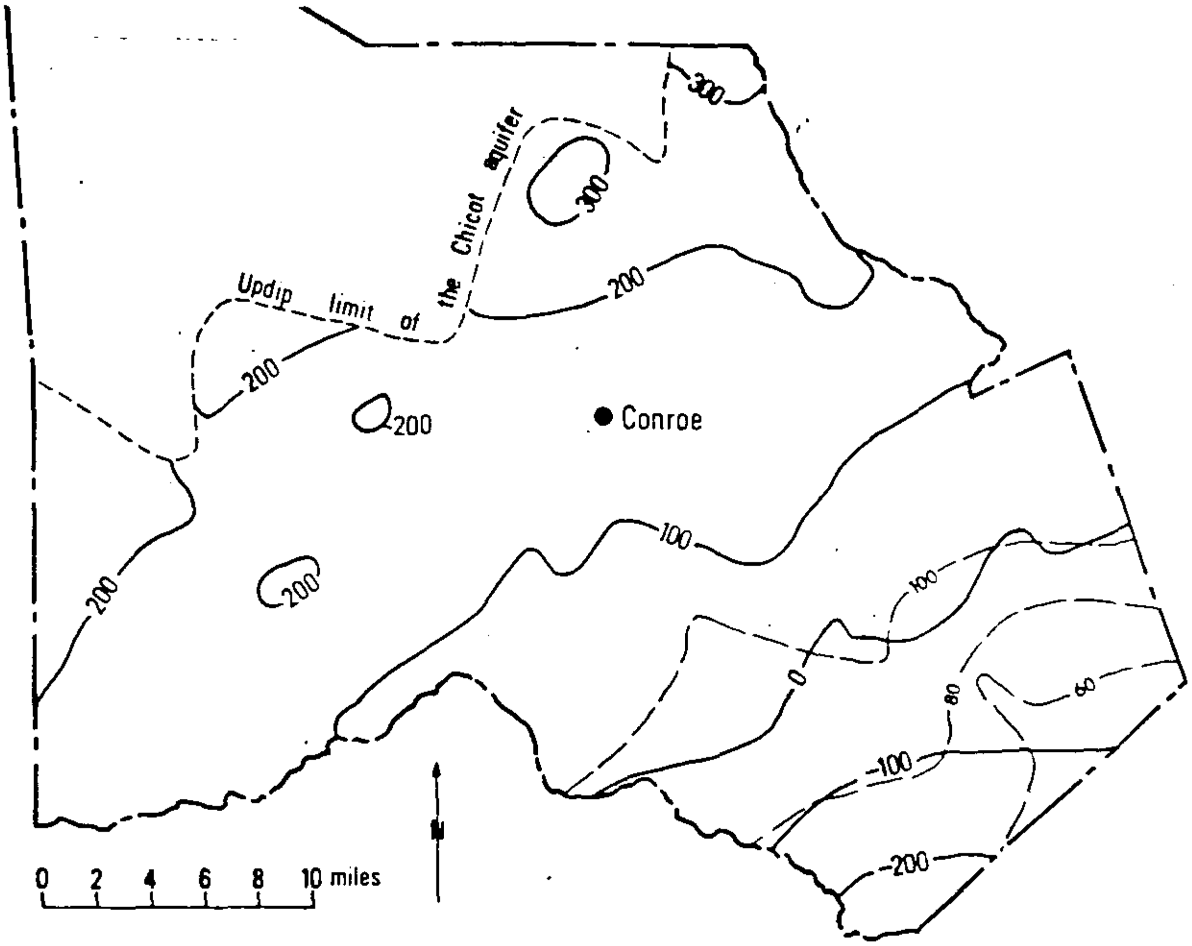
Groundwater--

Though several aquifers exist within the Tertiary and Quaternary rock sequences (Figure 48a), only the Chicot aquifer is presently threatened by the spread of creosote. The Chicot (Figure 48b) is the surficial aquifer in the area.



Hydrologic Section A-A′, Walker, Montgomery, and Harris Counties
(After Popkin, 1971)

Figure 48a



Number indicates altitude of base of Chicot aquifer

——— 200 ———

Structure contour
Shows approximate altitude of base of Chicot aquifer

Contour interval 100 feet

Number indicates altitude of water level

— —100 — —

Water-level contour
Shows approximate altitude of water level

Contour interval 20 feet

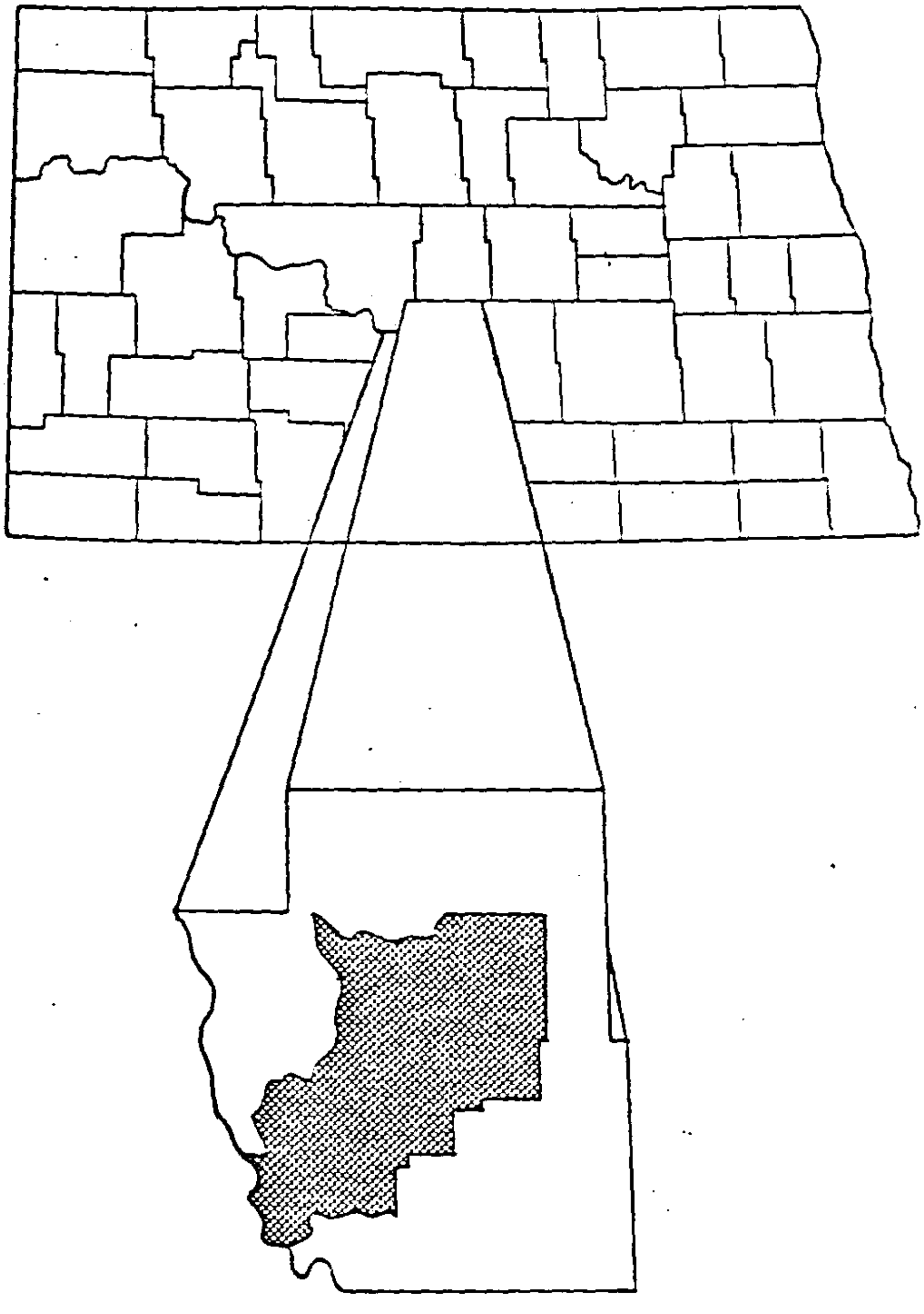
Approximate Altitude of the Base of the Chicot Aquifer and the Approximate Altitude of Water Levels in Wells Screened in the Aquifer, 1966-67
(After Popkin, 1971)
Figure 48b

The Chicot aquifer consists of the Willis, Bentley and Montgomery Formations, and younger deposits. Though the Willis sand forms the base of the Chicot in Montgomery County, the Alta Loma sand becomes the basal unit towards the south.

Bedient (1982) tabulated field and lab data concerning permeabilities of the Chicot aquifer. Sand layers ranged between 1.0 x 10-3 cm/sec and 5.0 x 10-5 cm/sec. The hydraulic conductivities of the clay layers average about 6.0 x 10-9 cm/sec.

APPLE CREEK BASIN, NORTH DAKOTA

The study area (Figure 49) was selected for several important reasons. An agricultural soil was desired that was fairly loamy and contained a significant precentage of soil organic matter. Access to an undisturbed site for soil coring was easily obtained with Milton Lindvig, Director of the Hydrology Divison of the North Dakota Water Commision, acting as liaison. Preliminary field work regarding the geology, soils, and water resources of the area was unnecessary as the region is well documented in the literature (Kume et al., 1965 and Randich



Location Map Showing the Study Area Within Burleigh County, North Dakota

Figure 49

et al., 1966). A surface water control point exists near the mouth of Apple Creek where discharge and water quality data is available.

Much of the material presented in the sections concerning physiography and geology was taken from part 1 of a report entitled *Geology and Ground Water Resources of Burleigh County, North Dakota*. The treatment of these topics by the authors (Kume and Hansen) was excellent.

Part 3 of the same report, written by Randich and Hatchett, was used solely in the description of climate, and groundwater, and partially in the surface water section. Surface discharge and water quality data were taken from parts 2 and 3 of the aforementioned report on Burleigh County. The soils section was taken primarily from Aandahl (1982) and the Soil Conservation Service's *Soil Survey of Burleigh County, North Dakota*.

Several of the enclosed maps were found in the Oklahoma State University map room. The remaining figures were taken from the North Dakota Geological Survey Bulletin 42.

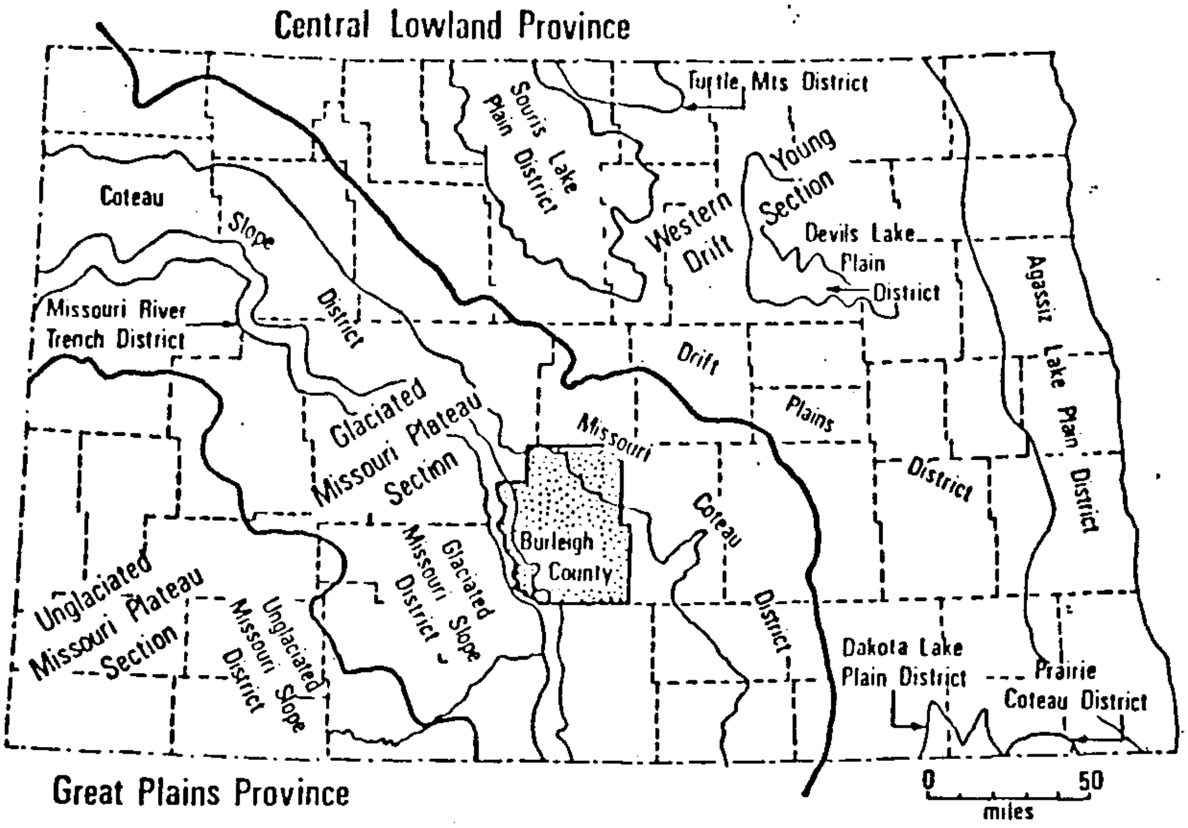
Geography

The Apple Creek basin lies primarily within the boundaries of Burleigh County in south central North Dakota. The drainage area covers 1680 square miles, though 500 square miles is probably noncontributing (Randich et al., 1966). The dynamic portion of the basin is confined within the ranges of 76-80 west and the townships 137-142 north.

Physiography and Topography--

Apple Creek falls into two physiographic districts (Figure 50). Through the majority of its length, the waterway is part of the Apple Creek Uplands Subdistrict of the Coteau Slope District. At the conjunction of Apple Creek and the Missouri River, the waterway enters the Missouri River floodplain and the Missouri River Trench (physiographic) district. These districts are part of the Glaciated Missouri Plateau Section of the Great Plains Province within the Interior Plains Major Division (Kume et al., 1965).

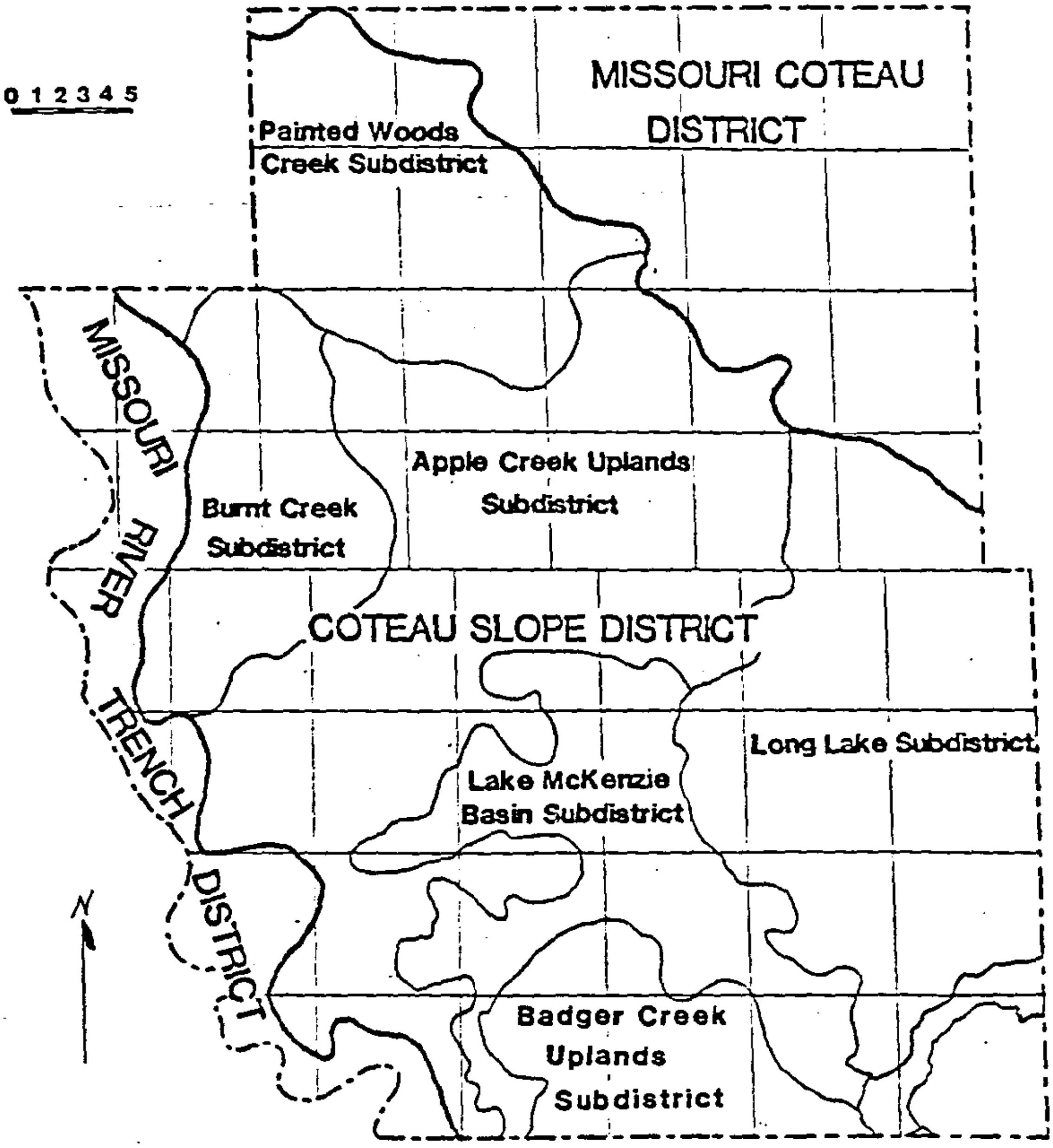
Stream eroded bedrock covered by sheet moraine is characteristic of the Apple Creek Uplands subdistrict (Figures 51 and 52). The overall hummocky topography is only disturbed by isolated bedrock buttes. Drainage is well integrated, and the glacial drift is thin in the north (<10 feet) becoming more



Physiographic Map of North Dakota

(After Kume et al., 1965)

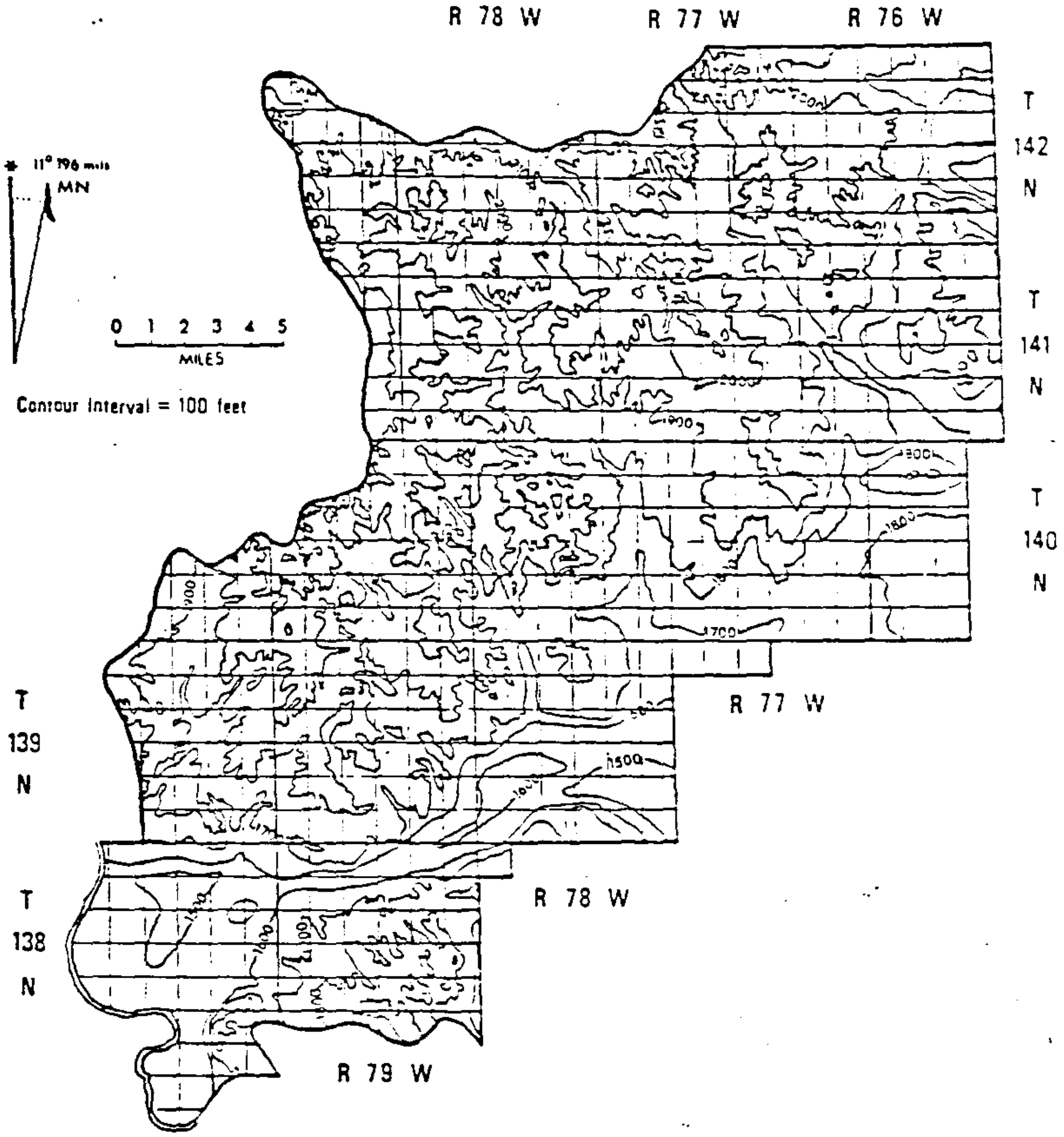
Figure 50



Map of the Physiographic Subdivisions of the

Coteau Slope District in Burleigh County, North Dakota

Figure 51



Bedrock Topographic Map
within the Apple Creek Study Area
(After Kume et al., 1965)

Figure 52

variable southward. Kames exist in the northeast, and dunes are abundant southeast of Bismarck. Most of the present drainage channels once carried glacial meltwater (Kume et al., 1965).

The Missouri River Trench District contains a trench floor and dissected valley walls. Terraces are well developed and occur at several elevations governing various flood stages.

The elevation of this region is greater than 2100 feet at the headwaters of Apple Creek and grades down to 1640 feet at the Missouri River. Local relief is generally less than 200 feet and is the result of stream valleys cut into bedrock. Apple Creek flows under a gradient of less than one degree through most of its course and thus meanders are well developed.

Soils--

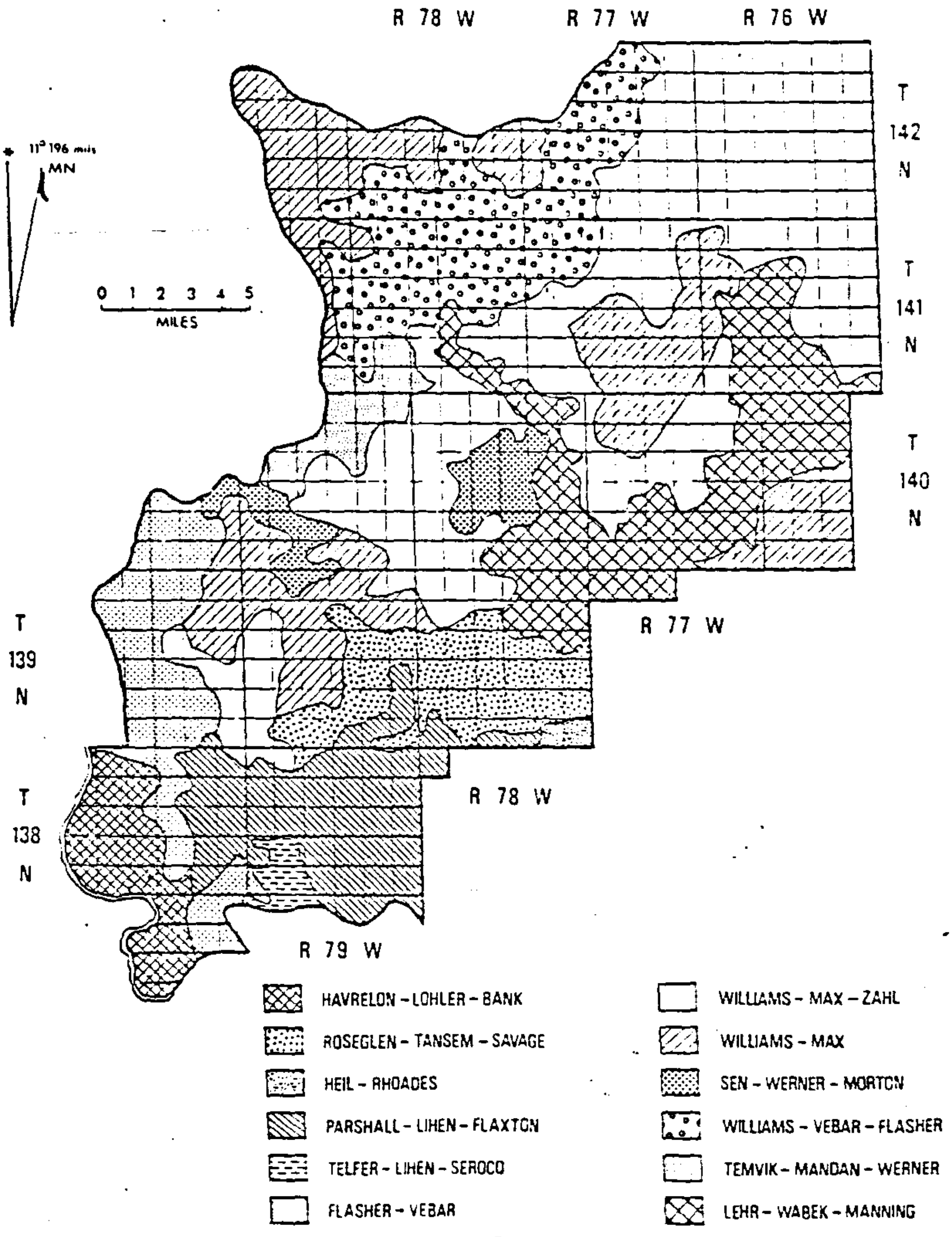
Aandahl (1982) divides the Apple Creek basin into three different soil regions. The upper basin region is composed of argiborolls, haploborolls and ustorthents. These are 'fine-loamy soils formed in glacial till on level to rolling slopes.'

The mid-basinal region contains primarily argiborolls, which have an argillic horizon. The lower basin region, which includes the Missouri River floodplain, is composed of haploborolls,

TABLE 3

4 Major Soil Associations of Apple Creek Basin, North Dakota

ASSOCIATION	ORDER	SLOPE	DRAINAGE PROPERTIES	TEXTURE	SOURCE ROCK	SOM CONTENT	WATER CAPACITY
Williams-Max-Zahl	Mollisol	Nearly level to steep	well drained	medium till plains	glacial	moderate	high
Lehr-Wabek-Manning	Mollisol	Nearly level to steep	excessively drained	medium and moderately coarse	outwash plains	moderate	very low to low
Roseglen-Tansem-Savage	Mollisol	Nearly level to rolling	well drained	medium	lake plains and terraces	moderate to high	moderate to high
Parshall-Lihen-Flaxton	Mollisol	Nearly level to rolling	well drained	moderately coarse	outwash plains and sand mantled uplands	moderate to	moderate



General Soil Map
within the Apple Creek Study Area
(After SCS et al., 1974)

Figure 53

argiborolls, and ustipsamments. These are most often 'loamy soils formed in residuum from sandstones and shales on level to rolling slopes' (Aandahl, 1982).

The Soil Conservation Service divided the Apple Creek basin into four major soil associations (Table 3, Figure 53). Many headwater tributaries of Apple Creek flow through the Williams-Max-Zahl soil association. These soils exist on nearly level to steep slopes and are very well drained (SCS, 1974).

Lehr-Wabek-Manning soils exist in the upper creek region just below the headwaters, slopes are variable as are soil textures. Medium to coarse textured soils predominate, however (SCS, 1974).

At the Random Creek conjunction, Roseglen-Tansem-Savage soils are prevalent. These well drained, medium textured soils occur on level to slightly rolling terrain (SCS, 1974).

The lower creek region is covered by Parshall-Lihen-Flaxton soils. They are well drained, moderately coarse textured, and occur in level to rolling areas (SCS, 1974).

During the course of the field study, an attempt was made to sample those solids which are most widespread within the drainage basin. The Williams series of soils are by far the most aerially extensive soil types. The Williams loam, undulating covers 20.7

percent of the county by itself. Besides the Williams series, the second largest soil type covers only 3.3 percent of the county (SCS, 1974). Thus the Williams loam is the only statistically significant soil type in the county.

The Williams loam developed on nearly level glacial till plains. Slopes generally range between 3 and 6 percent. These soils have deep profiles and are well drained.

The loamy surface layer is about 4 inches thick, and it is underlain by a friable, clay loam of moderate permeability. The C horizon is also a clay loam but has a moderately slow permeability. The water capacity of the soil is high as a result of the high clay fraction, and the percent organic matter is moderate (SCS,1974).

Vegetation--

Native vegetation on the predominant Williams loam soil series is as follows: 15-45% western wheatgrass, 15-25 needle and thread, 10-20% green needlegrass, 5-15% blue grama 5-10% prairie junegrass, 0-30% rough Fescue, 0-20% blue bunch wheatgrass, 10-20% other grasses, 5-10% forbs, and 0-5% shrubs (Aandahl, 1982).

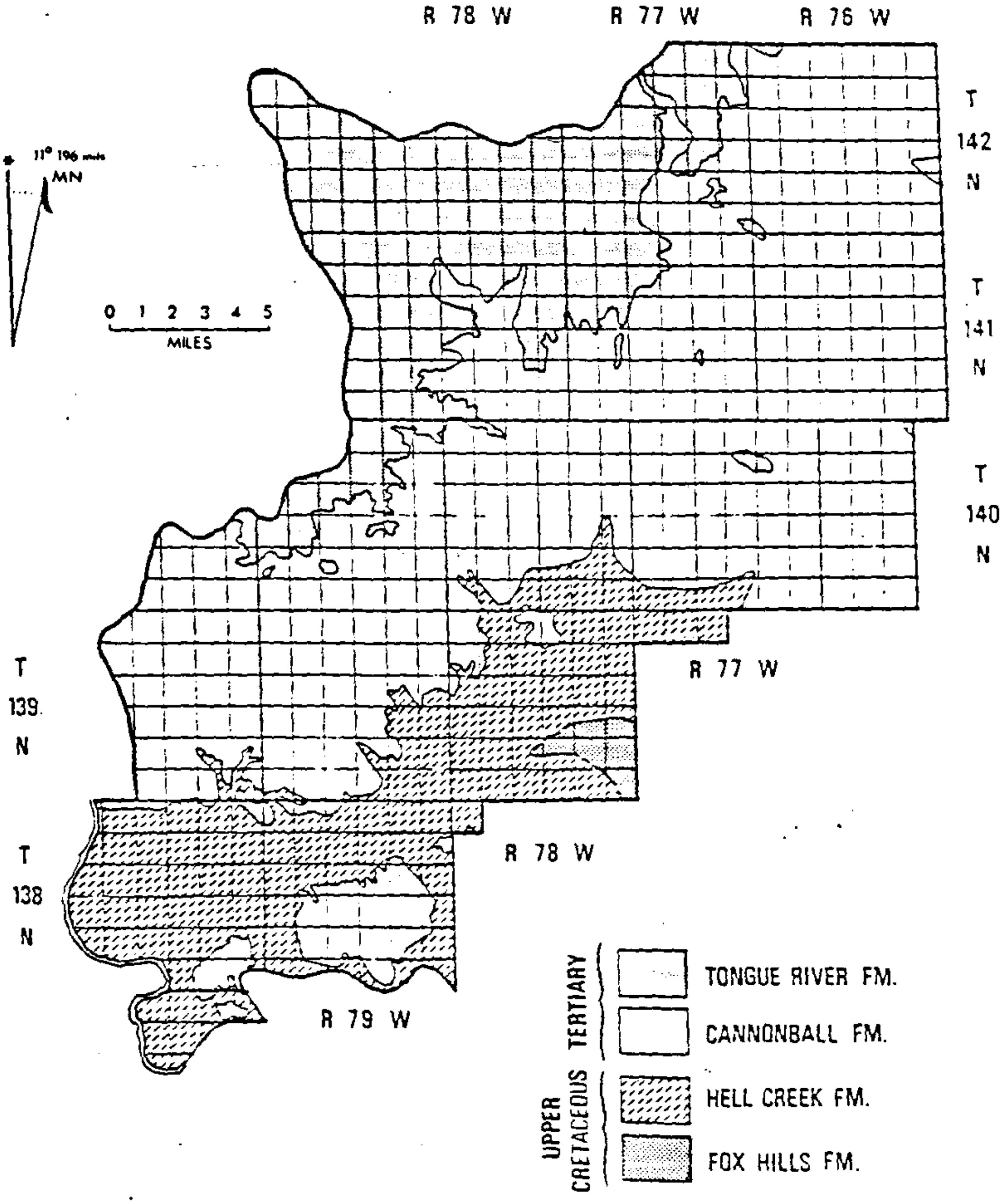
Principal crops on these soils are wheat, oats, barley, flax alfalfa, hay, and corn. Some acreage is used as summer fallow (Aandahl, 1982).

Geology

Only those formations exposed at the surface within the study area (Figure 54) will be discussed under 'Geology'. Older formations will be discussed where appropriate, as in the section describing the hydrogeologic properties of bedrock aquifers. Those rocks that outcrop in the area range in age from upper Cretaceous to Quaternary.

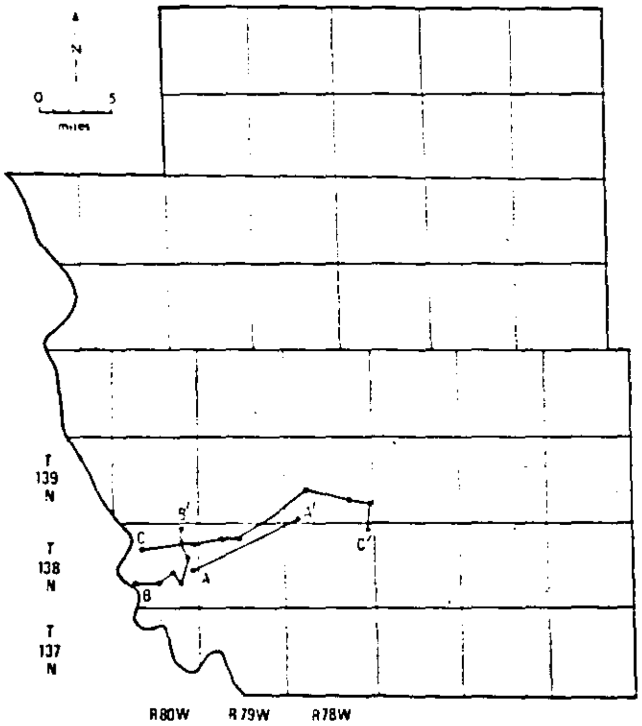
The Late Cretaceous age Fox Hills Formation is a marine sandstone. Except for siliceous beds which contain ferruginous concretions, the sandstone is friable. This formation dips to the northwest. The contact between the Fox Hills and the overlying Hell Creek Formation is gradational (Kume et al., 1965).

Above the Fox Hills Formation lies the Hell Creek Formation of the Montana Group (Figure 55). A regressive sequence exists between the two formations as the Hell Creek is of continental origin. Outcrops of the unit are composed of sandstone,



Bedrock Geologic Map
of the Apple Creek Study Area
(After Kume et al., 1965)

Figure 54



Location of Geologic Cross Sections
Burleigh County, North Dakota
(After Kume et al., 1965)

- ▨ Sand, Sandstone
- ▨ Gravel, Conglomerate
- ▨ Clay, Shale
- ▤ Sand and Clay Sandstone and Shale
- ▨ Silt, Siltstone
- ▨ Silty Clay Silty Shale
- ▨ Silty and Sandy Clay Silty and Sandy Shale
- ▨ Glauconitic and Shaly Sandstone
- ▨ Till
- ■ Lignite Coal (Detrital or in Place)

Figure 55

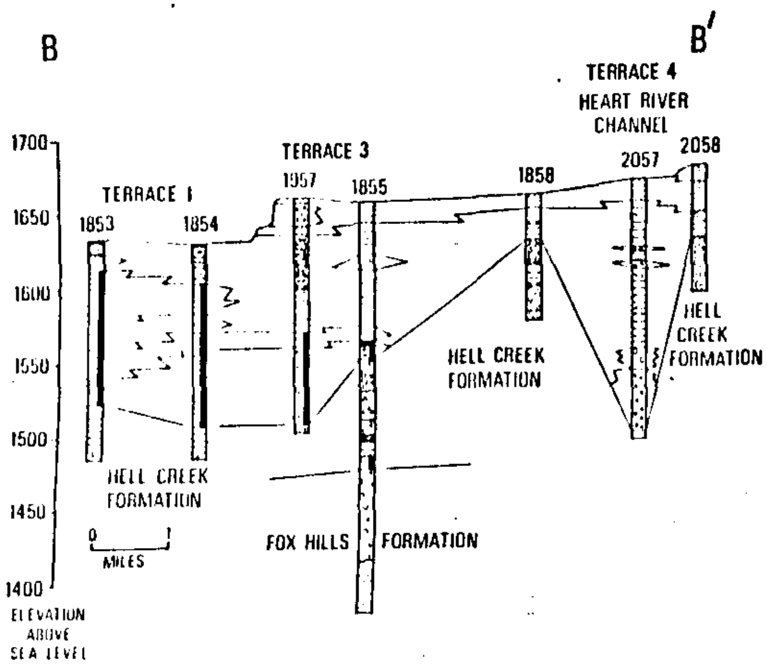
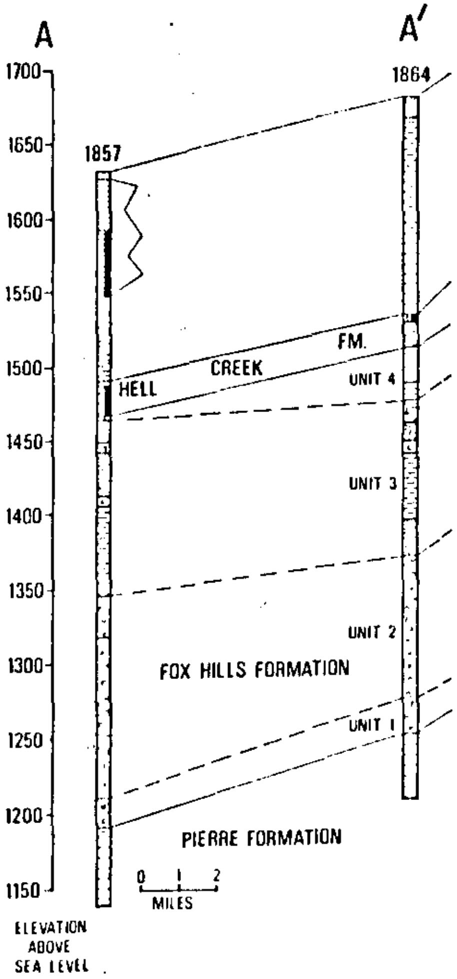


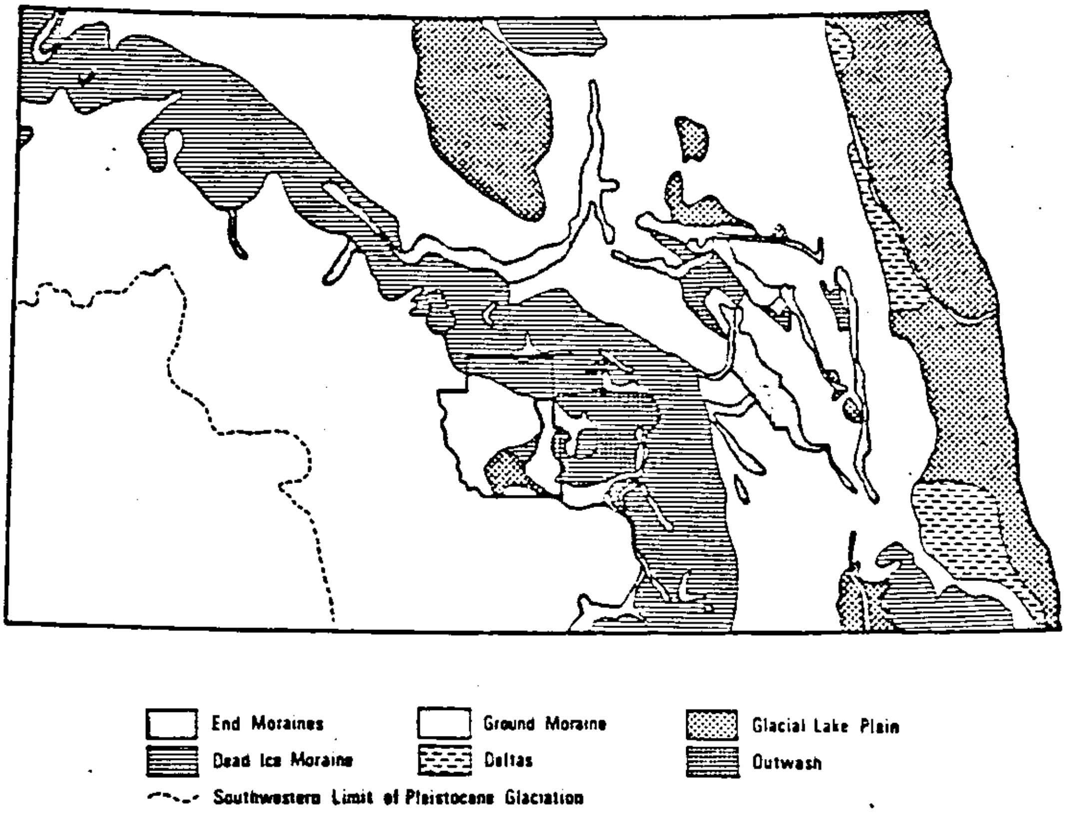
Figure 55 (continued)



mudstone, siltstone, carbonaceous shale, and lignite. The formation consists of shale, siltstone, and sandstone in the subsurface. The upper and lower contacts are both conformable and gradational. A transgressive sequence is indicated as the overlying Cannonball Formation is a marine sequence (Kume et al., 1965).

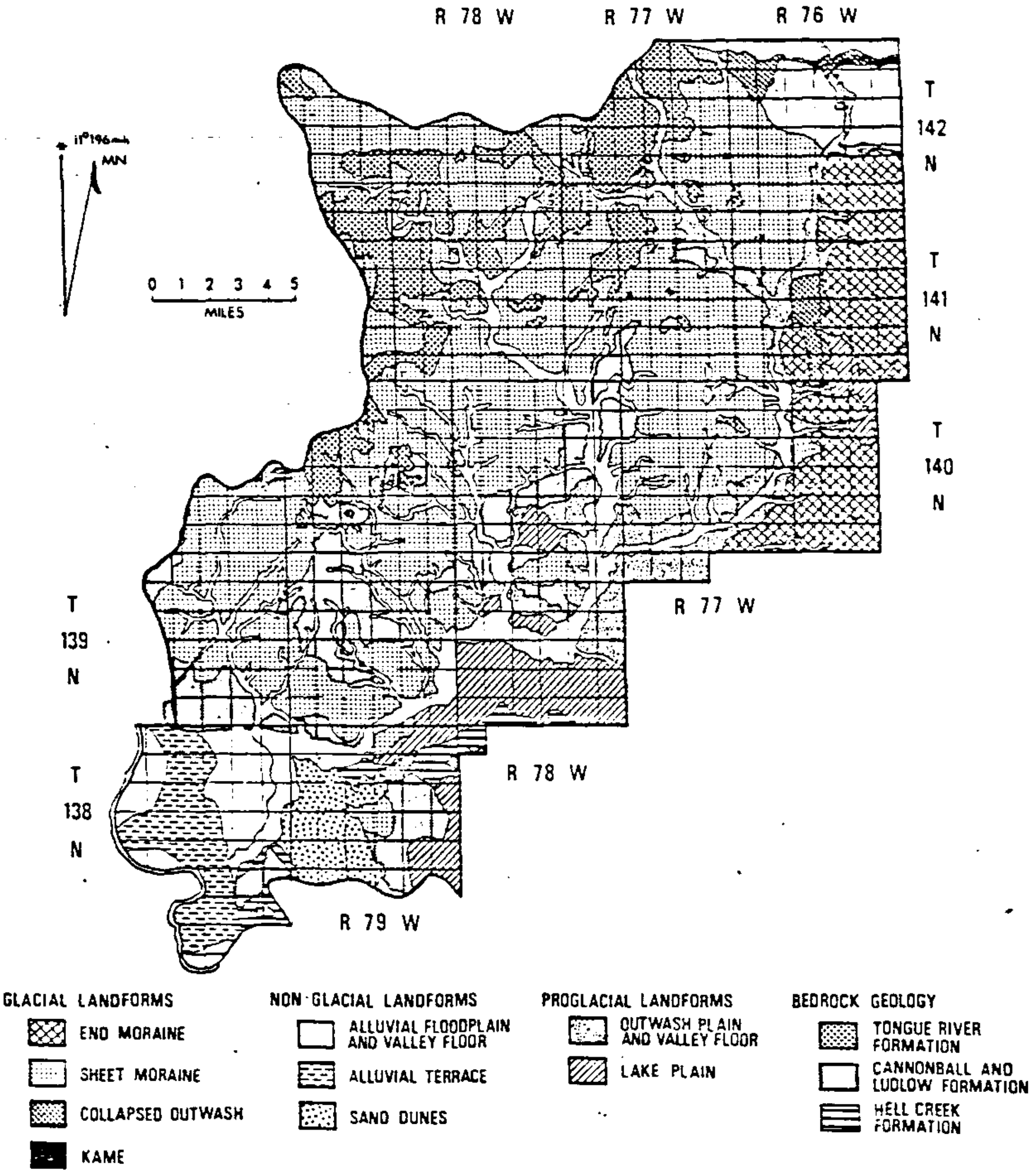
The Cannonball Formation of Paleocene age is part of the Fort Union Group. It is exposed throughout the mid-section of Burleigh County and dips to the northwest. Outcrops are composed of sandstone, siltstone, shale and lenticular limestone. In the subsurface record, the Cannonball consists of claystone, sandstone, siltstone and limestone. A regressive sequence exists resulting in a disconformity which overlies the Cannonball (Kume et al., 1965).

The Tongue River Formation, also a unit within the Fort Union Group is exposed in the highlands of the headwaters region within the study area. This terrigenous deposit reflects an alluvial plain environment. The basal sandstone member of the Tongue River Formation contains shale pebbles of Cannonball origin. Above the basal sandstone member lies interbedded sandstone, claystone, siltstone, shale, limestone and lignite (Kume et al., 1965).



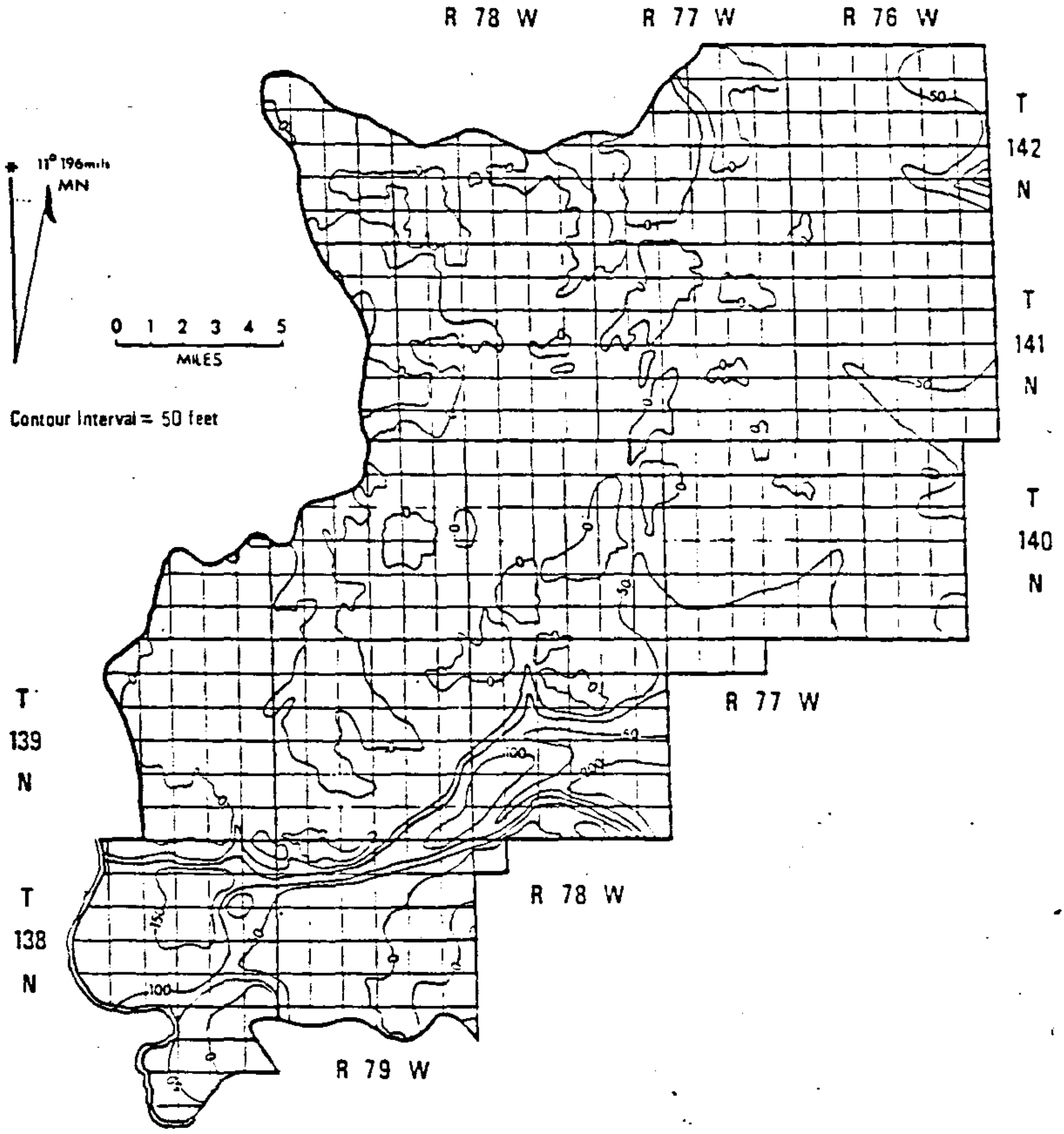
Generalized Glacial Map of North Dakota
(NDGS Misc. Map No.14)

Figure 56



Landform and Geologic Map
within the Apple Creek Study Area
(After Kume et al., 1965)

Figure 57



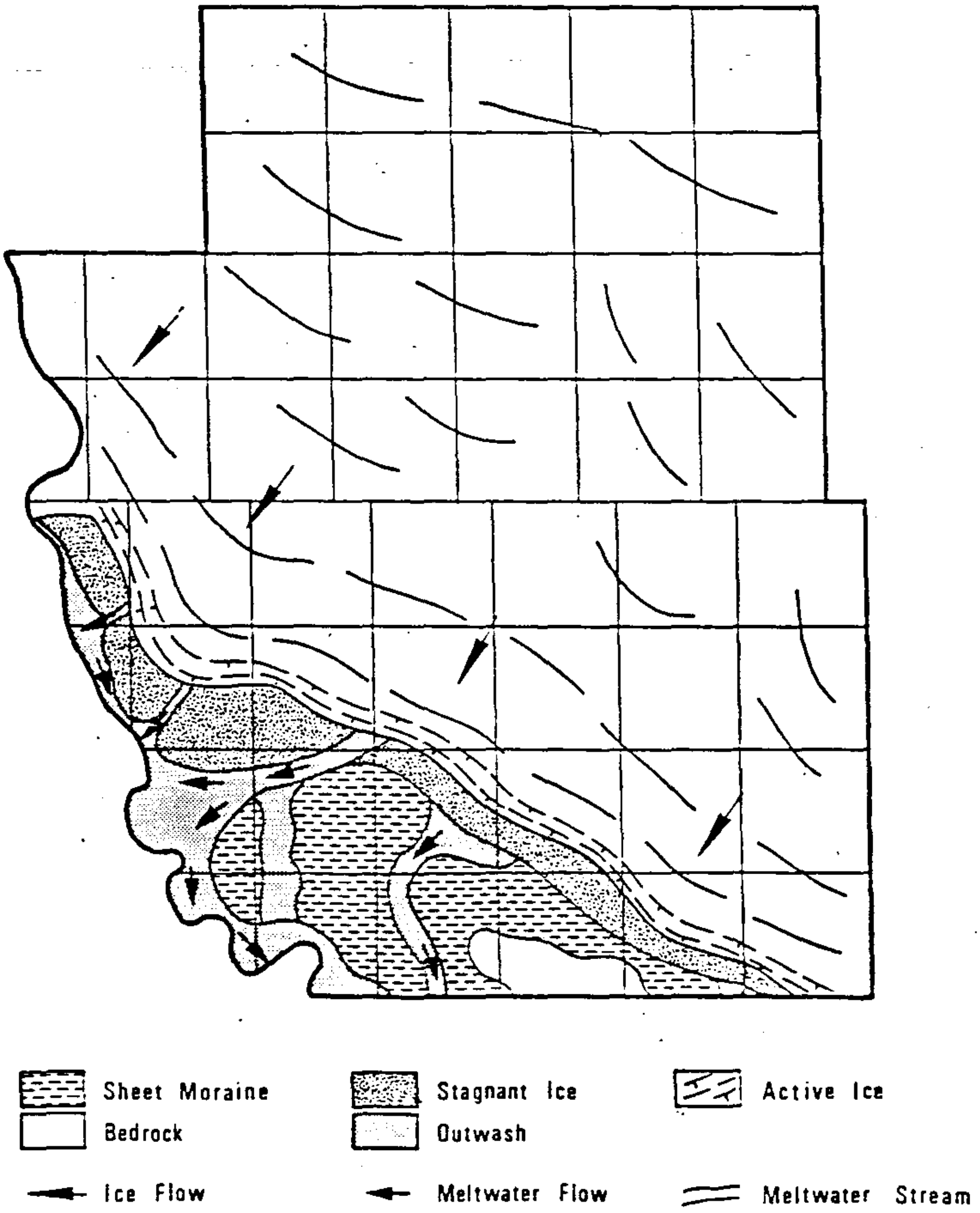
Drift Isopach Map
within the Apple Creek Study Area
(After Kume et al., 1965)
Figure 58

The generalized glacial map of North Dakota (Figure 56) illustrates that Apple Creek basin is covered predominantly by ground moraine. Terminal moraines, outwash deposits, and glacial lake plains flank the eastern margin of the basin (Figures 57, 58).

Earliest evidence of glaciation is represented by rocks of the lower Wisconsin Stage of the Pleistocene Series. The remnant of this event, called the Napolean Drift (Figure 59), is a sheet moraine which occurs in western and central Burleigh County. This glacier receded quickly as evidenced by the absence of a terminal moraine. The Napolean Drift contains a high percentage of local bedrock types and very little (<25%) erratics. If the gravel fraction is excluded, this till consists of between 22-52% clay, 26-36% silt, and 19-51% sand (Kume et al., 1965). Pebbles are usually oriented with their long axes in a northeast-southwest direction which correlates with the direction of ice flow (Holmes, 1941).

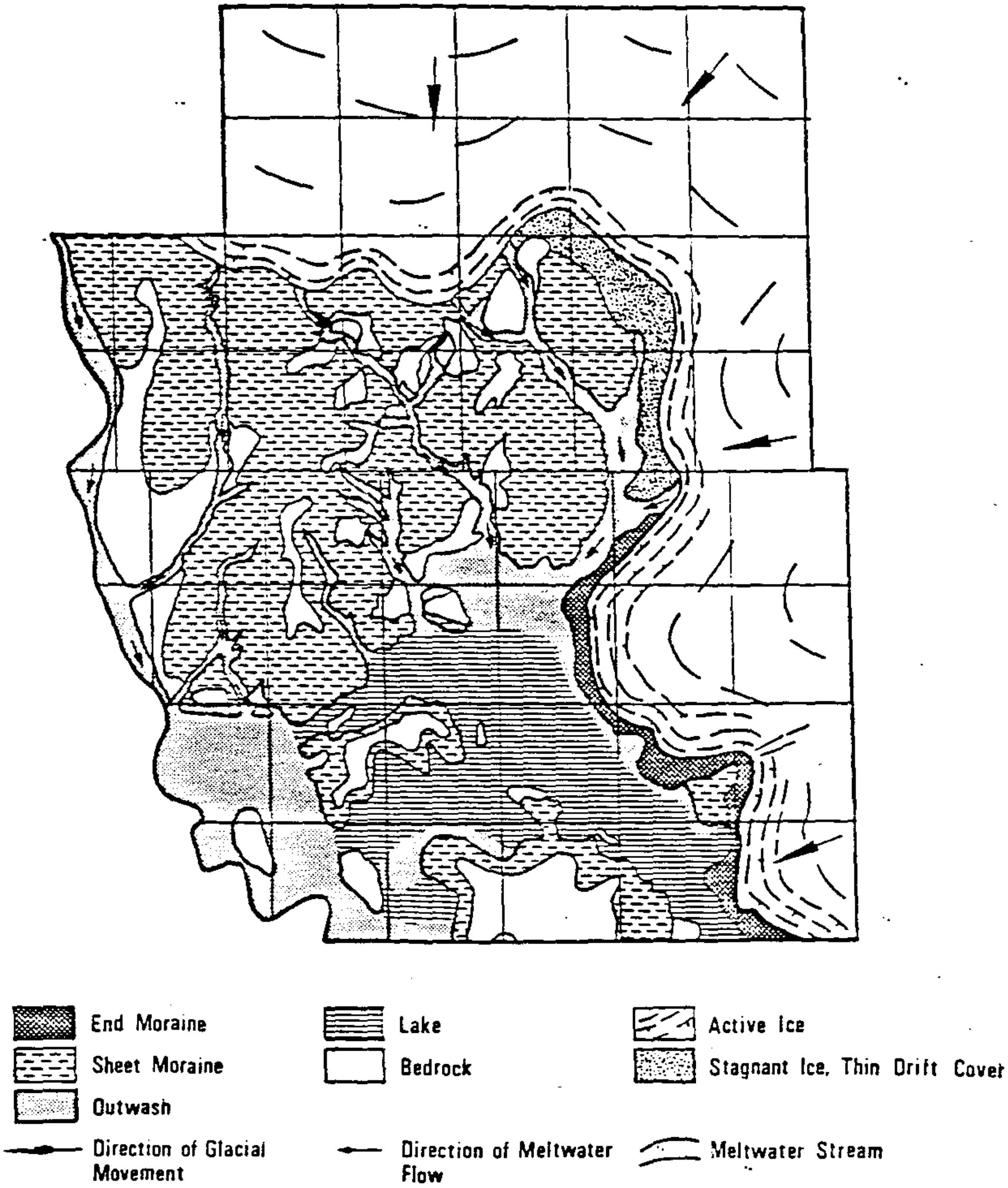
Clayton (1962) refered to a 25,000 year erosional period subsequent to the Napolean glacial advance. The uniform thickness and slight degree of weathering of the till led Kume et al. (1965) to suggest a lower figure, however.

The upper Wisconsin Stage Long Lake glacial advance



Napoleon Glacial Advance with the Deposition of Sheet Moraine.
(after Kume et al., 1965)

Figure 59



Long Lake Glacial Advance with the Deposition of the Long Lake End Moraine and the McKenzie Lake Plain.

(after Kume et al., 1965)

Figure 60

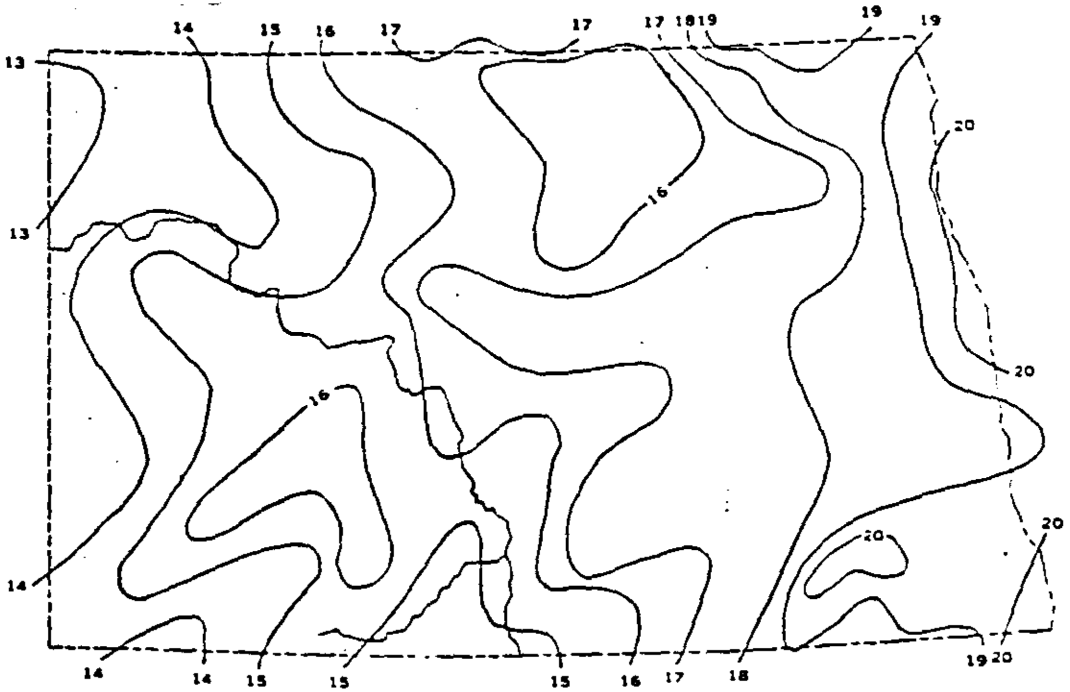
deposited terminal and ground moraines (Figure 60), and glacial lake sediments throughout eastern Burleigh County. The Long Lake Drift is an erratic influenced deposit. The increased percentage of erratics as compared to the earlier Napolean Drift is the result of a different ice flow direction. The Long Lake Drift consists of 26-35% clay, 24-42% silt and 28-44% sand (Kume et al., 1965).

Eolian deposits of Recent age exist primarily in southern Burleigh County along the margins of the Missouri River. Alluvial, sheetwash and colluvial sediments occur throughout the study area, primarily in or near current channels (Kume et al., 1965).

Hydrogeology

Randich et al. (1966) best describes Burleigh County as having a semi-arid continental climate. It is characterized by generally low relative humidity, light rainfall (confined largely to the warmer part of the year) (Figure 61), abundant sunshine, prevailing northwesterly winds, moderate snowfall, wide diurnal range in temperature, and pronounced seasonal extremes of temperature (Table 4).

North Dakota Generalized Precipitation Map



AVERAGE ANNUAL PRECIPITATION, IN INCHES
(Data from National Weather Service-NOAA)

Figure 61

Climatological Data for Bismarck Airport, 1980

Month	Precipitation (mm)	Temperature (°C)
January	18	-12.9
February	7	-9.2
March	8	-4.0
April	11	9.3
May	27	15.6
June	42	19.0
July	80	22.2
August	128	18.7
September	82	12.4
October	59	7.6
November	2	2.2
December	5	-7.5

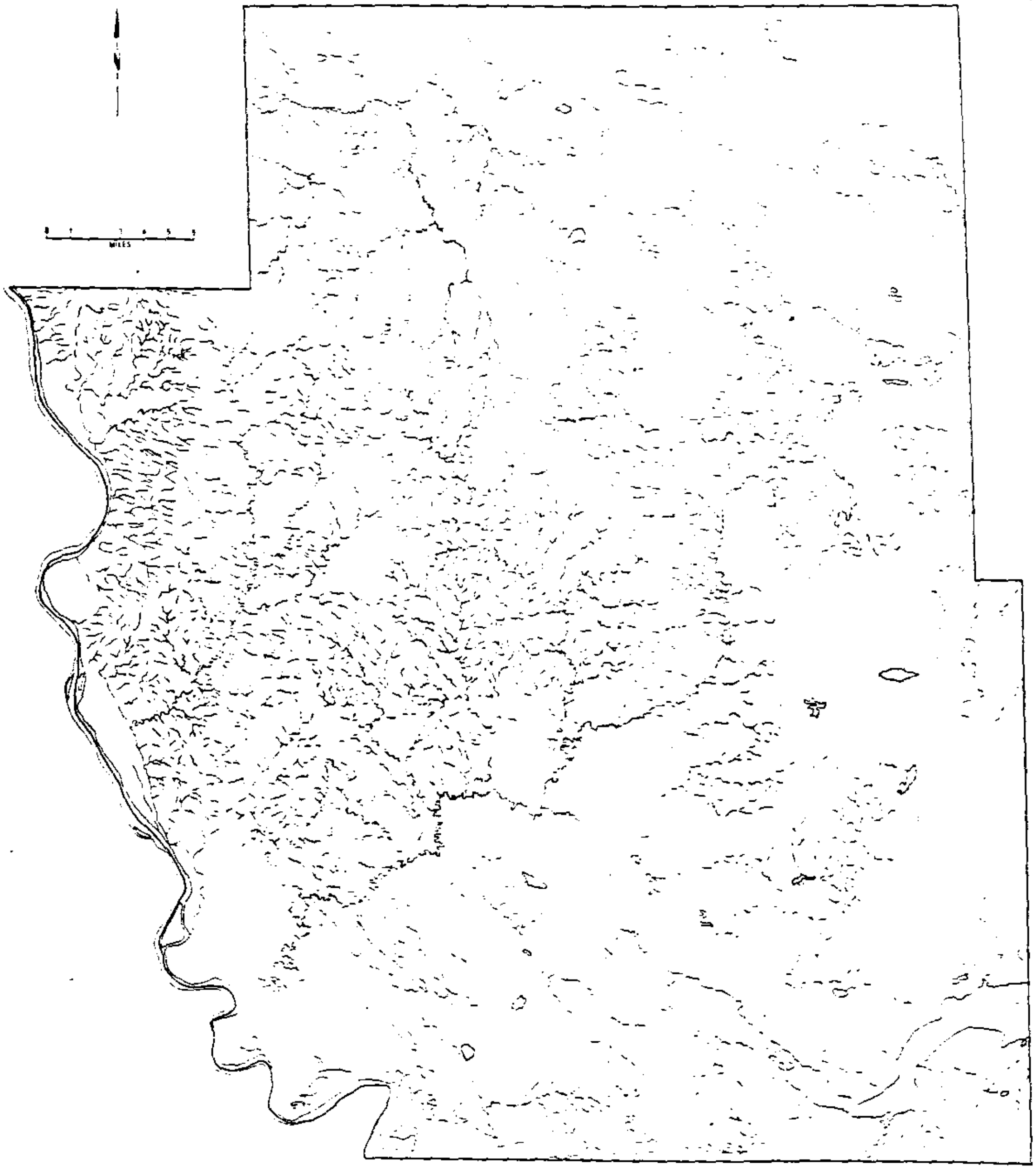
Table 4

DRAFT ONLY

Late September and mid-May mark the first and last frosts, respectively. This yields a growing season of about 135 days. Frost generally penetrates to five feet below land surface. The average annual precipitation is 16.5 inches and is due to cyclonic storms. The mean annual temperature is 43oF.

Surface Water--

Active surface and stream runoff is limited to a 400 square mile area which is contained within the study area. The only city or industrial area near Apple Creek is Bismarck, North Dakota which derives its water requirements from groundwater aquifers rather than surface sources. The creek flows unhindered in that no dams or obstructions block its channel. A dendritic pattern is well developed (Figure 62). As the gradient is less than one hundred feet per mile, a meandering channel geometry exists. About midway through its length, the East and West Branches of Apple Creek merge. Just south of this conjunction lies the McKenzie Slough which is fed by Random Creek to the east. It is suspected by the author that little interaction between the waters of the McKenzie Slough and Apple Creek occurs. Hay Creek is the last major tributary which feeds Apple Creek



Surface Drainage Map of Burleigh County, North Dakota

(after Kume et.al., 1965)
Figure 62

just east of Bismarck. Apple Creek enters the Missouri River floodplain immediately south of Bismarck.

A Stream discharge and water quality station sponsored by the USGS is located 2 1/2 miles upstream from the Hay Creek conjunction. Water quality records are available for water years 1974 to the current year. Steam discharge records exist for the periods March through June of 1905, and October, 1945 to the present (USGS, 1981).

The average discharge, measured over a thirty-five year period, is 33.8 cubic feet per second (cfs). The maximum discharge on record occurred on April 18, 1950 and was 6,750 cfs. Periods of no-flow are not uncommon during summer months of dry years (USGS,1981).

Samples are collected periodically by the USGS from a gaging station located near the mouth of Apple Creek. The water quality analyses from water year 1980 were run through a computer program to determine probable weathering scenarios.

All of the analyses (Table 5) indicated that the concentration of sulfate (SO_4^{-2}) was greater than calcium (Ca^{+2}). Randich et al. (1966) explains that SO_4^{-2} can result from the dissolution of the mineral mirabilite (Na_2SO_4) and that Ca^{+2} is often exchanged for sodium (Na^{+}). These conclusions also justify

TABLE 5

Date of Sample	Na+K	Ca	Mg	HCO3	SO4	Cl
10/25/79	69	14	17	56	36	8
11/30/79	66	14	20	49	45	6
12/31/79	66	15	19	54	40	6
1/31/80	62	17	21	55	39	6
2/22/80	61	20	19	58	35	7
3/27/80	53	23	24	43	54	3
5/7/80	61	20	19	46	49	5
5/30/80	65	18	17	49	45	6
6/27/80	69	16	15	55	36	9
7/30/80	74	13	13	58	33	9

Percent meq/l of cations and anions in
Apple Creek surface water samples

the high concentration of Na^+ in the stream.

The Apple Creek has Na-HCO3-SO4 type water with a fairly wide range of TDS values throughout the year.

Groundwater--

Water wells in the Apple Creek basin produce from bedrock aquifers (Table 6) in addition to Quaternary unconsolidated glacial deposits (Table 7)and Recent alluvial sediments.

Only the Fox Hills Sandstone is a reasonable water supply within the Cretaceous System. The Dakota Sandstone also yields significant quantities of water; however, the water must be treated to make it potable and suitable for agricultural use. The Tertiary System has two good aquifers, and, in fact, the Tongue River Formation is a major aquifer within the area. The Quaternary age glacial aquifers are the best with the highest yields and lowest TDS contents. The gradient of head is such that the bedrock aquifers constantly feed the glacial aquifers.

To understand the hydrogeology of the Quaternary age glacial aquifers within the basin it is necessary to examine pre-existing drainage systems. Prior to pleistocene modification, the drainage system in Burleigh County was significantly different

TABLE 6

Cretaceous System

Formation Name	Depth to Aquifer	Thickness	Water Type	TDS	Possible Well Discharge	Other
Dakota Ss	2800-3200'	250'±	Na-SO_4	2400 ppm	High permeabilities	High Flouride and iron
Pierre Sh	450'	1000'±			Relatively impermeable except for water from Sd lenses and fractures	
Fox Hills Ss	50-100'	300'±	Na-HCO_3-Cl Na-Cl-HCO_3	1500- 2700	Yeilds of 50-150 gpm	underlies Long Late and McKenzie aquifers
Hell Creek F.	at surface	200'±	Na-HCO_3 Na-HCO_3-SO_4 Na-HCO_3-CL	500- 200	Relatively impermeable	Water type on residence time
Tertiary System						
Cannonball F.	at surface	300'±	Na-HCO_3 Na-HCO_3-SO_4 Na-SO_4-HCO_3	1000- 1700	50 gpm	
Tongue River F.	at surface	215'±	Na-HCO_3-SO_4	500- 1900	20 gpm	major aquifer

than it is at present. Apple Creek was a tributary to the paleo-Heart River which, in turn, flowed into the Cannonball River and drained in an easterly direction (Figure 63).

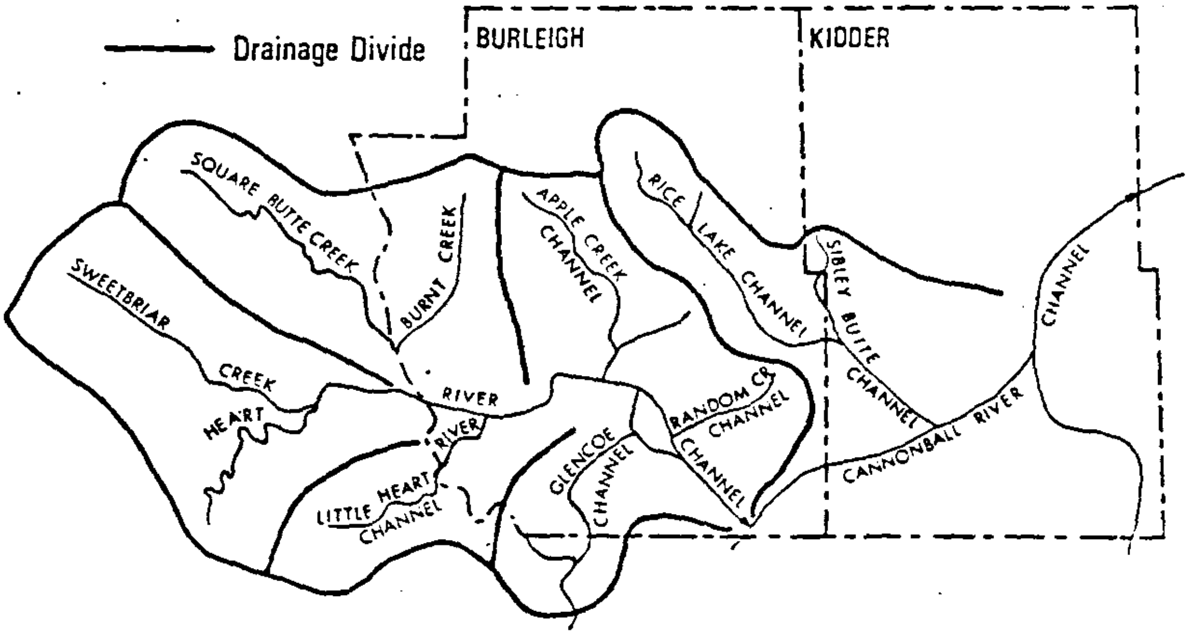
During glaciation, the Missouri River diverged to its present course (Figure 64). The Heart and Cannonball Rivers reversed their flow direction and the Glencoe and Soo Channels were cut into the bedrock by overflowing waters from the original channels. The new Heart River became the lower section of Apple Creek and that part of the Heart River upstream of its conjunction with Apple Creek became the McKenzie Slough. ´Later meltwater flowing from proglacial Lake McKenzie deposited most of the material (Figure 63) now comprising the Long Lake, McKenzie, Lower Apple Creek, Glencoe Channel, Soo Channel, and Bismarck aquifers (Randich et al., 1966).´

The sample designations for the ground-water analyses first list the number as it relates to the sample number on table 8. The next symbol gives the age and type of deposit (see table for key). The date of collection follows, and the last symbol signifies that it is a groundwater analysis.

Sample numbers 2, 5 and 24 are from the upper Cretaceous Fox Hills Formation. Analyses 2 and 24 are typical of this formation with total dissolved solids (TDS) values of between 1500 and

TABLE 7
Quaternary Age Glacial Aquifers

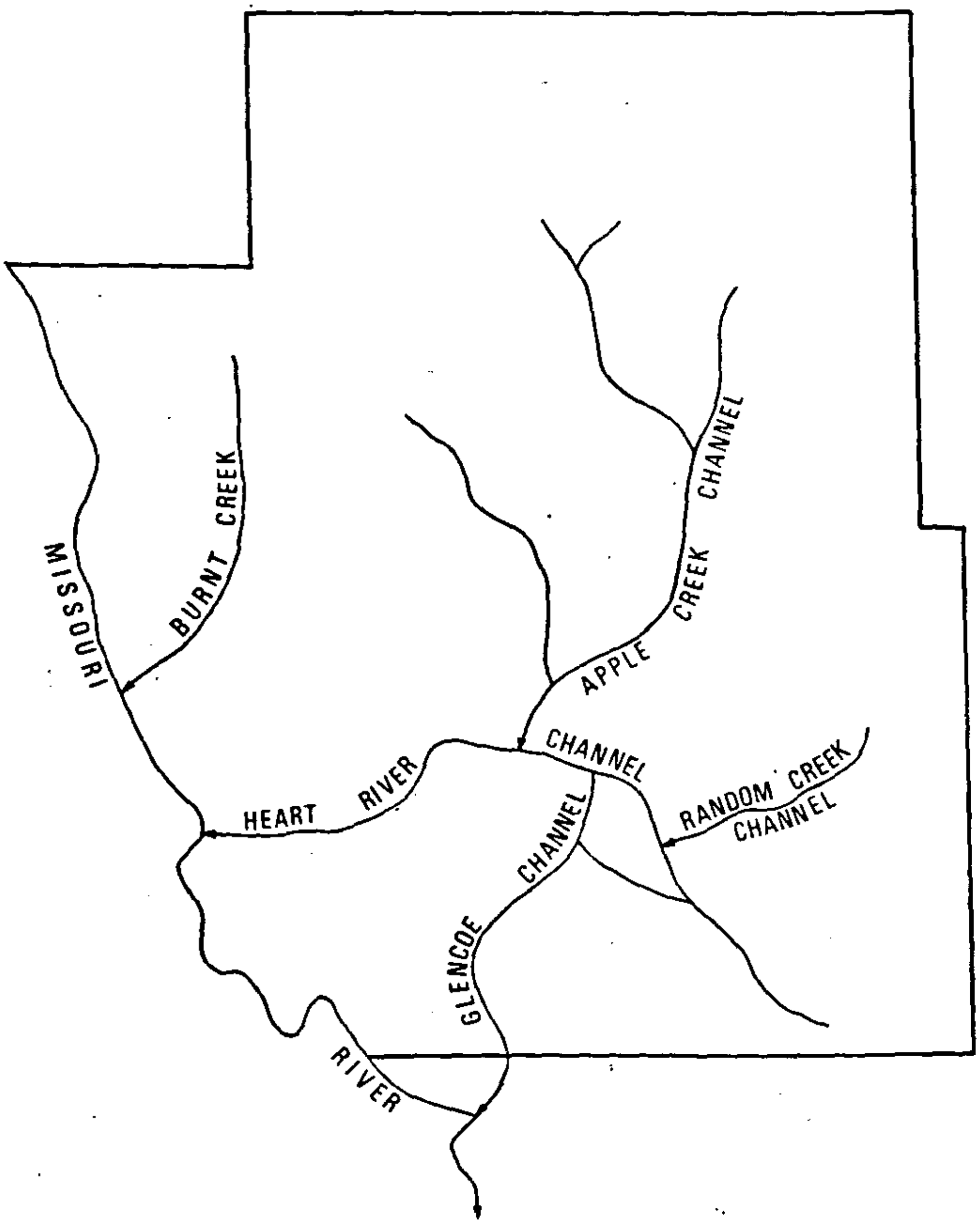
Aquifer Name	Areal Extent (sq.mi.)	Depth to Aquifer (ft)	Thickness (ft)	Lithology	T(gpd/ft)	S	Total Storage (acre-ft)	Type	TDS (ppm)
Lower Apple Creek	21	40-110	10-100	Sd&Gr	10,000	WT & L-Art	$6.2x10^5$	Na-HCO$_3$	<1000
Bismark	25	20-105	10-105	SD&Gr	350,000	L-Art	$5.1x10^5$	Na-Ca-HCO$_3$ Na-HCO$_3$-SO$_4$	800- 1800
Upper Apple Creek	19	at surface	<20	SD&GR		WT	3000	Na-HCO$_3$-SO$_4$	1000



Preglacial and Pre-Wisconsin Drainage

(After Kume et al., 1965)

Figure 63



Diversion and Wisconsin Drainage Map
Burleigh County, North Dakota
(After Kume et al., 1965)

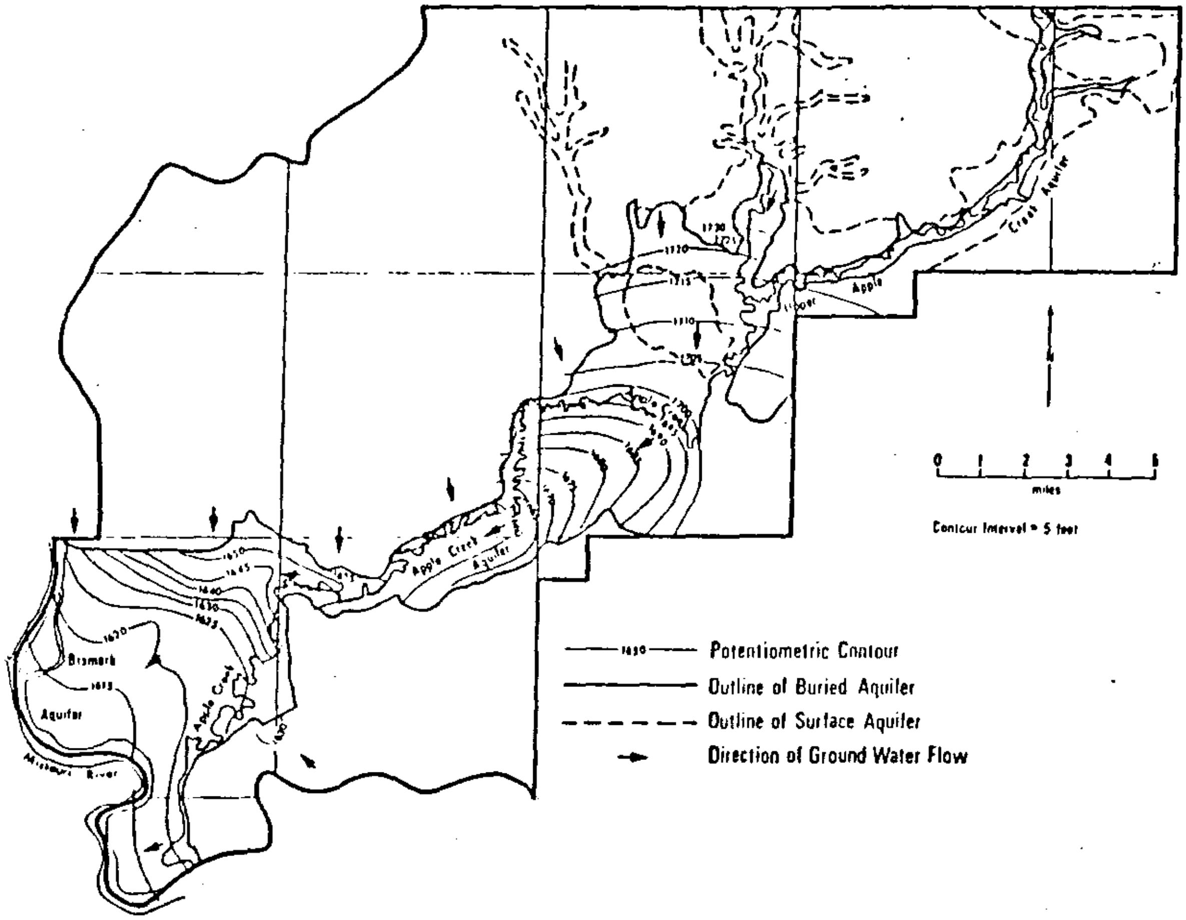
Figure 64

2900. Sample #2 is a typical Na-HCO3-Cl type water and #24 represents a Na-Cl-HCO3 type water. Cation exchange is indicated in both samples implying that the ratio of SiO2 to Na+K is less than one. Analysis #5 is atypical of the Fox Hills Formation. The author suggests that either (1) the analysis is from the Hell Creek Formation, or (2) the sample was collected near the contact between the two formations and that water from the Hell Creek Formation is leaking into the Fox Hills Formation. Ca removal is indicated implying that higher concentrations of sulfate exist.

Sample numbers 8, 9 and 20 were collected from the Hell Creek Formation of Upper Cretaceous age. TDS values fall in the range of 500 to 2000 mg/l. The water chemistry is primarily the Na-HCO3 type. In all cases the ratio of SiO2/(Na+K) is less than one. In addition, analyses 9 and 20 have a greater SO4 concentration than Ca.

Nearly all of the samples from Quaternary glacial drift indicate calcium removal. The main water type is Na-HCO3 which represents 82 percent of the samples. Most of the analyses show TDS values between 1200 and 2000 mg/l.

MACROPORE SITE, PAYNE COUNTY, OKLAHOMA



Potentiometric Surface Map of the Glacial Aquifers within the Southern Half of the Apple Creek Study Area
(After Randich et al., 1966)

Figure 65

TABLE 8

Groundwater Analyses within the Apple Creek Basin

#	Form	TDS	Na	K	Ca	Mg	HCO3	SO4	Cl	SiO2
1	QD	458	33	7	90	18	329	94	6	21
2	KFH	1510	610	1.8	5.6	1.2	1153	2.7	256	12
4	QD	829	246	13	23	8.5	641	112	2	1.34
5	KFH	503	76	3.6	40	43	356	149	2	44
8	KHC	720	212	9.1	31	16	641	72	6	21
9	KHC	466	155	6	8.8	6.1	354	98	8	18
10	QD	1280	410	7.4	43	15	828	312	29	30
11	QD	1392	500	20	12	4.9	940	335	30	16
12	QD	1340	394	7.6	65	21	829	360	23	31
14	QAL	1840	613	4.5	49	13	1120	492	35	28
20	KHC	1568	500	14	14	11	720	420	124	27
21	QD	1568	390	19	63	50	592	700	14	28
22	QD	1360	402	6.2	54	15	737	422	25	29
24	KFH	2335	905	25	9.6	6.1	1070	3.7	825	20
25	QD	602	60	10	79	33	390	150	4	31
26	QD	1270	277	9.8	103	36	588	486	8.2	30
27	QD	1280	353	8.9	74	28	744	381	19	29
28	QD	1210	331	7.5	70	22	713	353	24	28
32	QD	968	299	6.5	23	13	684	198	17	29
34	QD	980	260	6.6	71	21	736	202	15	29
38	QD	1260	423	5.6	33	10	856	278	24	30
40	QD	1400	423	7.2	53	16	814	402	27	30
44	QD	1410	420	8.1	60	23	768	438	51	27
47	QD	1630	375	6.8	134	50	882	514	68	25
48	QD	1050	299	6.4	80	26	680	245	41	26
49	QD	1050	253	7	85	27	687	235	47	29
51	QAL	832	134	5.8	113	39	596	201	17	25
52	QAL	555	135	6.9	141	49	672	248	18	24
53	QAL	911	133	6.4	125	46	640	229	17	26
55	QD	814	179	6.8	85	23	686	151	15	29
59	QD	855	222	6.6	66	20	647	170	20	49
61	QD	899	299	6.2	53	16	701	168	5.1	31

Legend

QD	Quaternary glacial drift
QAL	Quaternary alluvium
KHC	Cretaceous Hell Creek
KFH	Cretaceous Fox Hills

(after Randich et.al., 1966)

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This particular location was chosen for its easy accessibility, high water table and macropore development.

The main objective of this study is to develop a field method that will determine how macropores and fractures originate, what controls their size, and how water flows through macropores in the soil. It is hoped that ultimately one will be able to assess the movement of solutes through macropores plus any chemical interactions that may occur within the macropores. In monitoring the size and density of the "macro" pores over time, it will be shown that there is a tendency of microcracks to coalesce and form "macro " cracks, thus inferring a preferential formation of larger cracks in the direction of abundant interlocking microcracks. The soil moisture content versus depth during and after infiltration events will show how and where water flows, with time, through "macro" pores in the soil.

The presence of cracks seems to be related to the mineralogic content of the soil. The percentage and types of clays present will determine the change in the volume occupied by a unit weight of soil. Shrinkage has been shown to take place in two stages. The first stage is characterized by a change in the volume of the soil mass just equal to the volume of the water removed as the soil dries. As the moisture content is further reduced depletion may be at the expense of both capillary or film water and of water held in the lattice structure. The fact that the degree of swelling differs in clay minerals suggests that the shrinkage, which accompanies the drying of soil, is related to the character of the clay component or mixture of clay minerals constituting the clay fraction of the soil.

Soil cracks can range in size from a few micrometers to several thousand micrometers. Brewer (S.S.S.A. 1964) classified soil pores on the basis of size using field measurements for large openings and microscope measurements for smaller ones. Fractures or pores larger than 100 micrometers have been termed "macro" pores. Those ranging in size from 30 to 100 micrometers are "meso" pores, and "micro" pores measure less than 30 micrometers.

Anomalously high soil moisture contents at depth may be attributed to "macro" pores. However, thinking in terms of pore size alone may be too rigid. Relatively small pores can conduct as much liquid as "meso" or "macro" pores when continuous throughout the soil profile. Subsurface channels of continuously connected pores not visible on the surface may also produce anomalous soil moisture contents with depth.

Prior to 1960, relatively few investigators had examined soil-water interactions as a function of depth using measured values of hydraulic conductivity and hydraulic gradient. Nelson et al. (1964) began this work with a study on the redistribution of soil-water. Following his investigation, Rose et al (1965), Von Bavel et al (1968), and Larue et al (1968) examined the variability in hydraulic conductivity for different soils at depth. Beven & Germann (1981) discussed the importance of macropores on water flow through soils. Bouma et al. (1981) have investigated soil morphology with respect to preferential flow along macropores and concluded that characterization of the flow through macropores can only be accomplished using tracers. Earlier, Nelson (1962) used the distribution of tracers to explain the relative effects of pore geometry, diffusion rates, adsorption and exchange.

Geography

The experimental plot is located in the Enid quadrangle, North Central Oklahoma, 15 miles west of the city of Stillwater, in the NW1/4, NE1/4, sec.10 T19N, R1W of the Orlando East Quadrangle.

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The site lies on the upper floodplains of lake Carl Blackwell, city's water supply.

Physiography and Topography--

The study area lies in the Central Redbed Plains physiographic province (figure 1). Idling plains, broad valleys and low hills characterize the region, with topographic lows being formed by non-resistant red shales and uplands consisting of lenticular sandstone units (Curtis and Ham,1979). Continuity of the sandstone beds over distances of several miles has created cuesta-like ridges in some areas. This is especially evident in northwestern Payne County where one such ridge is over seven miles in length (Garden,1973). The study area has an elevation of 950 feet above sea level with topographic highs and lows ranging from 1080 feet in the area southwest of the site to 940 feet in the area north, east and southeast of the site. There is a regional dip to the southwest of about 40 feet per mile. Lake Carl Blackwell has an elevation of 944 feet at the spillway.

Soils--

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The soils of the study area are classified by Gray and Nance (1978) as broken alluvial land consisting of a mixture of loamy alluvial soils that are frequently flooded and small areas of occassionally or rarely flooded soils. This area is classified by the USDA Soil Conservation Service as being Pulaski Fine Sandy Loam, a variant of the Pulaski Soil Series. The Pulaski Fine Sandy Loam is a variant of the Pulaski in that its control section has a fine loamy texture. Inclusions in the mapping unit are:

30% - similar soils - except that the control section (10 to 40 inches) is fine silty

15% - soils that have a coarse-loamy control section (Gray and Nance, 1978)

The Pulaski Fine Sandy Loam variant can be described as a rapidly drained, moderately permeable soils located on flood plains with the surface layer typically being a reddish-brown fine sandy loam, the next layer being a reddish-brown loam and the underlying material being a reddish-brown fine sandy loam and loam and stratified sandy loam (USDA-SCS, unpublished).

At the study site the soil samples we collected do not fall into the above description but can be described as follows:

0 - 6 inches - dark reddish-brown, very fine sandy clay loam
6 - 24 inches - dark reddish-brown, clay loam
24 - 48 inches - dark reddish-brown, sandy clay
48 -121 inches - reddish brown, clay

Vegetation--

The native vegetation consists of tall and mid grasses and deciduous trees. Specifically the study area contains Post and Blackjack Oak, and American Elm trees with open areas having Bluestem, Western Ragweed and Bermuda grasses and Ashy Sunflowers. The study area is bounded by tree-covered ground to the north, east and west; grassland forms the ground cover at the site and extends to the south. Agriculturally the area is used for pastureland and small grain crops.

Geology

The site lies in Quaternary alluvium from the Holocene and recent times. The underlying geologic structure is the Wellington Formation which was formed about 170 million years ago at the beginning of the Jurassic period. The formation is mostly a fine grained lenticular sandstone and mudstone conglomerate with a maroon to red-brown color. The red-brown color is readily apparent in many of the soils of the watershed and bestows a murky color to the lake.

Hydrogeology

Payne county has a temperate climate characterized by seasonal variations in both temperature and precipitation. Temperatures vary considerably between winter and summer months and occasionally from day to day. The annual mean temperature is 61 degrees F with seasonal means ranging between 40 degrees F during the winter months, 60 degrees F during the spring months, 81 degrees F in the summer months and 62 degrees F during the fall months. The annual mean predipitation is 34 inches with seasonal variations of 41 inches during the winter months, 10 inches during the spring, 11 inches in the summer to 8.5 inches of precipitation during the fall months. The precipitation occurs primarily as localized showers and convective thunderstorms of shortr duration and high intensi8ty during the spring and summer months. Regional storms of longer during affect the region during cooler months, with thunderstorms and showers also occurring during these periods. The maximum or potential evaporation is 61.48 inches measured from April 1 thru October using a Class "A" NOAA evaporation pan (Myers, 1982)

Surface Water--

The study area lies in the Cimmarron River Basin and is drained locally by Stillwater Creek. The major tributaries to the Cimmarron River in this area are Stillwater Creek to the north, Lost Creek to the southwest, Wildhorse Creek to the south, and Clear Creek to the west. All of these tributaries have been classified as intermittent streams.

Lake Carl Blackwell is a man made lake comprising an area of approximately 3000 acres. The lake is fed principally by Stillwater creek which is fed by numerous shallow tributaries. The drainage basin is approximately 100 square miles. The lake is the principal water supply for the City of Stillwater. The storage capacity has been estimated at about 55,000 acre-ft.

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Measurements and samples for water quality analyses are taken from Stillwater creek from March of 1981 to July of the same year. Temperature, conductivity, and total alkalinity in Stillwater creek were slightly greatly than in Lake Carl Blackwell. Temperatures range between 9.5 and 28.1 degrees celcius. The range of pH is 7.8 to 8.6 with the highest values occuring in May as a result of algal blooms. The conductivity of the stream is about 447 mmhos/cm.

Groundwater--

The surficial aquifer below the macropore site consists of brown loamy surface layers and reddish-brown or yellowish-red clay loam or sandy clay loam layers (Howick et al.,1982). Aquifers with such textures generally have hydraulic conductivity values of approximately 10-4 gal/day/ft2.

The average depth to the water table is about five feet at the study site.

The quality of the lake water is good in most respects. Phosphorus or nitrogen do not produce algal blooms or excessive growth of hydrophytes. Concentrations of chlorinated hydrocarbon pesticides (i.e. chlorophenoxy herbicides) and trace elements in the water and in the fish of Lake Carl Blackwell are generally below detectable levels. Bacterial counts are relatively low. Though no chemical quality data is available presently for the surficial aquifer, the dynamic interaction between the lake and the aquifer would indicate similar water types.

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APPENDIX A
QUALITY ASSURANCE

The purpose of this proposed research is to evaluate a methodology for examining and characterizing subsurface samples of soils and sediments. In actuality quality assurance criteria will be one of the products of this research.

We are however making every effort to ensure the technical validity of our results. The methods we are using to do this are listed below.

1. Whenever possible we are acquiring standard mineral samples. We have obtained standard clay minerals from "The Clay Minerals Society" and other standard minerals from the National Bureau of Standards. We use these samples to calibrate our equipment and to ensure that our sample preparation and analysis procedures are adequate.

2. We have tried unsuccessfully to obtain a set of standard (well characterized) soils. As a substitute we purchased a set of soils collected from many parts of the world and are in the process of characterizing them by whatever procedures are available to us, using wherever possible methods different to those we are using for our research.

3. It must be emphasized that all analytical determinations using the FTIR and Raman spectrometers are the result of multiple and not single scans, in fact they may be a composite of up to several thousand scans in the case of the FTIR. In addition, replication of all significant experiments are made using different samples.

4. Chemical analyses made by more or less conventional procedures will all be replicated. Where possible standards or spiked samples will be analysed. Because of the unique nature of the samples being analysed quality assurance other than replication is frequently impossible. For example, the mixing of a standard clay or humic acid with a particular sample is impossible because of the inability to adequately blend them.

5. One of the important results of our research will be the establishment of detection limits for the important constituents of a large number of compositionally diverse subsurface samples using a variety of sophisticated instrumental techniques. In addition we will be documenting during the progress of this research all important interferences observed in the various analytical determinations.

APPENDIX B
DETERMINATION OF SOIL CATION EXCHANGE CAPACITY
(courtesy of Lester Reed, Oklahoma State University

Reagents:

A. Calcium Chloride Dihydrate:

1. Weigh 147.03 grams of reagent grade $CaCl_2$ $2H_2O$ and dissolve in de-ionized distilled water.

2. Dilute with de-ionized distilled water to two liters. This is 1N $CaCl_2$ $2H_2O$.

B. Sodium Nitrate:

1. Weigh 170 grams of reagent grade $NaNO_3$ and dissolve in de-ionized distilled water.

2. Dilute with de-ionized distilled water to two liters. This is 1N $NaNO_3$.

C. Silver Nitrate:

1. Weigh to five places, 1.6989 grams of reagent grad $AgNO_3$ and dissolve in de-ionized distilled water.

2. Dilute with de-ionized distilled water to one liter. (store in an amber bottle and never store in direct sunlight. It is preferable to store in the dark.)

3. Determine the normality of $AgNO_3$ with standard NaCl. This should be 0.01 N $AgNO_3$.

D. pH 10 buffer:

1. Dissolve 10.7 grams of reagent grade NH4LCl in one liter of de-ionized distilled water.

2. Carefully add 166.7 ml of concentrated reagent grade ammonium hydroxide (approximately 15 normal) and dilute the mixture to 2500 ml. This is a pH 10 buffer, pH should be checked with a pH meter.

E. Eriochrome - Black-T Indicator Solution:

1. Dissolve 0.5 grams of Eriochrome-Black-T indicator with 4.5 grams of hydroxylamine hydrochloride in 100 ml of reagent grade methanol.

F. Ethylene Diamine Tetraacetic Acid Disodium-Dihydrogen Salt (EDTA):

1. Dissolve 2 grams of reagent grade EDTA in 900 ml of de-ionized distilled water.

2. Add 0.05 grams of reagent grade $MgCl_2$ $2H_2O$ from a solution containing 10 milligram per milliliter, or 5 ml.

3. Standardize EDTA solution against a 25 ml portion of a standardized calcium solution. This should be approximately 0.01 N. EDTA.

G. Indicator for Mohr titration for chloride with silver nitrate:
1. Weigh 4 grams of K_2CrO_4 (potassium chromate) and dilute to 100 ml with distilled de-ionized water. Use 4 drops for titration of a 10 ml sample. It is advisable to titrate a blank of 10 ml of distilled water and subtract blank reading from sample titration. The titration is from bright yellow to a reddish turbid solution.

Procedure

1. Weigh 10 grams of soil that has been air or oven dried and passed through a 20 mesh sieve into a 200 ml Erlenmeyer Flask.

2. Add 50 ml of 1N $CaCl_2$, stopper and shake intermittenly for 4 hours or longer. (Preferably overnight) (constant shaking is unnecessary)

3. Filter the soil-salt mixture on a 5.5 cm Buchner funnel fitted with a Whatman #42, 5.5 cm filter paper. The funnel is fitted into a side-arm vacuum flask. (The filter paper is wetted and pressed by suction on the flask before adding the sample) (The sample must be added immediately or the soil will leak into the suction flask)

4. Rinse the 200 ml Erlenmeyer flask with three rinses of 50 ml of 1N $CaCl_2$ and gently pour the three 50 ml portions each through the funnel with little or no suction. (Note: It is very important that the $CaCl_2$ solution goes through the sample on the Buchner funnel slowly or even dropwise.) (The vacuum usually needs to be turned on and then turned off and the vacuum in the suction flask will be sufficient)

5. Slowly leach the sample on the Buchner funnel with three 50 ml portions each of de-ionized H_2O (use vacuum constantly if the water goes through too slowly).

6. Discard combined leachate of water and 1N $CaCl_2$.

7. Thoroughly rinse suction flask with distilled water and then leach soil with three washes of 50 ml each of 1N $NaNO_3$, <u>save leachate</u>. (It is imperative to leach slowly.)

8. Remove leachate from the suction flask and dilute with water to 200 ml in a 200 ml volumetric flask.

9. Remove 10 ml of the leachate and place in a 200 ml Erlenmeyer flask and add 10 ml of NH_4Cl - NH_4OH buffer. (This 10 ml sample = 0.5 gm)

10. Next add 8 to 10 drops of Erichrome-Black-T-indicator.

11. Titrate with standardized E.D.T.A. (.0100) to a bright blue end point. Express milliequivalents of calcium per 100 grams of soil. Using an illuminating stir plate helps with determination of end point.

12. Take an additional 10 ml/5 ml or other appropriate sample from the NaNO3 leachate and titrate with the (for chloride) Mohr titration. Express milliequivalents of chloride per 100 grams of soil and subtract from the milliequivalents of calcium per 100 grams as obtained with the E.D.T.A. titration.

Calculations:

1. For Calcium Determination:

$$\frac{\text{ml of E.D.T.A.} \times \text{normality of E.D.T.A.} \times 100}{0.5\ (10\text{ ml sample})} = \text{Milli-equivalent per 100 grams}$$

2. For Chloride Determination:

$$\frac{\text{ml of AgNO3} \times \text{normality of AgNO3} \times 100}{0.5\ (10\text{ ml sample})} = \text{Milli-equivalent of Chloride/100 gms}$$

3. Cation Exchange Capacity:

Milliequivalents of Calcium/100 gms - (minus) milliequivalents of Chloride/100 gms = Cation Exchange capacity (CEC) /100 gms.

APPENDIX C

DETERMINATION OF PERCENT ORGANIC MATTER

(courtesy of Lester Reed, Oklahoma State University)

Reagents:

A. Potassium Chromate:

1. Weigh 19.164 grams of reagent grade K2Cr207 and dissolve in de-ionized distilled water.

2. Dilute with de-ionized distilled water to one liter in a volumetric flask. This should be 0.4 N K2Cr207.

B. Ferrous Ammonium Sulfate:

1. Weigh 78.44 grams of reagent grade Fe (NH4)2(S04)2 and dissolve in de-ionized distilled water.

2. Add 20 ml of H2S04 and dilute with de-ionized distilled water to one liter in a volumetric flask. This should be a .2N solution.

C. Orthophenan throline:

1. Weigh 1.485 grams of o-phenanthroline and 0.695 grams of reagent grade Fe2S04 and dissolve in de-ionized distilled water.

2. Dilute with de-ionized distilled water to 100 ml in a volumetric flask.

Procedure:

1. Grind soils to approximately 60 mesh.

2. Weigh 0.5 grams of air-dried soil into a 250 ml beaker.

3. Add 10 ml of 0.4N Potassium Dichromate.

4. Add 15 ml of concentrated H2S04.

5. Slowly heat on a hot plate to 161oC while slowly stirring.

6. Remove beaker, cool and wash thermometer and the inside of beaker with water.

7. Add 100 to 125 ml of distilled water, 2 drops of orthophenanthroline and titrate excess dichromate with a 0.2N Fe(NH4)2 (S04)2 solution. Solution should turn red at endpoint.

8. Carry 10 ml of the 0.4N K2Cr207 solution through the same procedure except that no soil is added.

DRAFT ONLY

Calculations:

1. For present organic carbon determination:

$$\text{TOC} = \frac{(\text{Blank Reading}-\text{Reading}) \times (.00336) \times (100) \times \text{N.FAS}}{\text{Weight of soil}}$$

2. For percent organic matter determination:

$$\text{POM} = \text{TOC} \times (1.72)$$

or

$$\text{POM} = (\text{Blank Reading} - \text{Reading}) \times (1.156)$$

DRAFT ONLY

APPENDIX D
DETERMINATION OF PERCENT ORGANIC MATTER
(courtesy of the Agronomic Services Lab,
Oklahoma State University)

Reagents:

A. Potassium Dichromate:

1. Weigh 49.04 grams of reagent grade K2Cr2O7 and dissolve in de-ionized distilled water.

2. Dilute with de-ionized distilled water to one liter in a volumetric flask. This should be a 1.0N solution.

B. Barium Diphenylamine Sulfonate:

1. Heat BDS for 30 minutes at low heat in an oven and then place in a desicator for 30 minutes.

2. Weigh 1.60 grams of reagent grade BDS and place in a one liter volumetric flask.

3. Dilute with de-ionized distilled water to one liter adding water at 200 ml intervals.

C. Phosphoric Acid:

1. Use reagent grade, concentrated H3PO4.

D. Ferrous Sulfate:

1. Weigh 278.0 grams of reagent grade Fe(SO4) and add de-ionized distilled water. Then add 15 ml reagent grade H2SO4.

2. Dilute with de-ionized distilled water in a one liter volumetric flask. This should be a 1N solution.

Procedure:

1. Pour a one gram soil sample into a 250 ml Erlenmeyer flask.

2. Add 10 ml of K2Cr2O7.

3. Add 10 ml concentrated H2SO4 and shake mixture.

4. Cool for 45 minutes, then add 5 ml concentrated Phosphoric Acid and 50 ml of de-ionized distilled water.

5. Add 10 drops of BDS indicator.

6. Titrate to green color with Fe (SO4).

7. Run three blanks through the above procedure.

Calculations:

For percent organic matter determination:

$$POM = 0.69\left(\frac{Blank1 + Blank2 + Blank3}{3} - Sample\right)$$

Appendix E
Procedure for Exchangeable Cations in Soil
(courtesy of Lester Reed, Oklahoma State University)

Solutions

1. Ammonium acetate - pH 7 (Neutral), 1 Normal
   - Weigh 77.08 grams of Reagent Grade ammonium acetate
   - Weighed ammonium acetate into a 400 ml beaker and dissolve with distilled water
   - Dissolve and dilute to 1 liter volumetric flask with distilled water
   - Check solution for a pH 7 with a pH meter

**This solution is dangerous: care should be taken when pouring and never mouth pipetted.

<u>Procedures</u>:

1. Weigh 10 grams of 20 mesh dried soil on a sensitive quantitative balance
2. Pour weighed soil sample into a 200-250 ml Erlenmeyer
3. Measure 50 ml of Neutral (pH 7) 1N ammonium acetate in a volumetric flask---pour into the Erlenmeyer containing the soil
4. Stopper and shake occasionally for 4 hours (Preferably overnight)
5. Then pour onto a 5.5 cm Buchner funnel fitted with a #2 Whatman filter paper, (it should be wetted and firmed on the funnel by suction). Use a 500 ml filtering flask. Momentarily pull suction
6. The ammonium acetate extracting solution should come through the Buchner funnel <u>dropwise</u>, <u>not</u> as a continuous stream
7. Before all of the solution has run through the Buchner funnel <u>add</u> an additional 50 ml of ammonium acetate solution (measured in a volumetric flask). Pour the measured solution into the 200-250 ml Erlenmeyer, rinse then pour into the Buchner funnel
8. Add two additional 50 ml portions of ammonium acetate for a total of 200 ml. Use each of the 50 ml portions for rinsing or washing the 200-250 ml Erlenmeyer flask.
9. When the entire 200 ml of ammonium acetate solution has been leached through the soil sample, rinse with distilled water the 200-250 ml Erlenmeyer sample flask.

10. Pour the leachate from the suction flask into the rinsed sample flask and stopper

11. Save leachate for elemental analysis by A.A.

APPENDIX F
DETERMINATION OF TRACE ELEMENT CONCENTRATION
(from Baker-Blocker, et al., 1975)

Reagents:

A. Hydrochloric Acid:
   1. Create a 10% HC1 solution

B. Hydrogen Peroxide:
   1. Create a 30% H202 solution

Procedure:

1. Weigh 1 gram of soil and place in a 250 ml Pyrex beaker.
2. Add 50 ml of HC1 and 5 ml of H202.
3. Heat for 8 hours at 80oC.
4. Add 5 ml H202 and heat for 8 more hours at 80oC.
5. Add 5 ml H202 and heat for 8 more hours at 80oC allowing solution to boil down to 15 ml.
6. Centrifuge sample in a 50 ml centrifuge tube at 1750 rpm for 10 minutes.
7. Decant the supernatant.
8. Rewash and centrifuge sample with HC1 until there is 50 ml of solution.
9. Save solution for analysis on the A.A. spectrophotometer.

APPENDIX G
QUANTITATIVE X-RAY DIFFRACTION

The method we use for quantitative x-ray diffraction analysis is the one developed by Hooton and Giorgetta which is based on the assumption that all components are identifiable and are to be analysed for. This method avoids the use of internal standards, calibration curves, and mass absorption coefficient measurements.

The x-ray diffraction trace of any sample is unique to that sample composition therefore it should be possible, at least in principle, to determine the composition from the trace along without adding standards. Hooton and Giorgetta (1977) altered Klung's basic equation to achieve this goal.

The equation is: Ii = (Ki.Wi) / (pi. ui.Wi) (1)

Ii = intensity of diffraction pattern of component i;
Ki = a constant depending on the nature of the component and the geometry of the apparatus;
Wi = Weight fraction of component is in the sample;
pi = density of component i;
ui = mass absorbiton of coefficient of component i;
um = mass absorbtion coefficient of the whole sample.

Solving for Wi we have Wi = (pi.Ii.um)/Ki (2)

In equation (2), Wi is the unknown to be determined, pi is known, Ii can be measured, for any component i. The unknowns um and Ki must be determined. Since pi and Ki are both constants for any mineral (in a given instrument configuration), they are combined and represented by a single symbol.

When this substitution is made Hi = pi/Ki,

Wi = Hi.Ii.um (3)

Assuming that Hi, a constant, can be determined for each mineral, and that the sum of the weight fractions is equal to 100%k it is possible to determine weight fractions of individual components, without references to calibration, curves and mixing standards.

One disadvantage in that (H) may have to be determined for some of the components in the sample. If this is the case only the relative amounts of the components for which H is known can be caluclated directly. This problem is alleviated by a procedure similar to the internal standard method. Any mineral for which H is known, and which is not already in the sample, can be added in a known proportion to act as a standard. Each mineral can then be dtermined by comparison with the standard, using Eqn (3) as follows:

Wi = Hi.Ii.um component 1
Ws = Hs.Is.um (Standard)

Dividing:

W1/Ws = (H1.I1)/(Hs.Is)

or W1 = (Ws.H1.I1)/(Hs.Is)

Recalculating W1 to correct for the presence of the standard in the sample:

$$W1 \text{ (original)} = W1.(1-Ws)$$

This gives absolute weight fractions for those components for which H is known.

Determination of H

H is only constant for a mineral in an instrument with a given configuration and with a constant Beam intensity. However, relative values of H for different minerals do not change, this is why EQ(3) must use ration of H rather than absolute values.

An easy method to determine relative values of H is to select one mineral as a reference standard, assign a value to H for that mineral, and determine H for all other minerals by mixing them in known proportion with the standard and using the following equations:

$$Wr = Hr.Ir.um \quad \text{(reference standard)}$$
$$W1 = H1.I1.um \quad \text{(component 1)}$$

Dividing:

$$Wr/W1 = (Hr.Ir)/(H1.I1)$$

or

$$H1 = (W1.Ir.Hr)/(Wr.I1)$$

W1 AND Wr are known, Ir and I1 can be measured from the diffraction trace and Hr is assigned a value (i.e. 1). This gives a value for H1 from a single run, although an average of multiple determinations may improve the results.