THE SPATIAL VARIATION OF SEVERAL HYDROGEOCHEMICAL PARAMETERS WITHIN THE APPLE CREEK DRAINAGE BASIN, NORTH DAKOTA

By

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PREFACE

The aerial and vertical variation of soil organic matter (SOM) was determined within the Apple Creek basin, North Dakota. SOM is a primary constituent of soils responsible for the adsorption of organic chemicals. Contour maps of predicted SOM values were produced by horizon and were used to generate a general SOM map which can be used in land-use decisions.

Several problems were encountered during the analytical phase of the study. Refining the SOM procedure resulted in 'starting from scratch' numerous times. Initially, an ammonium electrode was being used to determine CEC. When we could not stabilize the readings, we contacted the electrode manufacturer, Orion, who told us that they have had problems only with Dakota soils. For a while, the headaches involved seemed to outweigh the apparent benefits of the study. It is appropriate at this point to thank my friends who kept me smiling (and working) when things looked dismal.

I would like to thank Dr. Arthur W. Hounslow for acting as my thesis advisor and for providing the initial premise for my thesis and guidance throughout the study. Dr. Hounslow was especially helpful with chemistry related problems. Dr. Wayne A. Pettyjohn and Dr. Douglas C. Kent also deserve my appreciation for serving as committee members. Dr. Pettyjohn was instrumental in initiating activities in North Dakota. He also served as my primary hydrogeologic consultant throughout the project. Dr. Kent suggested excellent ideas for presentation of material contained herein. He also detailed the implications and potential uses of the maps generated. This project would not have been possible without funding from the U.S. Environmental Protection Agency's Robert S. Kerr Environmental Research Laboratory.

Without the help of Cindy Patterson and Tom Acre, my field work would have been unbearable. Ray Powers coordinated and modified many of the analytical procedures, and he provided a 'scientific approach' which I certainly benefitted from. Kathy McBride and Dr. Ronald McNew, professor of statistics, guided me through the extensive SAS procedures used in the interpretive stages of my thesis. Milton Lindvig, Director of the Hydrology Division of the North Dakota State Water Conservation Commission, helped considerably in organizing the drilling activities during the summer of 1983, and he provided me with an invaluable insight into the region during both field excursions. I express my thanks to Roger W. Schmid and Lewis Knutson of Water Supply, Inc., in Bismarck, North Dakota, for extracting the Williams loam core. Roger Cosby of the USEPA R. S. Kerr Environmental Research Laboratory was extremely patient in helping with the SOM combustion procedure.

Often overlooked are those people who support daily activities. Without them, however, research could never be accomplished. In particular I would like to thank Talya Henderson and Romona Bissell who 'pulled through in the clutch' for me innumerable times. Gayle Maxwell of the OSU cartographic service did an excellent job on many of the enclosed figures. The people at the OSU's motorpool are to be congratulated for keeping their vehicles in excellent shape and for providing helpful service.

The collection of data and analysis was largely a collective effort and the credit (or blame) should be distributed among those involved. The interpretations are my own, however, so I do deserve to have my name on the cover.

Although the research described in this thesis has been funded wholly by the United States Environmental Protection Agency through grant OU6931-15 to Arthur W. Hounslow, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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CHAPTER I

INTRODUCTION

Reason for Study

Organic chemicals in the subsurface are finally being treated as a serious threat to clean soil and potable water as the number of contaminated sites increases. It is becoming increasingly evident that the constituents and parameters which affect pollutant movement and attenuation must be quantified. This is required as a predictive as well as a remedial measure.

Adsorption of organic chemicals on soil constituents is recognized as a major factor in the attenuation of these contaminants in soils. The assumption that soil organic matter and clay minerals are primary adsorbing agents in the unsaturated zone is supported by recent literature. Little is known, however, of the aerial and vertical distribution of these constituents within the soil column.

The study area was selected for several important reasons. An agricultural soil was desired that was fairly loamy and contained a significant percentage of soil organic matter. The Apple Creek basin was chosen because the area represents glaciated terrain which is common to most of the northern United States. The Williams loam soil was chosen because it covers the largest area within the Apple Creek watershed. A second reason is that the Mollisol soil order, of which the Williams loam is a member, covers most of the Great Plains region. The area is well divided by section roads allowing easy access to all parts of the basin. Permission to enter an undisturbed site for soil coring was easily obtained.

Preliminary field work regarding the geology, soils and water resources of the area was unnecessary as the region is well documented in the literature. A surface water control point (sponsored by the USGS) exists near the mouth of Apple Creek where discharge and water quality data are available.

Objective

The objective of this thesis is to examine the aerial and vertical variations and importance of certain hydrogeochemical parameters (i.e. those that are responsible for the attenuation of certain organic chemicals in the subsurface) within the Apple Creek drainage basin, North Dakota. The final goal of this study is to target those areas which will be more susceptible to ground water contamination based on several confining conditions. It should be recognized immediately that this report is just the first stage in quantifying the physical and chemical parameters responsible for the adsorption of organic chemicals.

Scope

Statistical sampling designs have been used extensively by geochemists in mineral exploration, but their use in hydrogeochemical studies is rare. The basic methods of sampling have been applied to the Apple Creek basin. Data concerning the geography, geology and hydrogeology of the Apple Creek watershed were taken from published sources. Analytical methods were also taken primarily from published material; however, minor variations were made when necessary.

All of the samples were collected during the two field expeditions which occurred in the summers of 1983 and 1984 and will be referred to as phase one and phase two, respectively. The variation of analytical values obtained from phase-one formed the basis of sampling during phase-two. A single core to a depth of 15.5 feet was extracted from the unsaturated zone during phase-one.

Analysis of hand-collected specimens from phase-one consisted of percent organic matter determinations and bulk x-ray diffraction analyses. The core samples were analyzed for percent organic matter and trace element concentration.

Phase-two included a more detailed approach to sampling. A twofold soil collection method was pursued in that both regional and localized sampling schemes were set up. The A, B and C soil horizons were sampled at each site.

The phase-two soil samples were all analyzed for organic matter content, exchangeable acids, exchangeable bases, and cation exchange capacity. In addition, clay extractions were done on some of the regional samples to determine clay type, or clay quantity variation within the basin.

All of the raw data were statistically analyzed using the Statistical Analysis System (SAS). Three programs were used extensively to (1) characterize the normality of the data distributions, (2) generate linear regressions between different parameters, and (3) determine correlation coefficients indicating interrelationships of parameters and constituents.

CHAPTER II

REVIEW OF LITERATURE

Soil Organic Matter / Organic Chemical Interactions

An excellent summary of organic chemical - SOM interactions is included in Hounslow (1983) as well as Hounslow et al. (1984). The author of this study has completed a first hand analysis of the original articles referenced in the aforementioned summaries. Additional pertinent references have also been included.

The idea that soil organic matter was partially responsible for adsorption of organic chemicals in soils was first noticed in the field of agriculture. Loustalot et al. (1953) recognized that the organic chemical 3(p-Chlorophenyl)-1,1 dimethylurea retained its toxicity longer in sandier soils than in heavier, clayey soils. The implication was made that the organic and inorganic constituents (clay minerals) in the heavier soils hastened decomposition, though no experimental evidence was produced at this time. Sherburne and Freed (1954) followed this report with a study which distinctly related adsorption to organic matter content. Clays were also noticed as being related to adsorption though their correlation coefficients did not imply as clear a relationship. Harris (1964) noted that soil organic matter is the primary constituent involved in adsorption in moist soils, whereas inorganic minerals, including clays, are more active in adsorption in dry soils. Bailey and White (1964) gave a summary of adsorption on soil constituents which included the effects of soil organic matter, clays, and amorphous hydroxides.

Four proposals for possible mechanisms involved in adsorption were summarized by Khan (1978). These included Van der Waals forces, hydrophobic bonding, hydrogen bonding, and charge transfer. He also quoted earlier works as saying that at organic matter contents higher than 6%, most adsorption will occur on organic surfaces.

The distribution coefficient, Kd, is the most common measure of partitioning between the solid phase (by adsorption) and the liquid phase (pure solute, or in solution). Though Freeze et al. (1979) and Fetter (1980) treat adsorption as occurring on all solid surfaces, Drever (1982) considers adsorption as an ion exchange process affecting only clay minerals. Soil organic matter has the effect of increasing the concentration of adsorbed solute while increasing Kd values (Rao et al., 1979). The retardation factor, Rd, as described by Freeze et al. (1979), would likewise increase in proportion to the SOM content. Attenuation of certain organic chemicals is thus directly related to SOM content.

Apple Creek Basin, North Dakota

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 in the description of climate, groundwater, and surface water. Surface water statistics were also obtained from USGS (1980).

The soils section was derived from Aandahl (1982) and the Soil Conservation Service's Soil Survey of Burleigh County, North Dakota. The data concerning vegetation were also taken from these two sources. Most of the figures are from the North Dakota Geological Survey's Bulletin 42. The remaining figures were found in the Oklahoma State University map room.

Geochemical Sampling

Journals covering exploration geochemistry of primarily minerals were consulted for the 'state-of-the-art' in sampling designs. Only in the most recent publications have sampling techniques been treated in the context of hydrogeology. Mason (1983) noted four sampling methodologies. These are simple random, stratified random, systematic, and judgmental.

'Simple random sampling is the basis for all probability sampling techniques . . . and serves as a reference point from which modifications . . . are evaluated (Mason, 1983, p. 2).' Most of the theoretical sampling literature revolves around simple random techniques. The basic concepts of sampling were also derived from this method. A summary of these concepts is included below.

Miesch (1967) pointed out the difference between target population, which is 'the population of interest', and sampled population, which is 'the population that can be sampled.' This distinction arises from 'the fact that some potential specimens cannot be obtained.' So that the sampled population is representative of the target population, hierarchical sampling designs were proposed by Krumbein and Slack (1956), Miesch (1967,1976), Tourtelot and Miesch (1975), and Klusman (1979), among others. In this manner, the total error could be characterized at the different levels of sampling. Sampling constants and equations have been proposed by Ingamells and Switzer (1973), Visman (1969,1972), Duncan (1971), and Ingamells (1974a,1974b).

Stratified random sampling entails breaking up the target population into several strata which independently 'are more homogeneous than the total population (Mason, 1983).' Each stratum is then sampled by simple random methods. Krumbein and Slack (1956) also treat the topic of stratification.

Systematic sampling involves randomly superimposing a grid over the area of interest and sampling at each node. Judgmental sampling is a fourth method which tries to concentrate on specific areas of interest. Often, a bias is introduced which can be partially compensated for by replicate analyses.

Many variations exist within these four basic frameworks. Miesch (1967) proposed the term 'sampling locality' which is defined as a part of the target population larger than a single specimen. This method is usually employed in a hierarchical analysis. The variation between locality means is determined in this manner. Visman (1969) described the 'sampling by increments' method whereby a series of small samples are combined into a 'gross sample'.

Several terms which evaluate the validity of geochemical data are noted by Miesch (1967,1976). 'Accuracy...implies close agreement between the average of a large number of estimates and the correct value (Miesch, 1967).' The difference is called bias. 'Precision implies reproducibility, or close agreement among replicate estimates (Miesch, 1967).'

Resolution and stability are used to describe geochemical map characteristics. 'The resolution of a geochemical map is determined by the spacing between the centers of the sampling localities (Miesch, 1976).' In general, resolution is forfeited for increased stability.

'The variability among the sampling locality means and the confidence intervals, the degree to which the means are known, determines the geochemical map stability (Miesch, 1976).'

CHAPTER III

METHODS AND PROCEDURES

Geochemical Sampling

Statistical sampling generally requires at least two sampling periods. This is particularly important when utilizing a random sampling scheme as the variation determined from initial sampling allows for more representative sampling during secondary sampling. Phase one of the Apple Creek study was primarily a scouting expedition to sample several soil types and to determine access to different parts of the basin. Phase one sampling did not involve a preplanned sampling design other than to try to equally distribute sites throughout the drainage basin. Based on practical considerations determined from phase one sampling and consultation with Ronald W. McNew, Professor of statistics at Oklahoma State University, a stratified systematic sampling network was designed for phase two.

As a result of the large area of interest, fifty-eight 'sampling localities' were set up on a regional scale. Each sampling locality represents approximately a nine square mile area (9 sections). At the local scale, two, five-by-five plots with spacings of one foot and 50 feet were randomly superimposed on a Williams loam outcrop.

Regional sampling was done using a method introduced by Visman (1969). 'Sampling by increments' is where a series of small samples is combined into a 'gross sample'. In the Apple Creek basin study, all of the exposures of the Williams loam, undulating type, and Parshall - Lihen fine sandy loam (SCS, 1974), were determined along the network of section roads. Each site was located by randomly choosing a direction and moving along that orientation to a point where influences from road construction and farming activities were minimal. Each soil site was sampled at the A, B, and C horizons and placed in a plastic bag of that particular sampling locality. As a result, each sample is a combination of generally three or more sampling sites. In this manner, resolution is sacrificed to obtain greater stability as described by Miesch (1976).

Local surveys were taken where drilling activities occurred during phase one. An exposure of the Williams loam in an area of approximately 500 feet by 600 feet was outlined. A 'buffer zone' was excluded from consideration which consisted of a 100 feet wide ring within the aforementioned area. As a result, a 300 feet by 400 feet area was made eligible for sampling. The stratified systematic sampling grid (five-by-five, 50 feet spacing) was superimposed on the area of interest by randomly selecting the coordinate for the central node within the 300 feet by

400 feet area. The orientation of the grid was arbitrarily chosen to be parallel to the soil boundaries. A smaller stratified systematic grid (five by five, one foot spacing) was randomly located with its central node being one of the 50 feet spacing sample sites in order to minimize sampling and analytical time.

Analytical Methods

It should be noted that only certain chemical characteristics of soils were determined during the course of this study. Analyses of physical parameters (ie. porosity, permeability, bulk density) is beyond the scope of this project.

Percent Organic Matter

SOM content is most often determined by multiplying total organic carbon (TOC) values by the factor 1.724. This 'Van Bemmelen' factor (Allison, 1965) arises from the assumption that 58% of SOM is composed of organic carbon. Several procedures for determining TOC have evolved which can be classified as either redox or combustion reactions.

Combustion procedures have developed as somewhat 'standard' methods which utilize expensive hardware such as the popular LECO total organic carbon (TOC) analyzer. The advantage of the combustion methods is that all of the SOM is burned off. These methods generally purge inorganic carbon from solution and distinguish between dissolved (DOC) and suspended (SOC) organic carbon.

Redox-type TOC methods use either potassium or sodium dichromate to oxidize SOM. At this point, either the unreduced chromate complex is quantified by titration via the Walkley-Black method (Allison, 1965), or the reduced chromate is quantified by colorimetric techniques (Metson et al., 1979). An additional factor, 'f', is often introduced to account for the unoxidized organic matter. This factor is included so that values from redox and combustion methods are comparable (Allison, 1965).

Three samples were run on the LECO TOC analyzer at the Robert S. Kerr Environmental Research Laboratory (RSKERL) under the supervision of Roger Cosby. These samples represented high, medium, and low SOM contents. A linear regression was calculated between the LECO and redox results which was used to calibrate subsequent redox determinations.

The LECO method required a 1.0 g, air-dried sample. This was placed in a porous crucible and leached with 12 mls of 5% hydrochloric acid in a beaker and allowed to soak overnight. Suction was then applied to the crucible and 25 mls of deionized water were leached through (This leachate was saved for DOC analysis on a Beckman Model 915 TOC analyzer after purging the inorganic carbon dioxide with nitrogen gas). The crucibles were then oven dried at 105 degrees celcius overnight. Copper and iron accelerator chips were added to the crucibles prior to analysis on the LECO WR-12 carbon determinator, Model 761-100.

The modified Walkley-Black method involved mixing a 1.0 g sample with 30 mls of concentrated sulfuric acid and 10 mls of sodium dichromate. Deionized water was added to just below the 200 ml mark, and the solution was allowed to sit overnight. Dilution with water volumetrically to 200 mls was followed by centrifugation at 4000 rpm for five minutes. The supernatent was analyzed for optical density at a wavelength of 600 nm, which is characteristic of the reduced chromate ion, on a Bausch & Lomb Spectronic 21 spectrophotometer.

Cation Exchange Capacity (CEC)

This is a measure of the number of negatively charged sites on clay minerals and soil organic matter to which positively charged ions are attracted. The CEC is a function of pH, soil texture, quantity of SOM, and types and amounts of clays. A lowering of pH generally is followed by a decrease in CEC. The hydrogen ions bond to the negatively charged sites and are only mildly subject to cation exchange (Brady, 1974).

The method that is developing as a standard for CEC measurements utilizes an ammonium electrode (Busenberg et al., 1973). This procedure was attempted, but wetting of the electrode membrane led to the mixing of the electrode and sample solutions causing erroneous values. As a result, CEC was calculated by summation of the exchangeable bases (Ca, Mg, K, Na) and acids (H, Al).

The method for determining exchangeable bases was taken from Chapman (1965). A 0.20 g sample was allowed to soak overnight in 25 mls of 1.0 N ammonium acetate. The sample was then filtered and the soil was leached with three subsequent 25 ml aliquots of the extracting solution. The leachate was diluted to 100 mls volumetrically with 1.0 N ammonium acetate including 3.0 mls of a 35% lanthanum chloride solution in deionized water. The exchangeable bases were determined using a Perkin Elmer Model 403 atomic absorption spectrophotometer.

Exchange acidity was determined by a procedure based on that described in Peech (1965). A 4.0 g sample was allowed to sit in 25 mls of extracting solution overnight followed by filtering and three subsequent 25 ml washings with extracting solution. After diluting volumetrically to 100 mls, five drops of indicator solution were added and the sample solution was titrated with 0.8 N hydrochloric acid, using a Hach digital titrator, to a pink end point. The extracting solution was made by dissolving 1100 g of barium chloride, 500 mls of 2 N triethanolamine and 72 mls of 6 N hydrochloric acid in deionized water and diluting to 18 liters. The indicator solution was composed of 0.22 g of bromocresol green and 0.075 g of methyl red in 96 mls of 95% ethanol containing 3.5 mls of 0.1 N sodium hydroxide.

Clay Analysis

Clay extractions were completed by mixing a 20.0 g sample in 500 mls of a deflocculating solution (3 g calgon per liter of deionized water) which was placed in an ultrasonic bath for five minutes then allowed to sit overnight. This solution was then placed in a 1000 ml graduated cylinder and filled to the 1000 ml mark with the calgon solution. After a period of 17 hours, the top 700 mls were siphoned off. Several drops of the clay extract solutions were placed on porcelain plates and allowed to dry under a heat lamp. These were then kept for x-ray diffraction analysis. In some cases, the samples were heated for one hour at 500 degrees celcius, or they were glycolated overnight at 25 degrees to help distinguish various clay peaks.

Quality Assurance

The quality of scientific research is based entirely on care exercised during data generation. This includes sampling, analysis, and interpretation of data. Reproducibility of results is the most common measure of the quality of research. This area is most often called quality assurance.

Sample Precision

Since little is known about the distribution of constituents involved in adsorption, a three tier sampling scheme was designed for the Apple Creek basin study. A regional study was conducted with poor resolution but high stability to establish background trends. Two local studies with higher resolutions (one foot, 50 feet) were also conducted to determine at what spacing an actual trend begins to occur. These local studies also lend validity to the distribution of values encountered at the regional scale.

Generally, at least 25% of the samples were run as duplicates to test sample precision. A guideline of 10% sample error was allowed between duplicates. When this cutoff was exceeded, additional replicates were run to establish an accurate mean for the sample. This was only required for phase one samples.

Analytical Precision

When separate aliquots from the same sample were analyzed to determine analytical precision, invariably the same value was obtained. This pertains to optical density readings for the SOM procedure and absorbance readings for the atomic absorption spectrophotometer used in the analysis of exchangeable bases. As titration was used in the determination of exchangeable acids (EA), this test of analytical precision could not be applied (The EA content was near detection limits so dividing the extractant into multiple aliquots would reduce analytical accuracy).

Optical density measurements for the SOM samples were taken relative to a sucrose standard of known carbon concentration; thus analytical accuracy was insured. In addition, these redox values were applied to a linear regression established between the redox method (Sodium dichromate) and a LECO combustion procedure (as described in the analytical methods section). As a result, the arbitrary 'f' factor accounting for the unoxidized organic matter was eliminated.

Another undesireable trait that has been attributed to the redox procedure for SOM determination is the effect of carbonates and oxidizable minerals. By adding sulfuric acid to the soil before the dichromate solution, inorganic forms of carbon are driven off as carbon dioxide. The acid also oxidizes those minerals that would otherwise be oxidized by the chromate ion. In order to dismiss the idea of interference by carbonates, sucrose standard solutions were spiked with sodium carbonate. A stock solution containing 100 mg/ml of sodium carbonate in deionized water was added to the 'standard series' of sucrose standards at several volumes. The control series represented five solutions with sucrose contents of 0.0 mg, 20.92 mg, 41.94 mg, 62.91 mg, and 83.88 mg. These were all sulfuric acid - sodium dichromate - deionized water solutions. The three test series used the same solutions except that the sodium carbonate stock solution was added in volumes of 0.1 ml, 0.3 ml, and 0.6 ml, respectively. The resultant optical density readings were fed into the LECO - redox linear regression program to determine if the slope of the relationship changed. The results are listed in Table 1.

Comparison of the slopes and intercepts indicates no significant trends as the carbonate concentration increases.

TABLE I

EFFECTS OF CARBONATE SPIKED SUCROSE STANDARD SOLUTIONS

Series Name	Volume of 100 mg/ml Sodium Carbonate Added Per Sample	LECO-Redox Linear Regression Parameters	
		Slope	Intercept
Control	0.0 ml	.0125	.0126
Test #1	0.1 ml	.0120	.0124
Test #2	0.3 ml	.0116	.0242
Test #3	0.4 ml	.0117	.0206

Statistical Reduction of Data

Most of the data generated during this study were run through various statistical programs contained within the Statistical Analysis System (SAS) available on Oklahoma State University's mainframe computer. The actual equations which are used in SAS programs can be found in SAS manuals and are beyond the scope of this section. Each program used in the Apple Creek study is described qualitatively below. The actual program statements are listed in Appendixes A through C.

Gaussian Statistics

All of the data collected were tested for normality by the program PROC UNIVARIATE. The Shapiro-Wilk statistic, W, is computed within the range zero and one. As W approaches a value of one, the null hypothesis (stating that the data is normally distributed) is verified (SAS, 1982).

The mean, standard deviation, variance and other statistics were obtained by applying the program PROC UNIVARIATE. An analysis of variance is particularly important when comparing data from different soil types and resolutions.

Interrelationships

Correlation coefficients and linear regressions were determined using the SAS programs PROC CORR and PROC GLM, respectively. Most of the relationships tested were known to exist (i.e. CEC vs. exchangeable cations), but they were verified by these programs.

'Correlation analysis is used to measure the strength of the relationship between two variables (SAS, 1982).' A positive correlation coefficient implies a direct relationship whereas a negative coefficient indicates inverse proportionality. The program PROC GLM tests for linear relationships also, but it is especially helpful in pointing out regional trends.

Sample Error

Error between duplicate analyses can be examined by a standard deviation, or variance, of cumulative errors. The standard deviation is equal to the square root of the ratio of the sum of the squared differences between duplicates divided by twice the number of duplicates (personal communication, Arthur W. Hounslow, 9/12/84). The variance is the square of the standard deviation.

CHAPTER IV

REGIONAL CHARACTERISTICS

Geography

The Apple Creek basin study area lies within the boundaries of Burleigh County in south central North Dakota (Figure 1). It is confined within the ranges of 76-80 west and the townships 137-142 north. The total area of the watershed, however, is 1680 square miles and extends into McLean, Kidder, and Emmons counties.

Physiography and Topography

Apple Creek falls into two physiographic districts (Figure 2). 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 (Figure 3) of the Great Plains Province within the Interior Plains Major Division (Kume et al., 1965).

Stream eroded bedrock covered by sheet moraine is

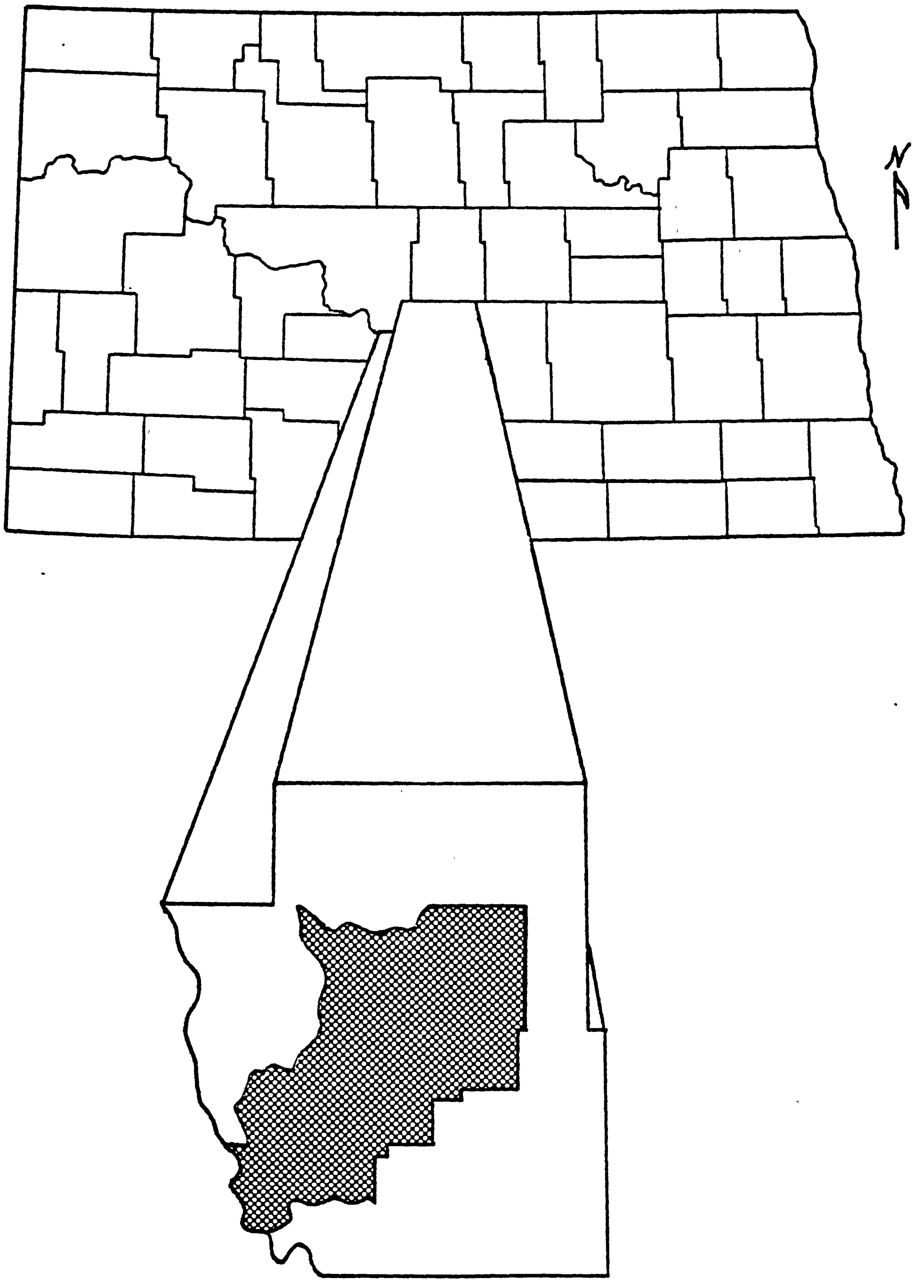
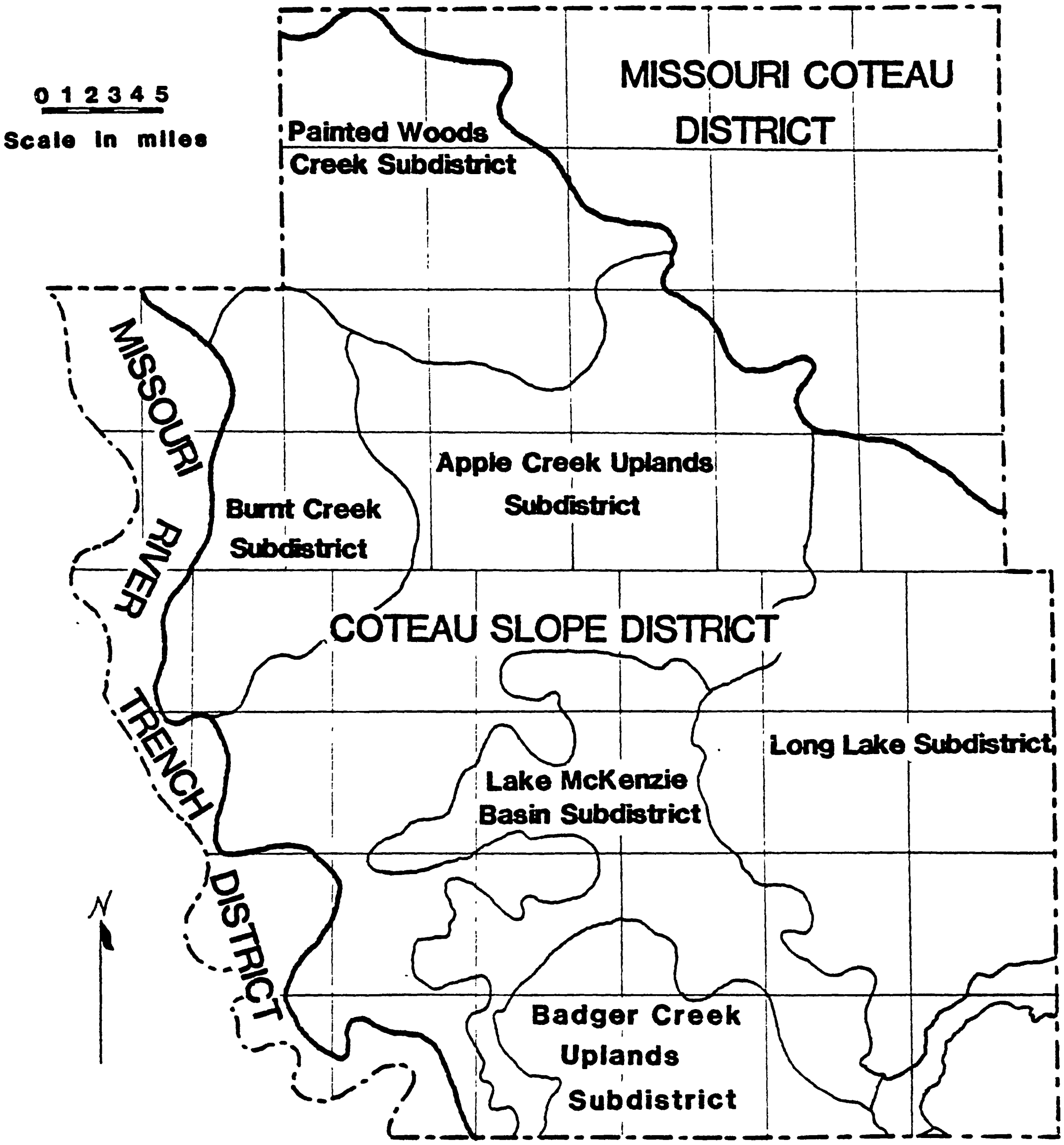
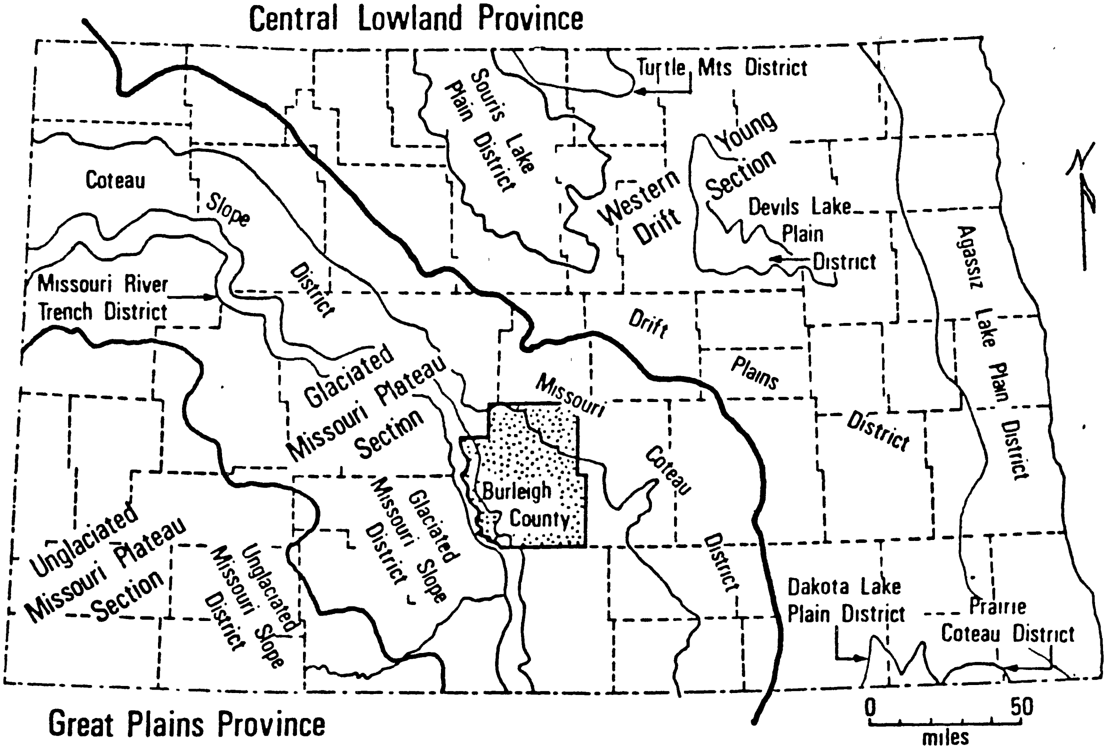


Figure 1. Location Map Showing the Study Area Within Burleigh County, North Dakota



Source: Kume, J., and Hansen, D. E., 1965.

Figure 2. Map of the Physiographic Subdivisions of the Coteau Slope District in Burleigh County, North Dakota



Source: Kume, J., and Hansen, D. E., 1965.

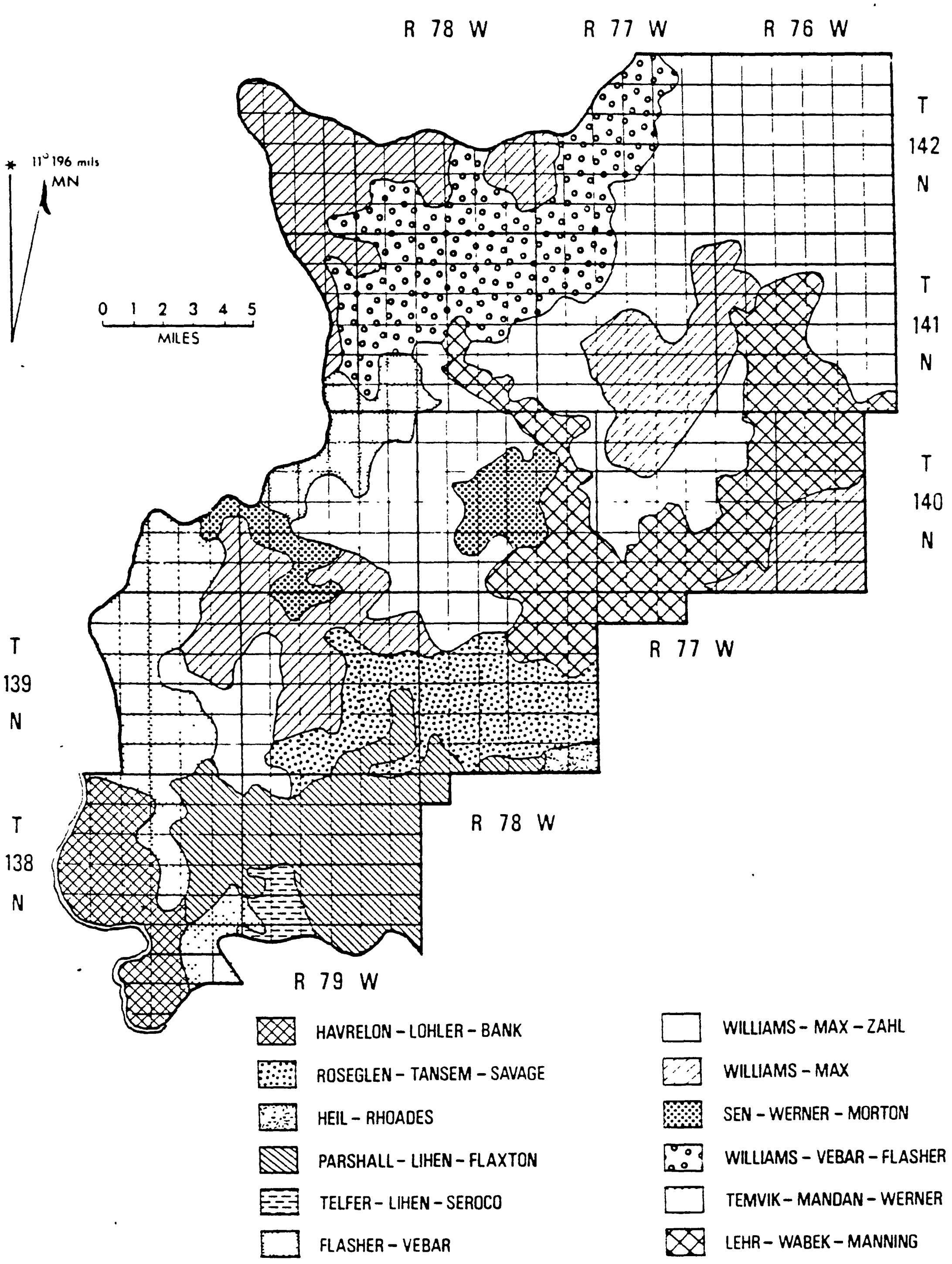
Figure 3. Physiographic Map of North Dakota

characteristic of the Apple Creek Uplands subdistrict. The overall hummocky topography is only disturbed by isolated bedrock buttes. Drainage is well integrated, and the glacial drift is thin in the north (less than ten feet) becoming more 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 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 meanders are well developed as a result.

Soils

The Soil Conservation Service divided the Apple Creek basin into four major soil associations (Figure 4). 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. Lehr-Wabek-Manning soils exist in the upper creek region just below the headwaters. Slopes are variable as are soil textures. At the Random Creek conjunction, Roseglen-Tansem-Savage soils are prevalent. These well drained, medium textured soils occur on level to slightly rolling terrain.



Source: Soil Conservation Service, 1974.

Figure 4. General Soil Association Map Within the Apple Creek Study Area

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

The Williams series of soils are by far the most aerially extensive soil types. The Williams loam (undulating type) covers 20.7 percent of the county. 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 in terms of drawing conclusions at the basinal scale.

The Williams loam developed on undulating glacial till plains of primarily the Napolean glacial advance. Slopes generally range between 3 and 6 percent. These soils have deep profiles and are well drained (SCS, 1974).

The A horizon of the Williams loam (undulating type) is a four to eight inch thick dark brown loam. The B horizon is a dark brown clay loam and is distinguished from the A horizon primarily by the change in clay content at the horizon contact. A gray-brown clay loam is encountered in the C horizon which generally grades into a light brown sandy loam. The contact between the B and C horizons is usually at a depth of two feet. The C horizon extends to a depth of about 60 inches (SCS, 1974). A calcium carbonate (caliche) zone was usually encountered during sampling near the B-C horizon contact.

The Parshall-Lihen fine sandy loam developed on nearly level lacustrine or glacial outwash deposits of the Long Lake glacial advance. Slopes range between 0 and 3 degrees. Permeabilities are high due to the large sand fraction (SCS,1974).

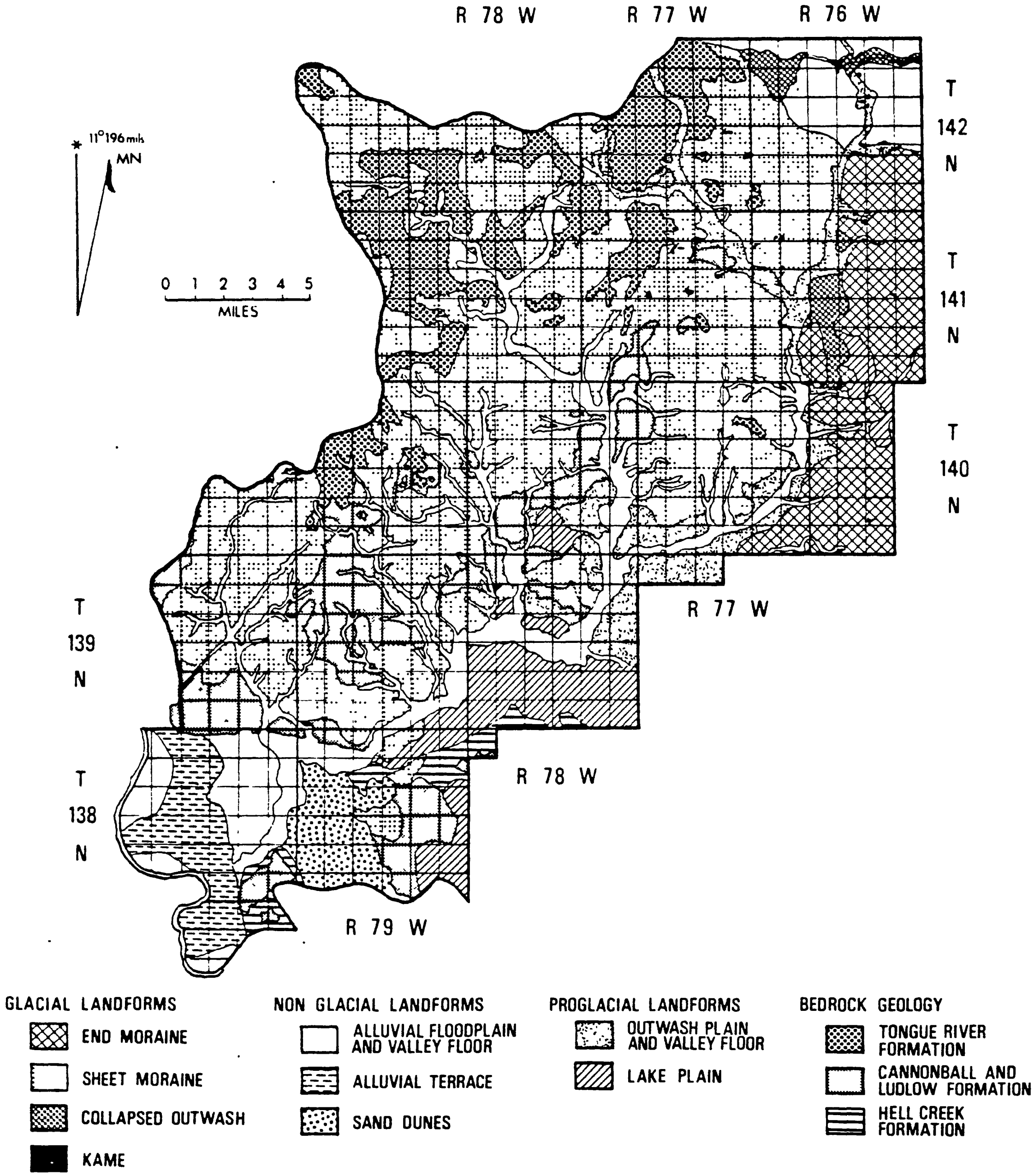
The Parshall-Lihen loam has a fifteen inch thick, dark brown, fine sandy loam A horizon. The B horizon has a brown, fine sandy loam texture, but it includes a higher clay content. The B-C horizon contact is variable between one and two feet in most cases. The C horizon is a tan colored, clean fine sand (SCS,1974). In several samples a buried A horizon was encountered in place of the C horizon.

Vegetation

Small grain native grasses such as western wheatgrass, needle and thread, green needlegrass, blue grama, prairie junegrass, rough fescue, and blue bunch wheatgrass are the major plants found in the study area (Aandahl, 1982). Corn, alfalfa, and flax are produced on the Williams loam soils (SCS, 1974).

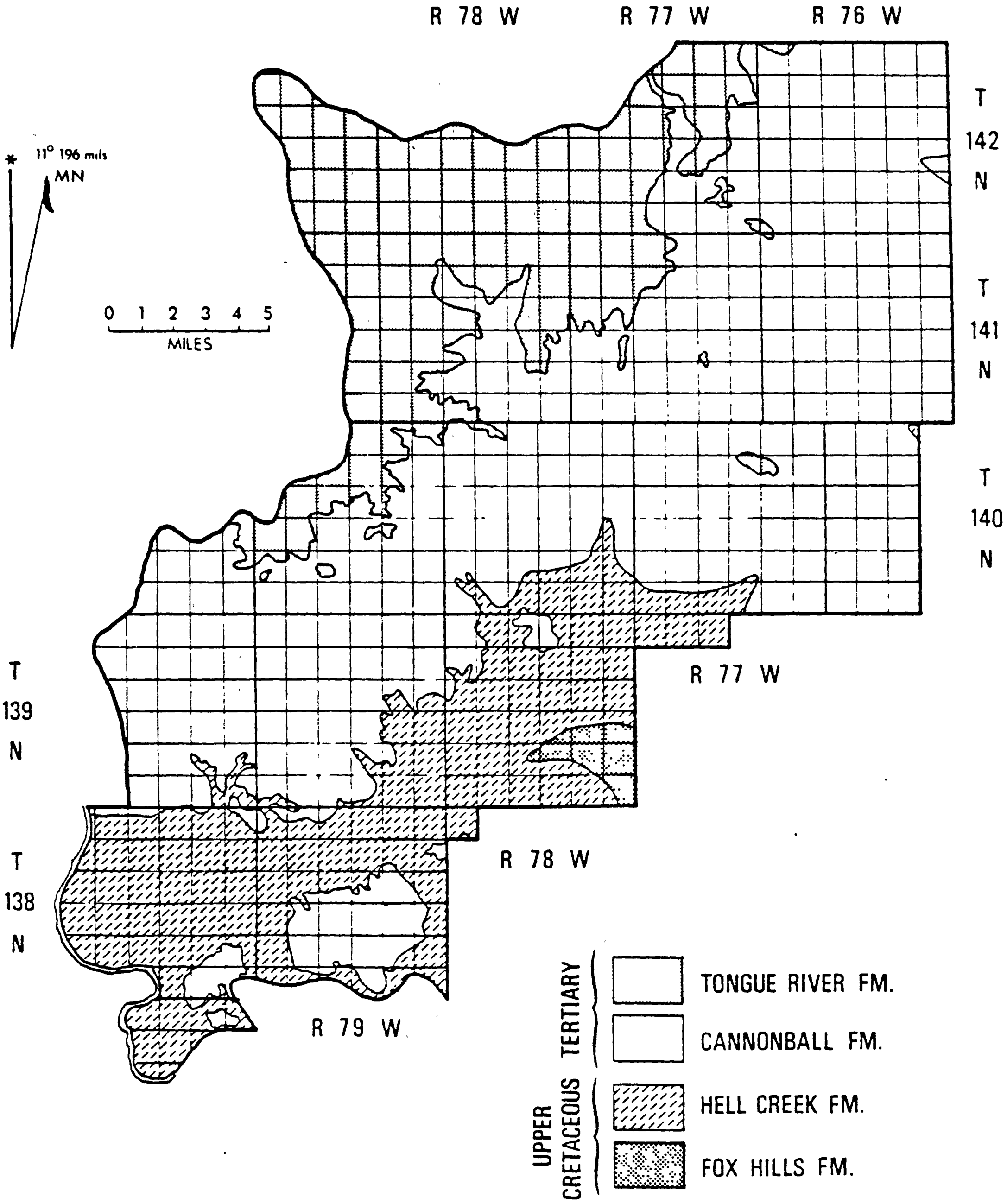
Geology

A geologic map for the area is shown in Figure 5. Detailed discussion will only cover the units shown in the bedrock geologic map (Figure 6). Outcropping formations in the area range in age from Upper Cretaceous to Recent.



Source: Kume, J., and Hansen, D. E., 1965.

Figure 5. Landform and Geologic Map Within the Apple Creek Study Area



Source: Kume, J., and Hansen, D. E., 1965.

Figure 6. Bedrock Geologic Map of the Apple Creek Study Area

Bedrock Geology

The Upper 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 northwest dipping Hell Creek Formation of late Cretaceous age. A regressive sequence exists between the two formations as the Hell Creek is of continental origin. Outcrops of the unit are composed of sandstone, mudstone, siltstone, carbonaceous shale, and lignite. The upper and lower contacts are both conformable and gradational. The upper contact represents a transgressive sequence from the terrigenous sediments of the Hell Creek to the marine dominated Cannonball Formation (Kume et al., 1965).

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

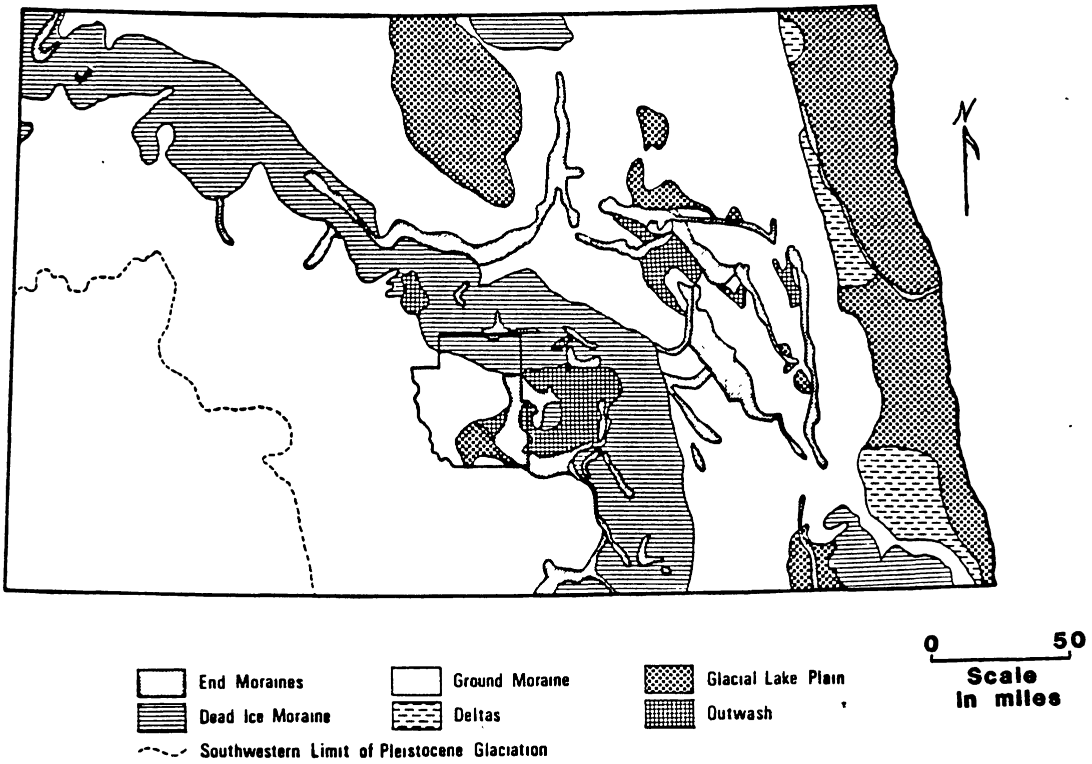
The Tongue River Formation is exposed in the highlands of the headwaters region within the study area. This Paleocene terrigenous deposit reflects an alluvial plain environment. The basal sandstone member of the Tongue River Formation contains shale pebbles of Cannonball origin. Above the basal sandstone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

Glaciology

The generalized glacial map of North Dakota (Figure 7) illustrates that the Apple Creek basin is covered predominantly by ground moraine. Terminal moraines, outwash deposits, and glacial lake plains flank the eastern margin of the basin.

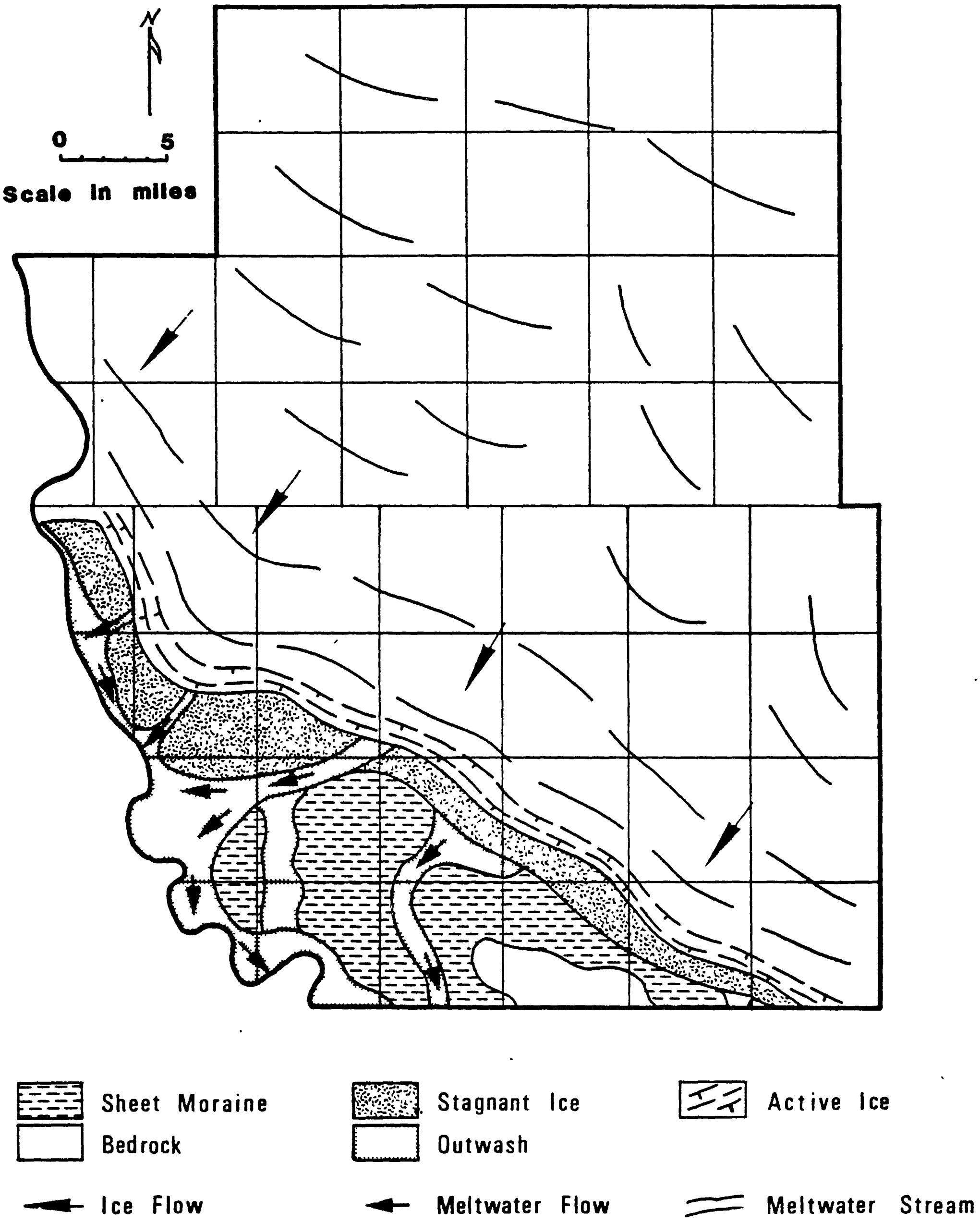
Earliest evidence of glaciation is represented by rocks of the Wisconsinian age of the Pleistocene Epoch. The remnant of this event, called the Napolean Drift, is a sheet moraine which occurs in western and central Burleigh County. This glacier receded quickly as evidenced by the absence of a terminal moraine (Figure 8). The Napolean Drift contains a high percentage of local bedrock types and very little (<25%) erratics. If the gravel fraction is excluded, the till texture 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



Source: North Dakota Geological Survey Miscellaneous Map No. 14.

Figure 7. Generalized Glacial Map of North Dakota



Source: Kume, J., and Hansen, D. E., 1965.

Figure 8. Napolean Glacial Advance With the Deposition of Sheet Moraine

uniform thickness and slight degree of weathering of the till led Kume et al. (1965) to suggest a lower figure, however.

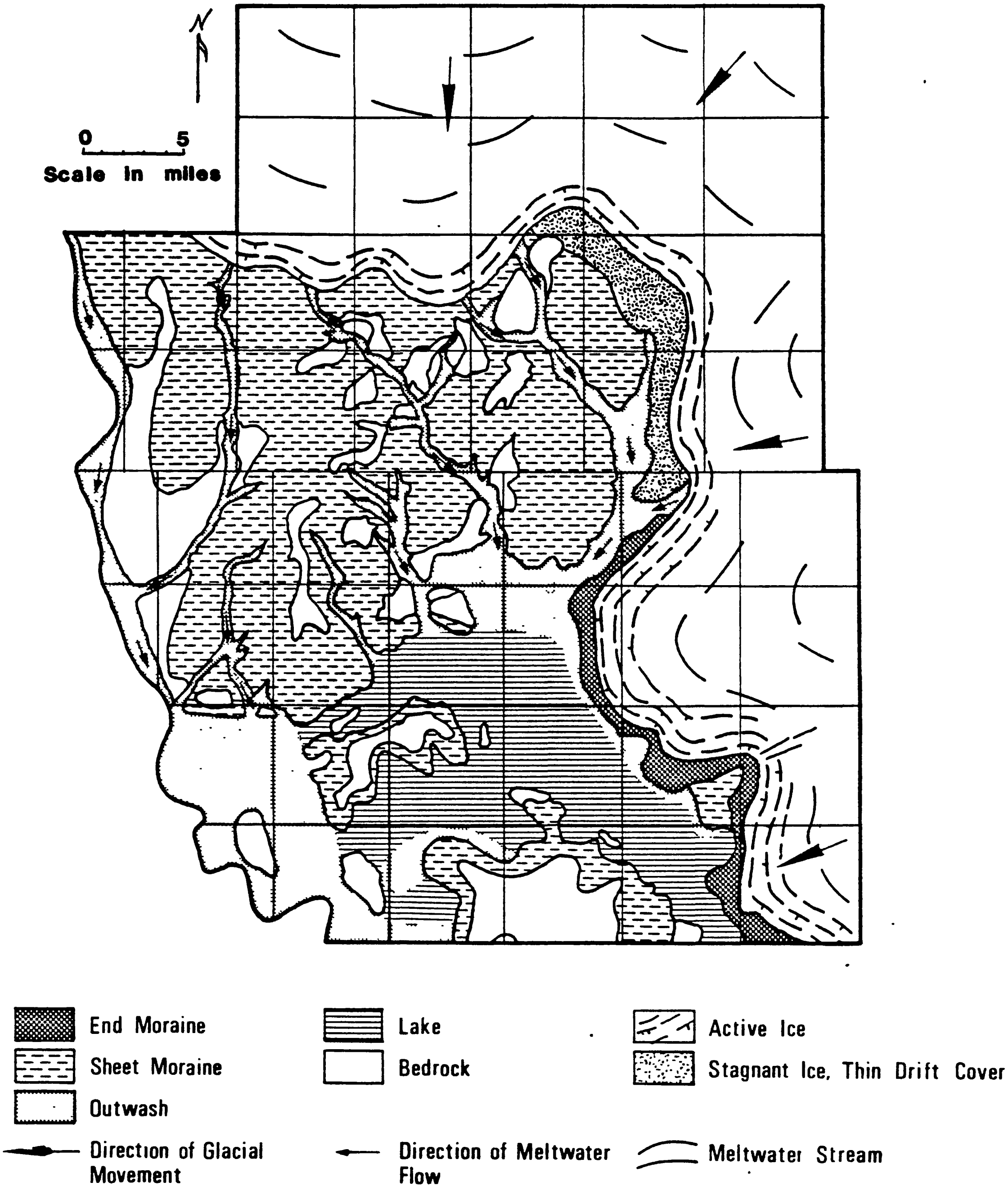
The Wisconsinian age Long Lake glacial advance deposited terminal and ground moraines, and glacial lake sediments throughout eastern Burleigh County (Figure 9). The Long Lake drift is an erratic influenced deposit. The increased percentage of erratics as compared to the earlier Napolean Drift is the result of a different ice flow direction as well as the redeposition of glacial material previously deposited north of the area. The Long Lake Drift consists of 26-35% clay, 24-42% silt, and 28-44% sand (Kume et al., 1965).

Figure 10 is a drift isopach map of the Apple Creek study area depicting the final distribution of glacial sediments.

Eolian deposits of Recent age exist primarily in southern Burleigh County along the margins of the Missouri River (Figure 5). Alluvial, sheetwash and colluvial sediments occur throughout the study area, primarily in or near current channels (Kume et al., 1965).

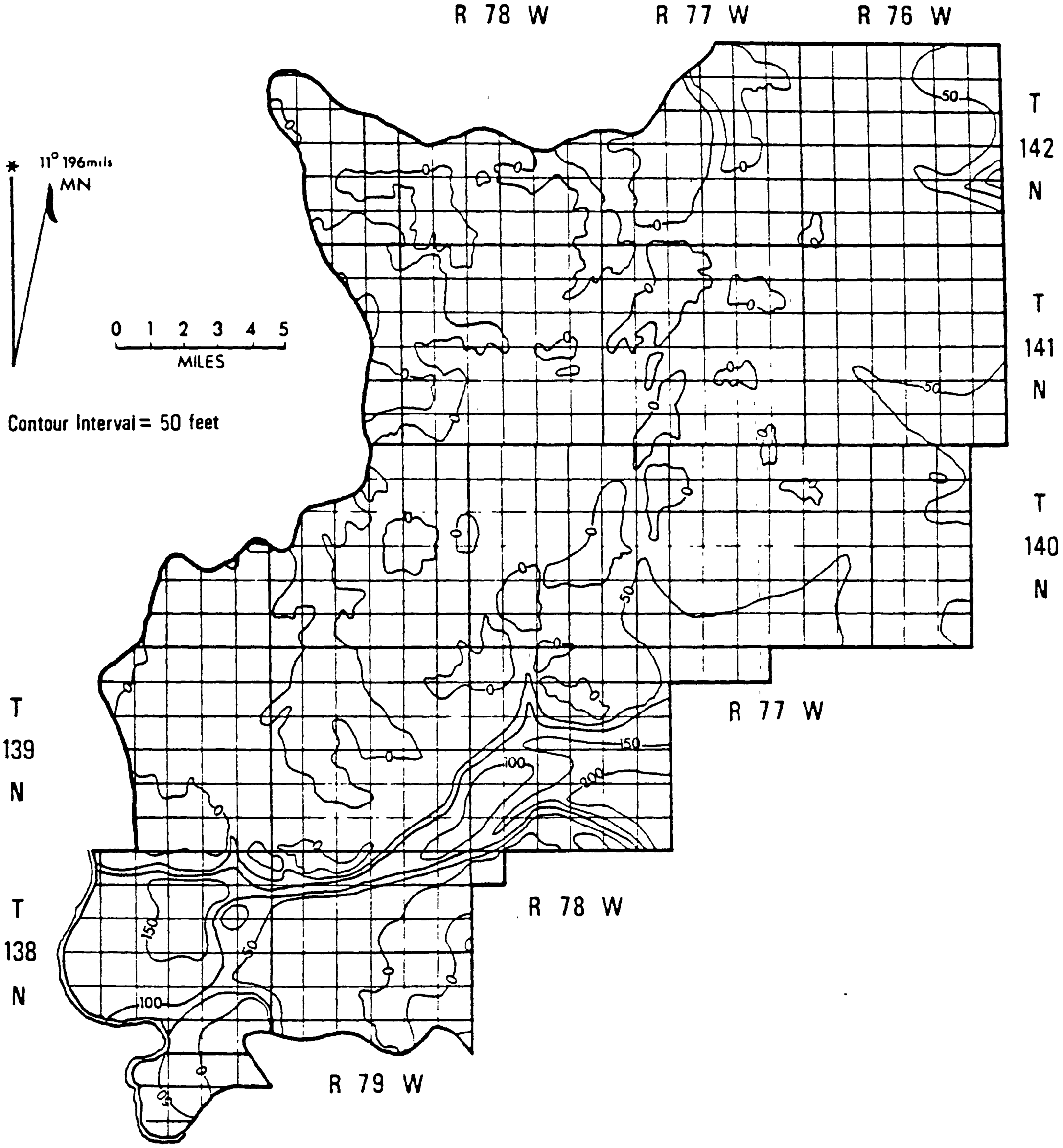
Hydrogeology

Randich et al. (1966) best descibes Burleigh County as having a semi-arid continental climate (Table 2). It is characterized by



Source: Kume, J., and Hansen, D. E., 1965.

Figure 9. Long Lake Glacial Advance With the Deposition of the Long Lake End Moraine and the McKenzie Lake Plain



Source: Kume, J., and Hansen, D. E., 1965.

Figure 10. Drift Isopach Map Within the Apple Creek Study Area

> . . . generally low relative humidity, light rainfall (confined largely to the warmer part of the year), abundant sunshine, prevailing northwesterly winds, moderate snowfall, wide diurnal range in temperature, and pronounced seasonal extremes of temperatures (Randich et al., 1966, pp. 4-5).'

TABLE II

CLIMATOLOGICAL DATA FOR BISMARCK AIRPORT, NORTH DAKOTA
FOR THE YEAR 1980

	Precipitation		Temperature	
	mm	(in)	C	(F)
January	18	0.71	-13	8.8
February	7	0.28	-9.2	15
March	8	0.31	-4.0	25
April	11	0.43	9.3	49
May	27	1.1	15	60
June	42	1.7	19	66
July	80	3.1	22	72
August	128	5.0	19	66
September	82	3.2	12	54
October	59	2.3	7.6	46
November	2	0.08	2.2	36
December	5	0.20	-7.5	19

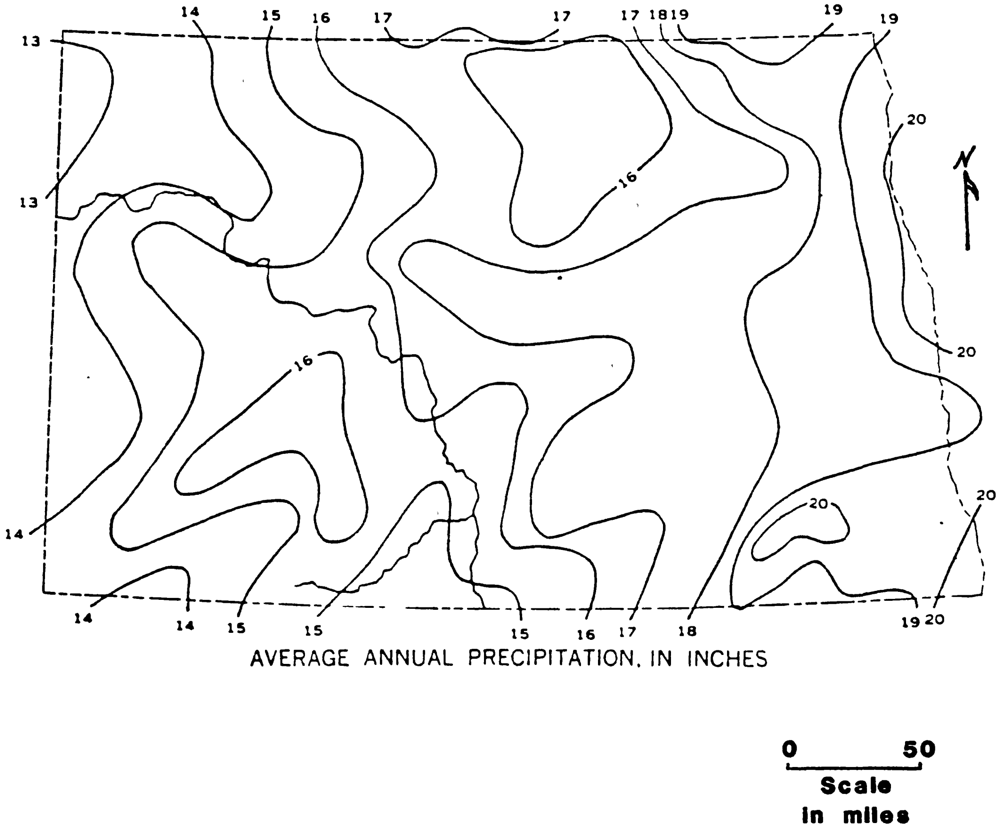
Source: United States Weather Bureau, 1981

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 (Randich et al., 1966). The average annual precipitation is 16.5 inches and is due primarily to cyclonic storms (Figure 11). The mean annual temperature is 43 degrees F (USDC, 1981).

Surface Water

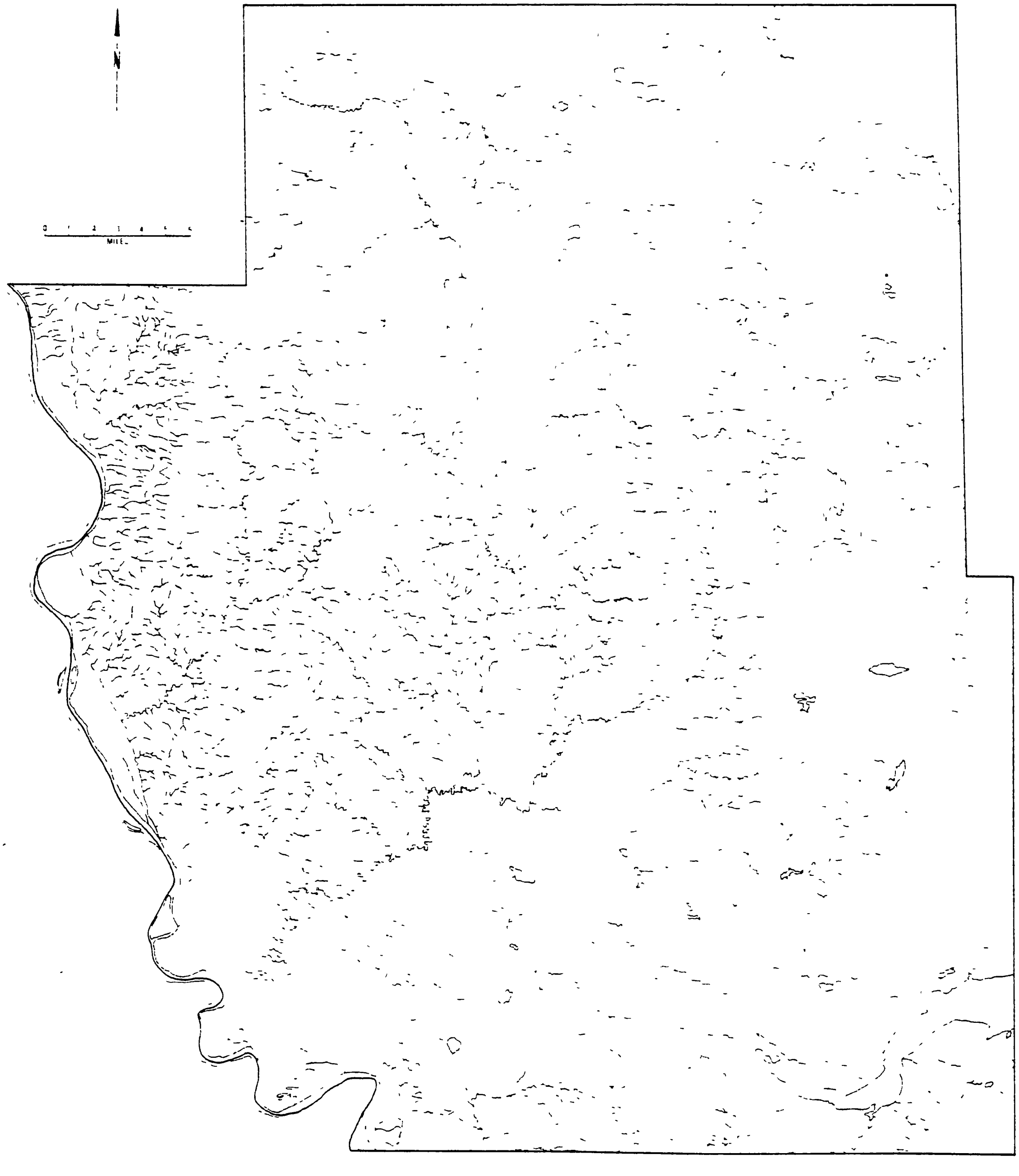
The active portion of surface and stream runoff of the Apple Creek basin is contained within the study area (Figure 12). The only city or industrial area near Apple Creek is Bismarck, North Dakota which derives its water requirements from the Missouri River (Personal Communication, Milton Lindvig, 5/24/84). The creek flows unhindered in that no dams or obstructions block its channel. A dendritic pattern is well developed. 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 just east of Bismarck. Apple Creek enters the Missouri River floodplain immediately south of Bismarck.

A stream discharge and water quality station sponsored



Source: United States Weather Bureau, 1981.

Figure 11. North Dakota Generalized Precipitation Map



Source: Kume, J., and Hansen, D. E., 1965.

Figure 12. Surface Drainage Map of Burleigh County, North Dakota

by the USGS is located 2.5 miles upstream from the Hay Creek conjunction. Water quality records are available for water years 1974 to the current year. Stream 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 common during the summer months of dry years (USGS, 1981).

Water quality analyses from water year 1980 were examined to determine probable weathering scenarios. All of the analyses indicated that the concentration of the sulfate ion was greater than the calcium ion (Table 3). This implies that either another source of sulfate is present or calcium removal is occurring as weathering of the common mineral gypsum would not produce this relationship. Randich et al. (1966) explains that sulfate can result from the dissolution of the mineral mirabilite (sodium sulfate) and that the calcium resulting from the dissolution of gypsum is often exchanged for sodium by multi-layered clay minerals. Either of these hypotheses are supported by the high concentration of sodium in the stream. The Apple Creek has Sodium-Bicarbonate-Sulfate type water with a fairly wide range of total dissolved solids (TDS) values throughout the year.

TABLE III

CONCENTRATIONS (%MEQ/L) OF MAJOR IONS IN THE APPLE CREEK

Date	Na+K	Ca	Mg	HCO_3+CO_3	SO_4	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
01/31/80	62	17	21	55	39	6
02/22/80	61	20	19	58	35	7
03/27/80	53	23	24	43	54	3
05/07/80	61	20	19	46	49	5
05/30/80	65	18	17	49	45	6
06/27/80	69	16	15	55	36	9
07/30/80	74	13	13	58	33	9

Source: Modified from United States Geological Survey, 1981

Groundwater

Water wells in the Apple Creek basin produce from bedrock aquifers (Table 4) in addition to Quaternary unconsolidated glacial deposits (Table 5) and Recent alluvial sediments (Randich et al., 1966).

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

TABLE IV

GROUNDWATER CHARACTERISTICS OF BEDROCK FORMATIONS WITHIN THE STUDY AREA

Formation Name	Age	Water Type	TDS(ppm)
Dakota Ss	Cretaceous	Na-SO_4	2400
Fox Hills Ss	Cretaceous	Na-HCO_3-Cl Na-Cl-HCO_3	1500-2700
Hell Creek Formation	Cretaceous	Na-HCO_3 Na-HCO_3-SO_4 Na-HCO_3-Cl	500-2000
Cannonball Formation	Tertiary	Na-HCO_3 Na-HCO_3-SO_4 Na-SO_4-HCO_3	1000-1700
Tongue River Formation	Tertiary	Na-HCO_3-SO_4	500-1900

Source: Randich, P.G., and Hatchett, J.L., 1966

TABLE V

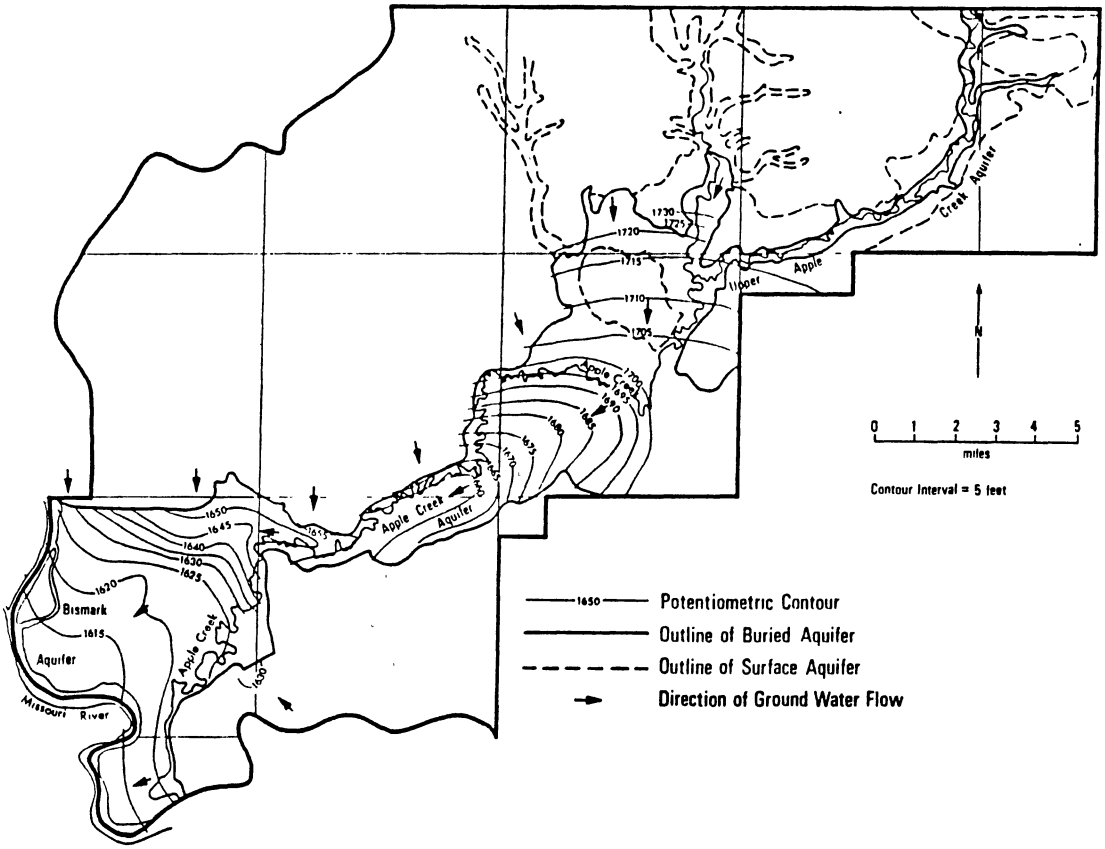
GROUNDWATER CHARACTERISTICS OF QUATERNARY AGE GLACIAL AQUIFERS WITHIN THE STUDY AREA

Aquifer Name	Lithology	Aquifer Type	T (gpd/ft)	Total Storage (acre-feet)	Water Type	TDS (ppm)
Lower Apple Creek	Sand and Gravel	Water Table and Leaky	10,000	620,000	$Na\text{-}HCO_3$	<1000
Bismarck	Sand and Gravel	Leaky	350,000	510,000	$Na\text{-}Ca\text{-}HCO_3$ $Na\text{-}HCO_3\text{-}SO_4$	800-1800
Upper Apple Creek	Sand and Gravel	Water Table	no data	3,000	$Na\text{-}HCO_3\text{-}SO_4$	1000

Source: Randich, P. G., and Hatchett, J. L., 1966 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 water supply within the area. The Quaternary age glacial aquifers are the most desireable with the highest yields and lowest TDS contents (Randich et al., 1966). The gradient of head is such that the bedrock aquifers constantly feed the glacial aquifers which feed the Apple Creek in the southern half of the study area (Figure 13).

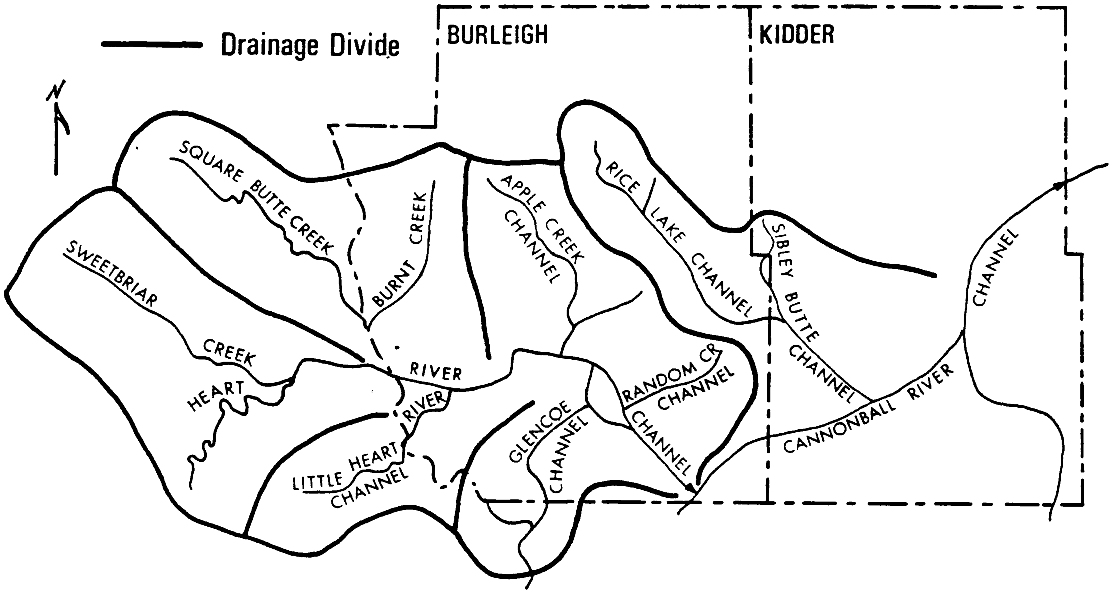
To understand the hydrogeology of the Quaternary age glacial aquifers within the basin it is necessary to examine pre-existing drainage systems. Prior to Pleistocene modification, the drainage system in Burleigh County was significantly different than it is at present (Figure 14). Apple Creek was a tributary to the paleo-Heart River which, in turn, flowed into the Cannonball River and drained in an easterly direction (Randich et al., 1966).

During glaciation, the Missouri River diverged to its present course (Figure 15). The Heart and Cannonball Rivers reversed their flow direction and the Glencoe and Soo Channels were cut into the bedrock. 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 now comprising the Lower Apple Creek . . . and Bismarck aquifers (Randich et al., 1966, p. 32).'



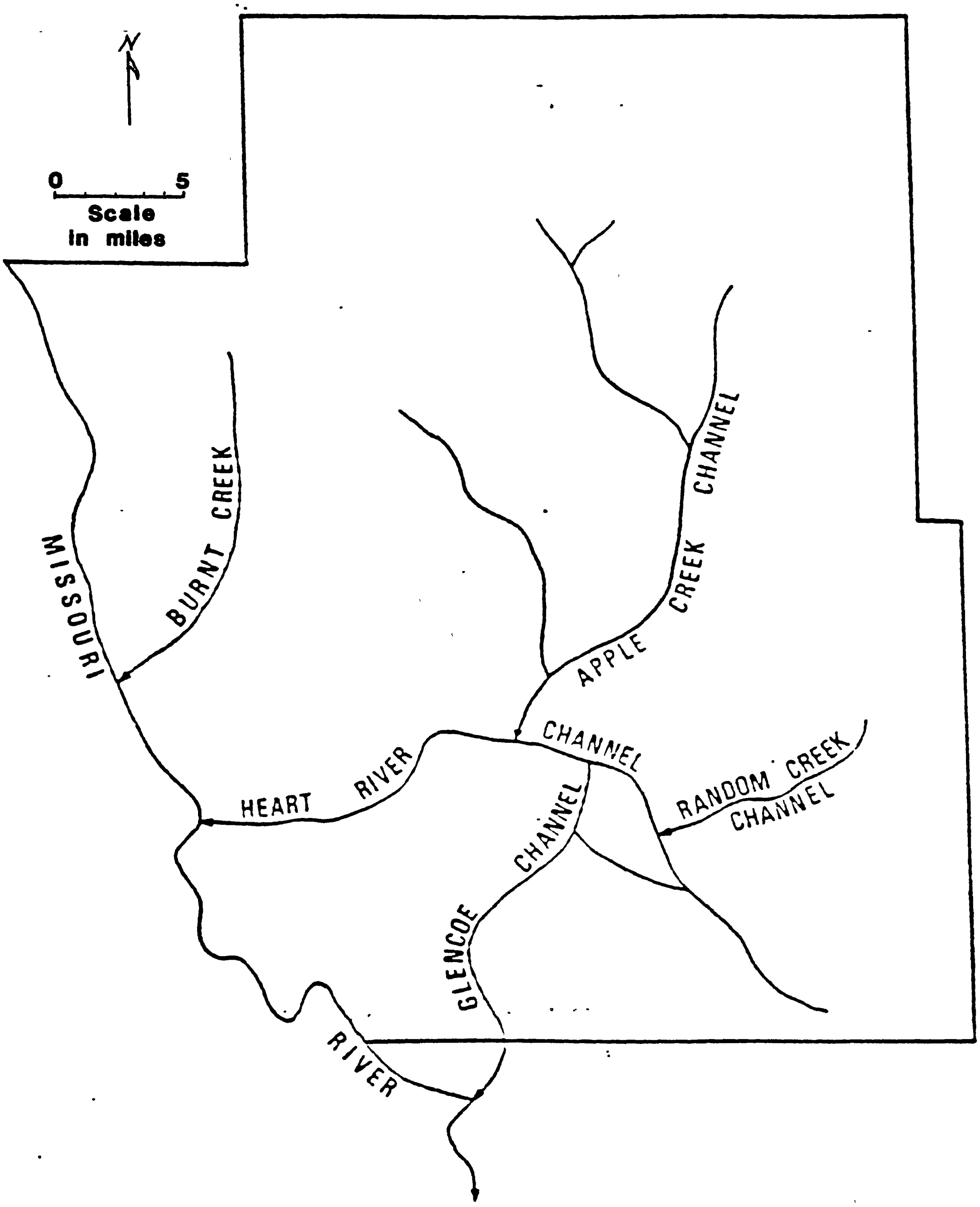
Source: Randich, P. G., and Hatchett, J. L., 1966.

Figure 13. Potentiometric Surface Map of the Glacial Aquifers Within the Southern Half of the Apple Creek Study Area



Source: Kume, J., and Hansen, D. E., 1965.

Figure 14. Preglacial and Pre-Wisconsinian Drainage



Source: Kume, J., and Hansen, D. E., 1965.

Figure 15. Diversion and Wisconsinian Drainage Map of Burleigh County, North Dakota

CHAPTER V

RESULTS AND DISCUSSION

Phase-One

As mentioned earlier, phase-one refers to those samples collected during the summer of 1983.

Aerial Soil Samples

A well defined sampling design was not used during the collection of phase one samples. The goal of this initial survey was to estimate the variance of SOM values found in nature so that a secondary survey could be designed to be more representative of the region. Determining the accessibility to various parts of the basin was also a goal of the first investigation. Shoveled samples were collected in plastic bags and air-dried before analysis. Considerable bias was probably introduced during sampling and therefore the results will not be reported.

Percent Organic Matter. SOM determinations were made using the Walkley-Black titration method as described in Allison (1965). The standard deviations generally exceeded the 10% sample error allowed in the colorimetric method of Metson et al. (1979).

Bulk X-Ray Determinations. Bulk soil samples were crushed and analyzed by x-ray diffraction for mineral content. Quartz was found to be the predominant mineral in the soils accounting for most of the peaks. Sodic plagioclase (albite) is the only accessory mineral present. The feldspar is probably due to the crushing of pebbles in the soil as feldspars leach out rapidly when exposed. The mineral mirabilite did not appear on the x-ray patterns; however, this only implies that the mineral is not in excess of five to ten percent of the bulk soil. Figure 16 shows a typical x-ray diffraction pattern.

Core Samples

A drilling site was chosen in sec 21, T139N R79W (0.29 miles south of the northeast corner of sec 21 along the section line). Drilling activities were performed by Water Supply, Inc. of Bismarck, ND. Continuous shelby tube cores were taken through the unsaturated zone.

Percent Organic Matter. SOM content was determined at two feet intervals to a depth of fourteen feet. The colorimetric method (Metson et al., 1979) was used for analysis. Figure 17 shows the change of SOM with depth. A gradual decrease exists to a depth of ten feet after which a subtle increase occurs. This distribution is to be expected as plant material is concentratd in the upper soil horizons. Leached organic matter dissipates with depth. The mild

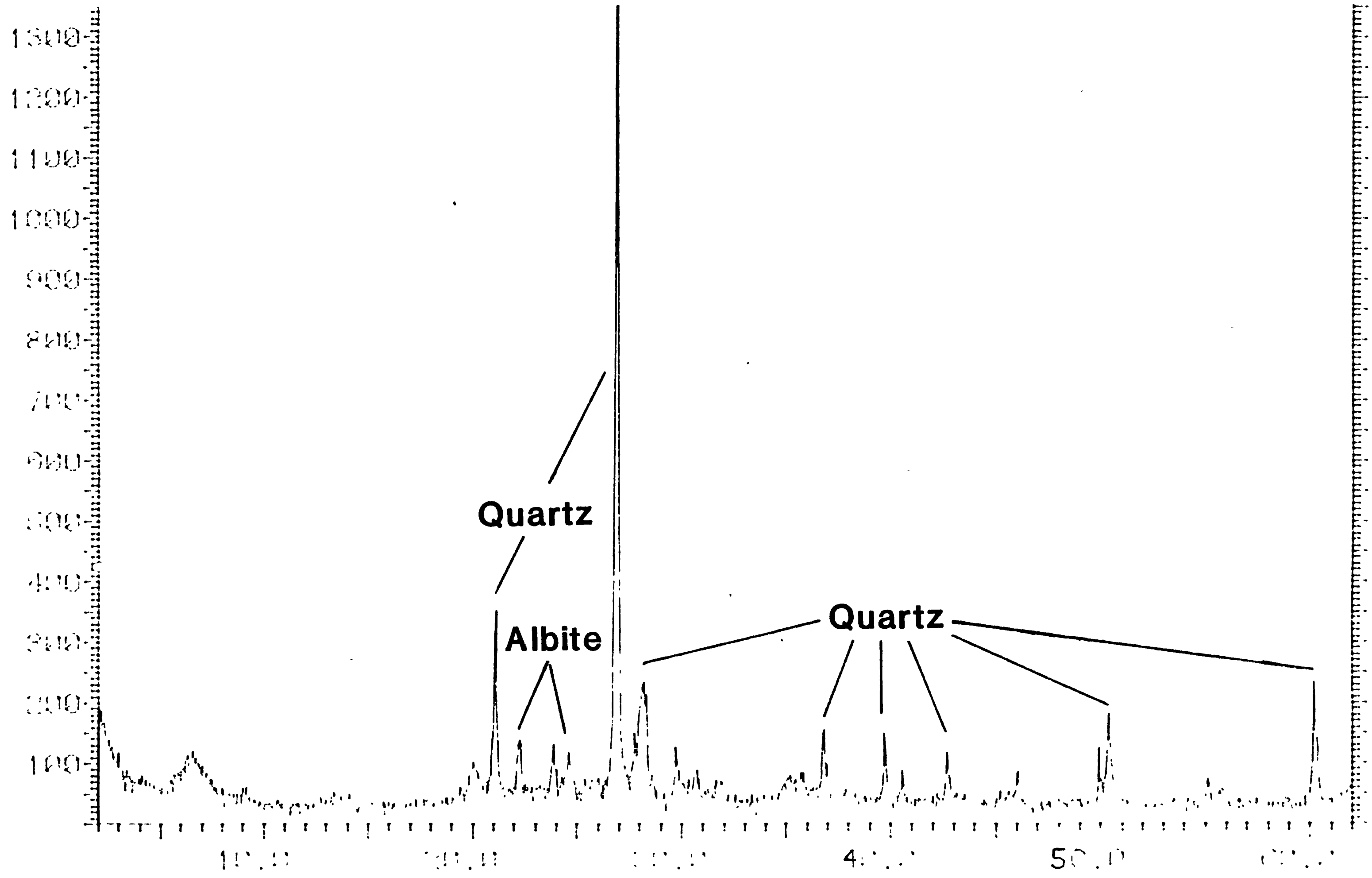


Figure 16. Typical Bulk X-Ray Diffraction Pattern for the Williams Loam

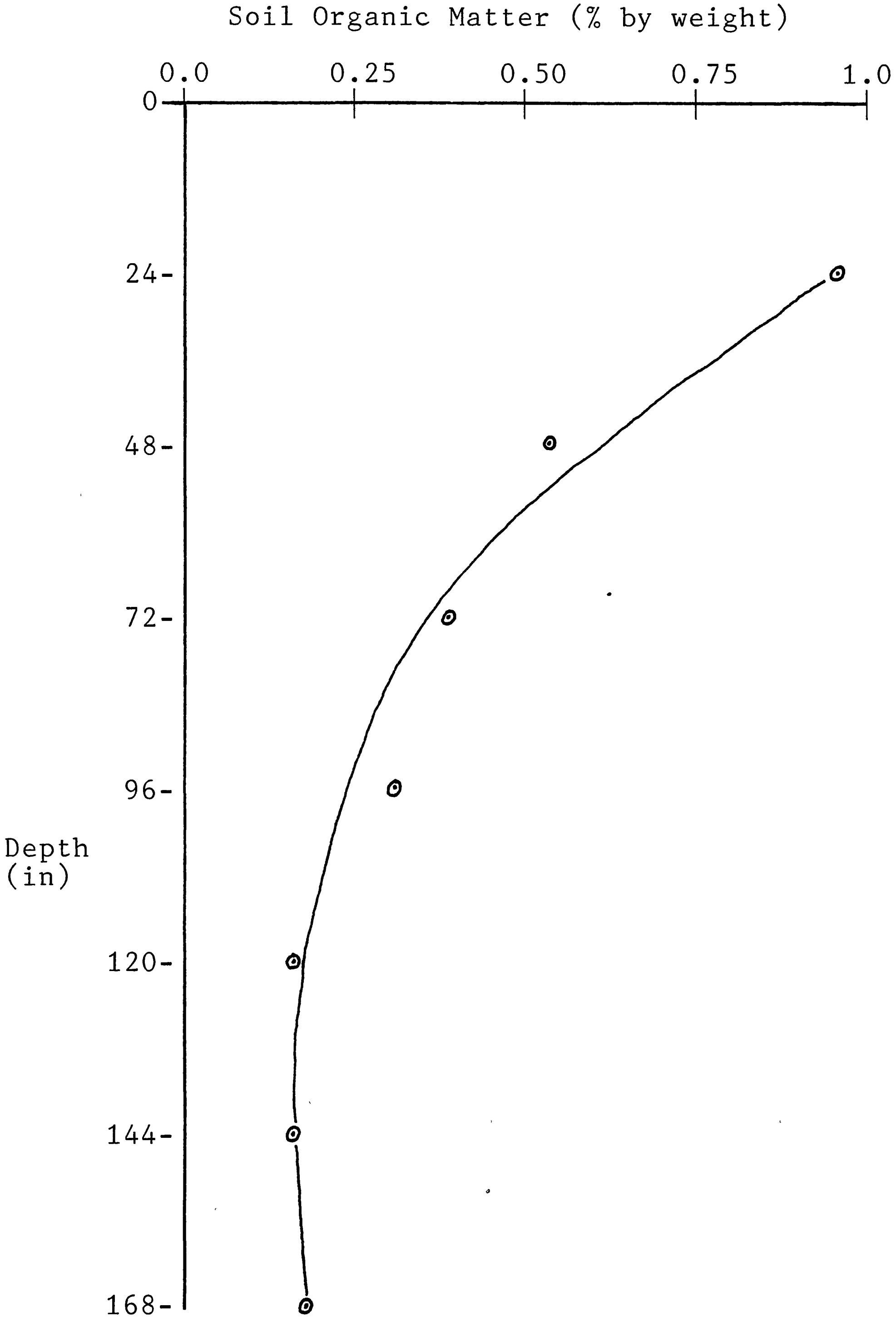


Figure 17. Plot of Soil Organic Matter Content Versus Depth Within the Williams Loam

increase after a depth of ten feet could indicate microbial activity in the glacial till within the capillary zone.

Trace Elements. X-ray fluorescence was used to analyze for trace elements. Fluo-X-Spec analytical laboratory in Denver, CO performed this service. As the analyses are semi-quantitative, the concentrations are probably only accurate to within an order of magnitude. Table 6 lists concentrations versus depth. None of the elements are related to depth of burial.

Phase-Two

Phase-two refers to the most recent samples collected in May, 1984. Most of the conclusions regarding the aerial distribution of constituents involved in the adsorption of organic chemicals will be drawn from these data.

Percent Organic Matter

The SAS program PROC UNIVARIATE was used extensively to test the normal characteristics of the SOM distribution. The Shapiro-Wilk statistic, W, was close to a value of one for all of the regional soil samples (Table 7) indicating normality. The localized soil samples also are normally distributed with respect to organic matter (Table 8) as indicated by the W test statistic. The mean values of SOM indicate a decrease with depth (Tables 7 and 8). Likewise, the standard deviations of SOM content also

TABLE VI

TRACE ELEMENT CONCENTRATIONS IN THE WILLIAMS LOAM

Depth	Trace Elements (ppm)									
(in)	Cu	Zn	Pb	Fe	Rb	Ba	Sr	Ti	Zr	Mn
2.1	64	105	17	19000	103	1650	435	730	570	560
16.0	70	115	80	20000	135	1055	225	1700	410	540
16.1	52	90	-	18000	110	1500	180	1100	400	330
47.0	80	125	-	17500	72	1550	235	1350	520	300
52.0	67	135	37	23500	165	1600	495	1040	390	86
54.2	56	140	78	20000	110	1700	260	970	350	420
60.2	84	77	39	24000	130	2500	610	810	500	88
64.0	75	120	250	28000	150	2000	460	1500	350	320
67.5	45	120	140	26000	130	1700	390	1700	410	390
76.0	110	140	98	29000	170	1200	490	1500	320	510
80.2	110	200	98	28000	140	1100	400	1100	300	690
88.0	100	-	46	29000	110	1300	510	1100	440	350
88.1	80	160	49	27000	170	1300	490	990	310	530
92.5	96	92	130	29000	63	990	600	820	360	330
112.0	56	81	70	21000	130	1400	640	810	460	150
121.2	45	130	37	21000	100	1500	510	-	360	180
148.0	45	170	160	37000	96	950	420	160	340	640

generally decrease with depth. The only exception is the Parshall - Lihen loam at the regional scale. This can be attributed to the limited number of sampling localities tested. The standard deviation of sample error is generally small relative to the sample standard deviation at the regional and local levels.

TABLE VII

REGIONAL SOIL ORGANIC MATTER STATISTICS

Soil	Horizon	Mean (a)	Standard Deviation (a,b)	W (c)	Standard Deviation of Sample Error (d)
W (e)	A	4.99	1.23	.934	.0671
W	B	1.39	.298	.988	.0701
W	C	.643	.181	.871	.0349
PL (f)	A	2.90	.362	.980	.0858
PL	B	1.17	.141	.957	.0421
PL	C	.612	.160	.835	.0371

(a) Values are in % by weight
(b) Parshall-Lihen standard deviations are corrected for 'sampling by increments' method as described in text
(c) Shapiro-Wilk test statistic (Statistical Analysis System, 1974)
(d) Equation for sample error described in Chapter III
(e) Williams loam, undulating type (Soil Conservation Service, 1974)
(f) Parshall-Lihen fine sandy loam (Soil Conservation Service, 1974)

TABLE VIII

LOCAL SOIL ORGANIC MATTER STATISTICS FOR THE WILLIAMS LOAM

Spacing	Horizon	Mean (a)	Standard Deviation (a,b)	W (c)	Standard Deviation of Sample Error (d)
50 feet	A	5.65	.314	.946	.0540
50	B	2.07	.141	.942	.0579
50	C	.856	.0702	.912	.0369
1 foot	A	6.39	.446	.971	.0988
1	B	2.24	.129	.961	.0579
1	C	.696	.0569	.918	.0604

(a) Values are in % by weight
(b) Williams loam standard deviations are corrected for 'sampling by increments' method as described in text
(c) Shapiro-Wilk test statistic (Statistical Analysis System, 1974)
(d) Equation for sample error described in Chapter III

Each local sample represents one soil core, whereas each regional sample represents one sampling locality. Within the Williams soil, an average of 4.15 sites (individual cores) were added together to form a sampling locality. Within the Parshall-Lihen soil this number was 1.80. This procedure, called 'sampling by increments', tends to sacrifice resolution in favor of stability. As a result, the sample variance is decreased (Personal communication, Ronald W. McNew, 9/21/84). In order to compare the local and regional distributions, the local standard deviation must be divided by the square root of the number of combined cores (4.15 in the case of the Williams soil). The standard deviations listed in Tables 7 and 8 reflect corrected values which are directly comparable. While the two local surveys have similar standard deviations, the regional distribution indicates a much broader range of standard deviation values. This lends credibility to the hypothesis that organic matter content does varies geographically.

The SAS program PROC GLM was used to determine regional trends in SOM content. Five tests were run to determine (1) linear east-west trends, X, (2) linear north-south trends, Y, (3) oblique trends, X*Y, (4) regional curvature in an east-west direction, X*X, and (5) regional curvature in a north-south direction, Y*Y. The program generates an 'F' value which 'tests how well the model as a whole accounts for the dependent variable's behaviour (SAS, 1978, p. 61).' The important statistic, however, is the 'significant probability', labeled PR>F. As this value approaches zero, the validity of the model is upheld (SAS, 1978).

Table 9 shows that the Williams loam PR>F values for SOM are significant in all three horizons with respect to the X, Y, and X*Y orientations at the regional scale. Regional (north-south) curvature is also indicated in the B and C horizons. The Parshall-Lihen loam, however, shows no aerial trends. This most probably can be attributed to the low number of actual sampling points. Ten localities will not, in most cases, yield an accurate distribution. At the local level, neither the one foot or 50 feet resolution samples showed any aerial trends.

TABLE IX

SIGNIFICANT PROBABILITY (PR>F) VALUES FOR REGIONAL SOIL ORGANIC MATTER VARIATIONS

		Aerial Variation Parameters (a)				
Soil	Horizon	X	Y	X*Y	X*X	Y*Y
W (b)	A	.0001	.0002	.0084	.9567	.6282
W	B	.0106	.0272	.0556	.5492	.0956
W	C	.0210	.0133	.0050	.9246	.0047
PL (c)	A	.3877	.4948	.9150	.4410	.7963
PL	B	.5459	.6676	.9726	.2341	.5802
PL	C	.8316	.5282	.0749	.4649	.5171

(a) See text for description of aerial variation parameters
(b) Williams loam, undulating type (Soil Conservation Service, 1974)
(c) Parshall-Lihen fine sandy loam (Soil Conservation Service, 1974)

The program PROC GLM was used to generate a data set of predicted SOM values based on the best fitting equations of the relationships SOM vs. various orientations. The resulting distributions reflect smoothed out data which are essentially background concentrations. Figure 18 is a contour map of the Williams loam, A horizon of predicted SOM values. A gradual decrease in values occurs from the northeast section of the study area to the southeast

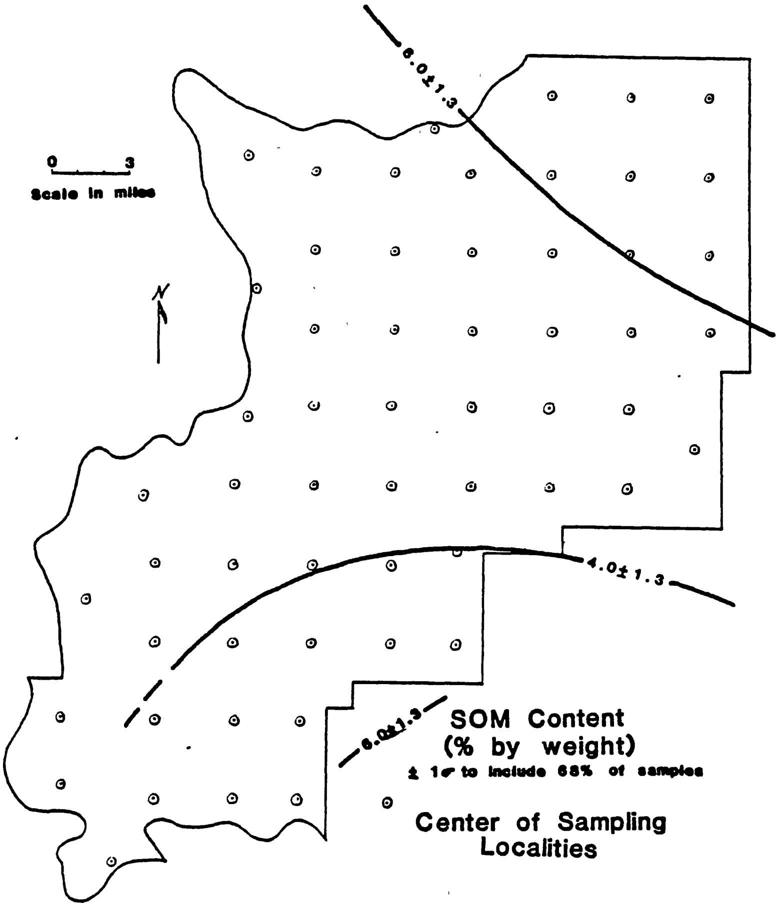


Figure 18. Variation of Predicted SOM Concentrations Within the Williams Loam, A Horizon

section. The B horizon (Figure 19) shows a concentric distribution centered around the far central eastern section of the basin, with values decreasing towards the center. Figure 20 shows the C horizon with a depression in predicted SOM values occuring in the north central region striking approximately east-west.

CEC / Exchangeable Cations

The exchangeable acid values are of dubious credibility because they approach detection limits. The analytical error involved also casts doubt because in most cases it puts the values beyond detection limits. Brady (1974) suggests that exchangeable acids are only mildly subject to cation exchange. Based on this statement and the results from phase two samples, exchangeable acids were not included in the calculation of cation exchange capacity. CEC,, as treated in this study, is solely the sum of exchangeable bases.

CEC values appear to be normally distributed as determined by PROC UNIVARIATE (Table 10). Mean values in meq/100g increase with depth which is expected as the clay content increases. The standard deviations likewise generally increase with depth. Anomalous calcium concentrations in some B and C horizon samples have led to abnormal standard deviations within these zones.

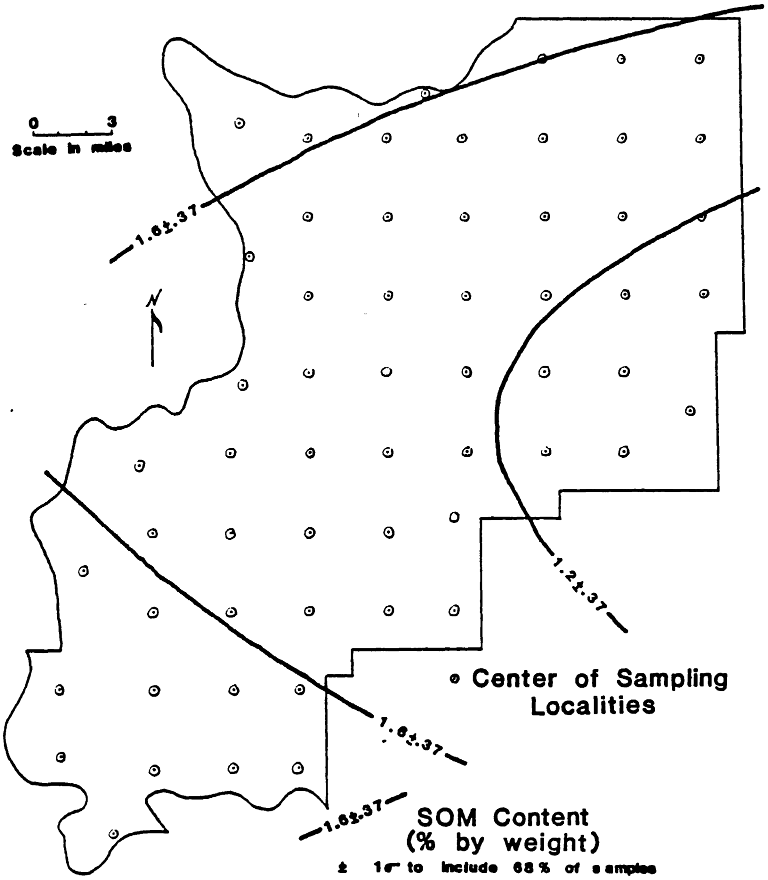


Figure 19. Variation of Predicted SOM Concentrations Within the Williams Loam, B Horizon

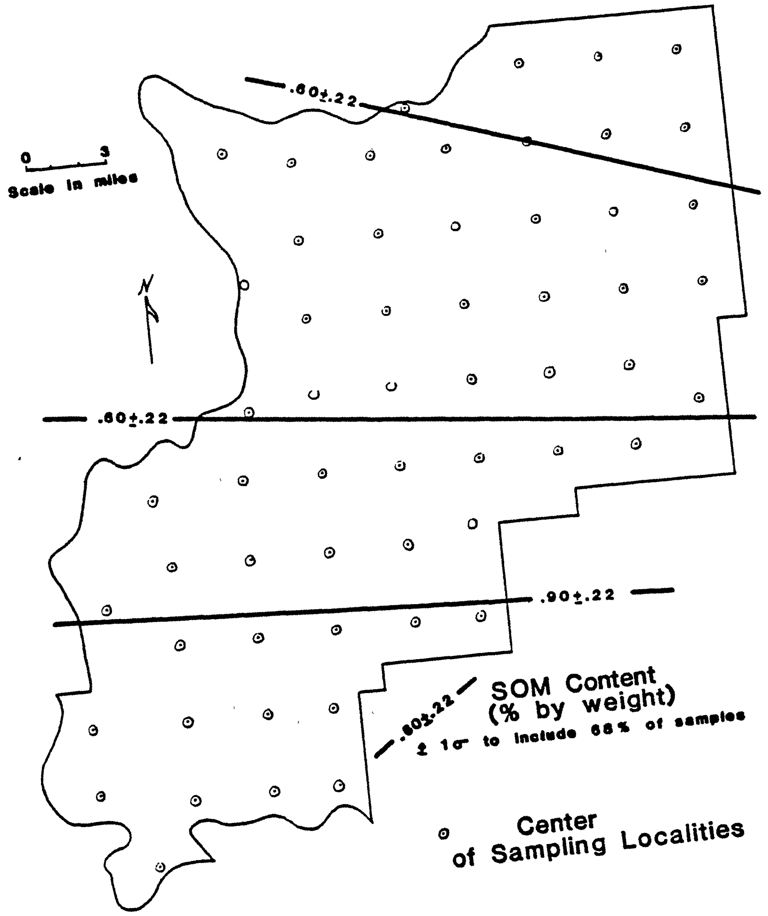


Figure 20. Variation of Predicted SOM Concentrations Within the Williams Loam, C Horizon

TABLE X

REGIONAL CATION EXCHANGE CAPACITY STATISTICS

Soil	Horizon	Mean (a)	Standard Deviation (a,b)	W (c)
W (d)	A	27.2	6.63	.853
W	B	74.3	51.0	.878
W	C	113.	47.2	.969
PL (e)	A	20.8	2.97	.953
PL	B	24.0	10.5	.788
PL	C	99.6	59.3	.871

(a) Values are in meq/100g
(b) Parshall-Lihen standard deviations are corrected for 'sampling by increments' method as described in text
(c) Shapiro-Wilk test statistic (Statistical Analysis System, 1974)
(d) Williams loam, undulating type (Soil Conservation Service, 1974)
(e) Parshall-Lihen fine sandy loam (Soil Conservation Service, 1974)

An artificial parameter, CCC, has been generated which is equal to the CEC minus the calcium concentration. Influences by calcium carbonate (caliche) on the CEC have prompted the author to consider this additional parameter. The distribution of the CCC parameter (which is primarily dependent on the magnesium concentration) begins to deviate from normality with depth (Table 11). This explains why the standard deviation also increases dramatically with depth. Examination of skewness and kurtosis shows an increasing affinity for a positively skewed, 'leptokurtic [Spiegel, 1961, p. 91]' (high peaked) distribution.

Aerial trends were tested by the program PROC GLM for CEC, CCC, and the exchangeable cations using the relationships described in the percent organic matter section. None of these parameters indicated a geographic variation.

TABLE XI

REGIONAL STATISTICS FOR CATION EXCHANGE CAPACITY MINUS THE CALCIUM INFLUENCE

Soil	Horizon	Mean (a)	Standard Deviation (a,b)	W (c)	Skewness	Kurtosis
W (d)	A	6.46	1.24	.971	.720	1.40
W	B	9.24	3.84	.764	2.53	8.28
W	C	14.8	7.78	.754	3.09	15.1
PL (e)	A	4.86	.603	.926	.0295	-1.55
PL	B	4.50	1.23	.874	1.19	.706
PL	C	6.60	3.99	.609	2.76	8.06

(a) Values are in meq/100g

(b) Parshall-Lihen standard deviations are corrected for 'sampling by increments' method as described in text

(c) Shapiro-Wilk test statistic (Statistical Analysis System, 1974)

(d) Williams loam, undulating type (Soil Conservation Service, 1974)

(e) Parshall-Lihen fine sandy loam (Soil Conservation Service, 1974)

Interrelationships

The CEC of soils is thought to be dependent upon the organic matter content. This relationship would be most evident in the A horizon where the SOM content is highest and clay content, especially montmorillonite, is lowest. SOM content decreases in the B and C horizons while the amount of montmorillonite increases. As a result, the effect of SOM on CEC is diminished in the lower horizons. Table 12 indicates the CEC values of several constituents involved in the adsorption of certain organic chemicals in soils.

The B and C horizons of the Williams and Parshall-Lihen loams showed no correlation between CEC and SOM, which is expected (Table 13). The A horizon of the Williams loam also did not show a relationship. This unusual occurence can be attributed to a higher-than-normal montmorillonite content. It could also indicate a form of organic matter less susceptible to cation exchange. Correlation coefficients indicated a typical relationship between CEC and SOM in the A horizon of the Parshall-Lihen loam, however.

Clay Extractions

In order to maximize the amount of information derived from clay extractions and minimize the analytical time involved, two samples from each soil type, representing high and low CEC values, were analyzed at the A, B, and C horizons. Clay types could generally be classified by running only the untreated samples (neither heated or glycolated). Special treatment of the extracts was only applied where peaks were superimposed.

TABLE XII

CATION EXCHANGE CAPACITIES OF CLAYS AND OTHER ADSORBENTS FOUND IN SOILS

Material	Cation Exchange Capacity (meq/100g)
Organic Matter (a)	200-400
Montmorillonite (a)	80-150
Illite (a)	10-40
Kaolinite (b)	1-10
Oxides & Hydroxides (a)	2-6

Source: (a) Drever, J. I., 1982
(b) Bailey, G. W., and White, J. L., 1964

X-ray diffraction patterns from the A horizons of the Williams and Parshall - Lihen loams were dominated by a low signal-to-noise ratio that made the clay peaks difficult to distinguish (Figure 21). Illite, however, emerged as the predominant clay type, with some samples containing

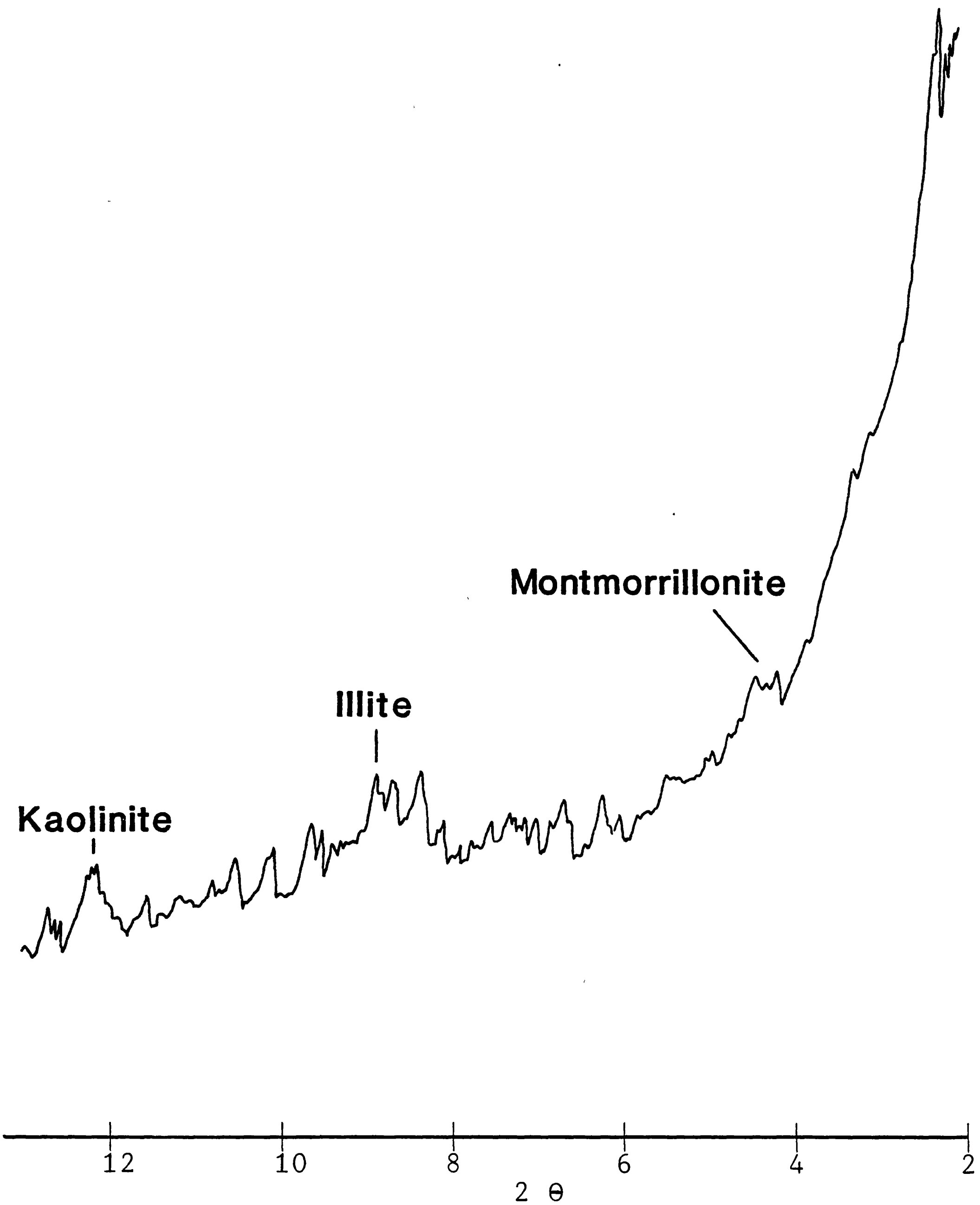


Figure 21. X-Ray Diffraction Pattern Typical of A Horizon Glycolated Clay Extracts of the Williams and Parshall-Lihen Loams

kaolinite. The B and C horizons almost invariably contained montmorillonite, illite, and kaolinite in that order of importance (Figures 22 and 23). Samples representing high CEC's differed from low CEC samples only by the peak intensity. This would indicate that the value of the CEC is due to the quantities of clays present, rather than the types of clays.

TABLE XIII

REGIONAL CORRELATION BETWEEN CATION EXCHANGE CAPACITY AND SOIL ORGANIC MATTER CONTENT

Soil	Horizon	CEC vs. SOM (Correlation Coefficients)
Williams	A	0.369
Williams	B	0.291
Williams	C	0.157
Parshall-Lihen	A	0.890
Parshall-Lihen	B	0.015
Parshall-Lihen	C	0.331

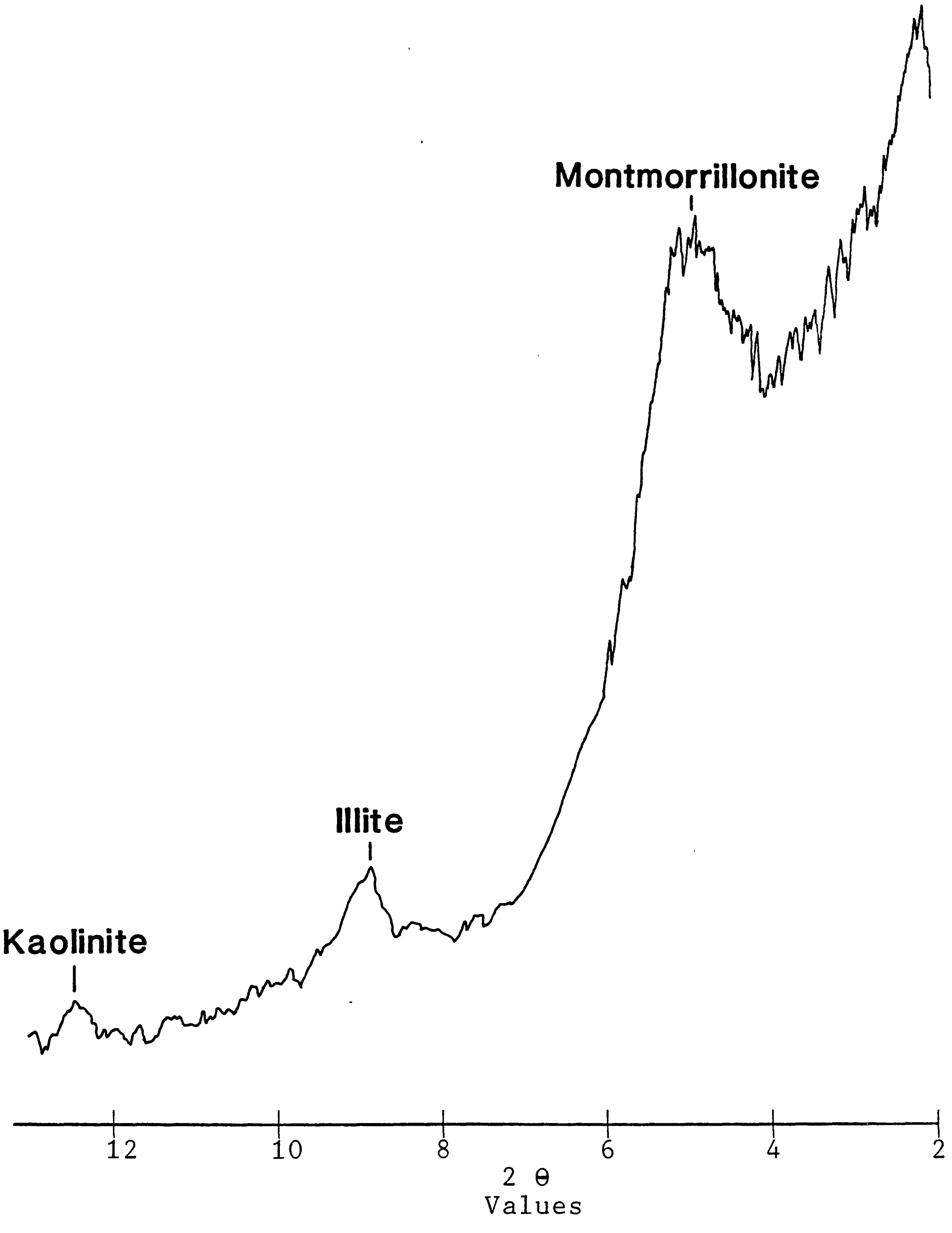


Figure 22. X-Ray Diffraction Pattern Typical of B Horizon Glycolated Clay Extracts of the Williams and Parshall-Lihen Loams

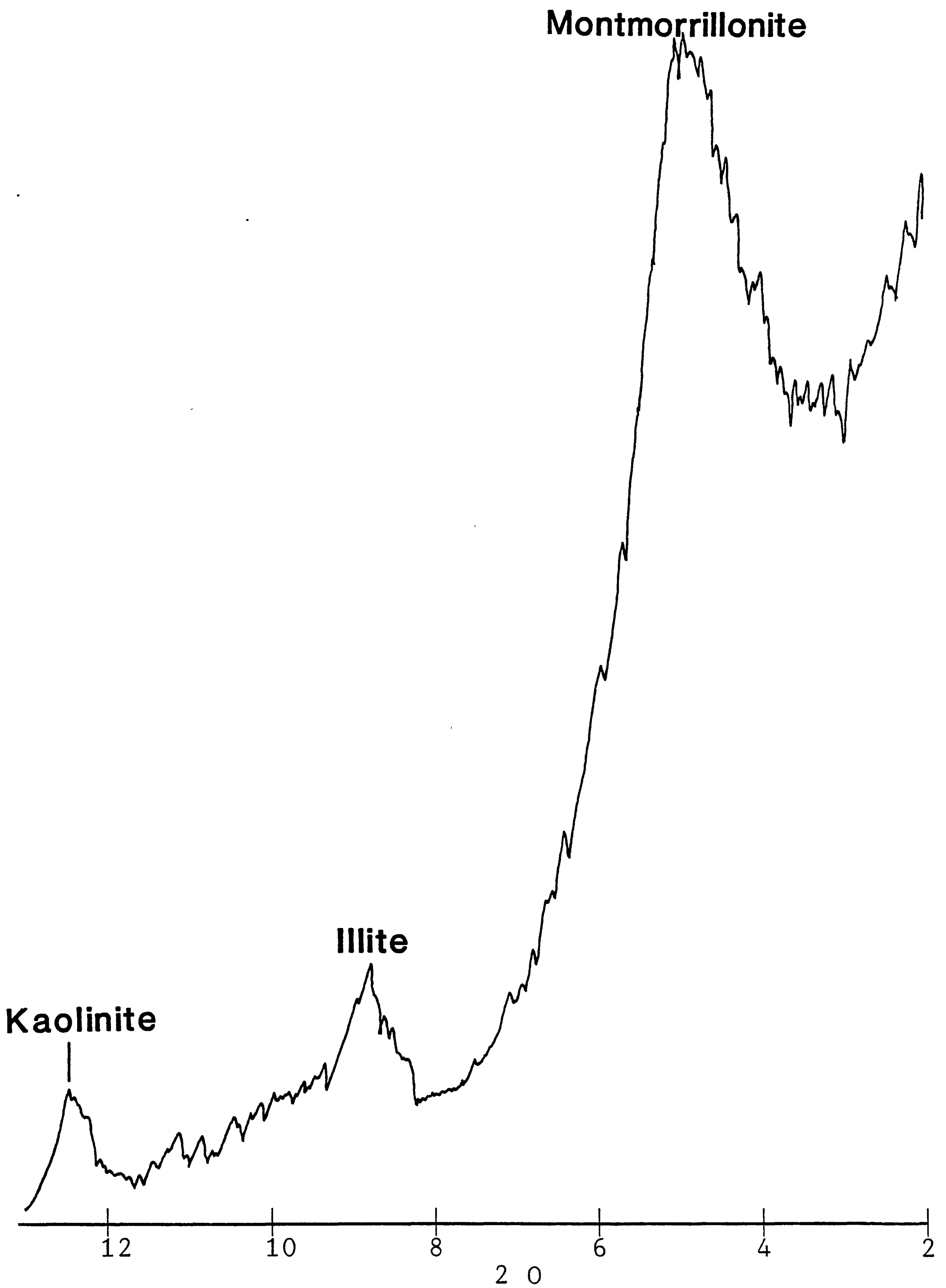


Figure 23. X-Ray Diffraction Pattern Typical of C Horizon Glycolated Clay Extracts of the Williams and Parshall-Lihen Loams

CHAPTER VI

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Summary

The present lack of data regarding the spatial distribution of the constituents and parameters involved in the adsorption of organic chemicals in soils provided the impetus for this study. The objective of this study was to determine the aerial and vertical trends of the soil organic matter (SOM) content, the cation exchange capacity (CEC), and the most prominent exchangeable cations. The scope of this investigation was limited to the statistical sampling of the Williams and Parshall - Lihen loams at three levels of resolution. Laboratory analysis of the aforementioned constituents was followed by statistical analysis to determine spatial trends and interrelationships. All information regarding the importance of these parameters in adsorption reactions, as well as the description of the study area's physical characteristics, was taken from published sources.

The Apple Creek basin in south central North Dakota was selected for several reasons. An extensive network of section roads allowed easy access to most parts of the basin. The prevailing soil types are Mollisols which have high organic matter contents and are representative of the Great Plains type soils. The area has been affected by glaciation which is characteristic of the northern United States. The acceptance by the land owners to sampling on their property, and the aid offered by the North Dakota Water Commission, mitigated many of the problems often encountered in field studies.

The physiography of the study area can be characterized by a hummocky topography. The Williams and Parshall - Lihen loams developed on glacial till and outwash deposits of the Napolean and Long Lake glacial advances, respectively. The Williams loam has by far the largest surface area within the region. The Parshall - Lihen loam is concentrated in the southern third of the study area.

Bedrock formations dip uniformly to the northwest with Upper Cretaceous to Paleocene units being represented. The surficial geology is indeed more complex and consists of a maze of glacial (ie. glacial lake, morainal, outwash) and alluvial unconsolidated deposits.

The Napolean and Long Lake glacial advances resulted in the deposition of a thin ground moraine in the northern half of the study area and thick outwash deposits in the southern half. These outwash channels are excellent aquifers which are fed by the surrounding bedrock. Potentiometric surface contours indicate that the Apple Creek is gaining (perennial) in the southern half of the study area. The lack of developed outwash channels in the north have resulted in losing (ephemeral) conditions.

The study area was divided into 58 sampling localities. Outcrops of the Williams and Parshall - Lihen loams were sampled at the A, B, and C horizons wherever possible. All sites located within a locality were combined and analyzed as one sample. This 'sampling by increments' method sacrifices resolution in order to obtain a more representative data base. The Williams loam was sampled in 47 localities confined to the northern two-thirds of the basin. The Parshall - Lihen loam was sampled in 10 of the southernmost localities.

At the local level, two - five by five plots were sampled at one foot and fifty feet spacings. These grids were superimposed randomly on a Williams loam outcrop. A continuous, shelby tube core was extracted to a depth of 15.5 feet adjacent to the local sampling grids.

Several methods were attempted to determine SOM content. Combustion methods, generally utilizing a LECO total organic carbon (TOC) analyzer, are becoming more prevalent because of the complete combustion of organic matter. Redox methods, using sodium dichromate as an oxidizing agent, remain as the faster, cheaper procedures, however, with comparable accuracy and precision. A linear regression was established by running samples through both methods, and subsequent redox values were standardized to combustion values for TOC. SOM contents (% by weight) were obtained using the assumption that 58% of organic matter consists of organic carbon. TOC values are multiplied by this 'Van Bemelen' factor (1.724).

The prevalent ammonium electrode determination of CEC could not be used on the North Dakota soils. As a result, each exchangeable cation was quantified individually using the atomic absorption (AA) spectrophotometer. The CEC was then calculated by the summation of these exchangeabble cations (Ca, Mg, Na, K).

Trace element concentrations were determined by x-ray fluorescence in the core samples.

Bulk x-ray diffraction analysis was completed on some of the aerial soil samples. Clay extracts were also prepared and analyzed by x-ray diffraction.

All of the raw data were statistically analyzed using the Statistical Analysis System (SAS) available on Oklahoma State University's mainframe computer. Three programs, PROC UNIVARIATE, PROC GLM, and PROC CORR, were used extensively to characterize the distributions and relationships of the geochemical parameters.

PROC UNIVARIATE tests for normal distributions by generating the Shapiro-Wilk test statistic. PROC GLM is an acronym for General Linear Model and determines linear regressions between different parameters, while PROC CORR calculates correlation coefficients between different parameters.

SOM contents were found to decrease with depth both in the aerial soil samples and in the Williams loam core. The data was found to be normally distributed with the sample error deviation being considerably smaller than the population standard deviation. The standard deviations of the local samples were smaller than the regional samples supporting the hypothesis of a regional variation. The program PROC GLM indicated aerial trends of SOM at the regional scale within the Williams loam but not at the local scale.

CEC values were also normally distributed and increased with depth. A geographic variation of CEC was not indicated, however, by the program PROC GLM.

CEC was only found to be a function of SOM content in the Parshall - Lihen A horizon where there is a limited clay content.

Illite and kaolinite were found in the A horizons of the Williams and Parshall - Lihen loams. Montmorillonite, illite, and kaolinite were present in the B and C horizons of both soil types. Changes in CEC appear to be related to clay quantity rather than clay type.

Conclusions

The five factors involved in soil formation must be considered to explain the variation of SOM within the Apple Creek basin, and elsewhere. These are parent material, climate, time, topography, and biological activity. The Williams loam developed on glacial till which, in general, varies aerially in both chemical and physical traits. The C horizon would be most affected by variations in parent material. The SOM distribution within the C horizon, however, does not correlate with any geologic trends, including changes in till origin.

Because of the low relief and mid-continental location, climate would not be expected to be a factor within the study area regarding SOM distributions. The time allowed for soil formation is also approximately equal for the area as the glaciers receded 12,000 to 13,000 years ago.

The effects of topography and biological activity on SOM content would be seen in the A horizon. Variations in the B horizon would be affected by both A and C horizon SOM distributions.

Topography appears to be a very important factor in the development of SOM in the A horizon. Predicted values of SOM show a general decrease in content with decrease in elevation. Actual SOM values further refine the downstream variation.

Dependence of organic mattter contents on biological activity would only be proven by a biological assay which is beyond the scope of this project.

The most significant result of this study is the characterization of the aerial and vertical trends of SOM. A composite map of relative SOM concentrations within the Williams loam is shown in Figure 24. This map outlines three broad regions as possessing high, medium, and low

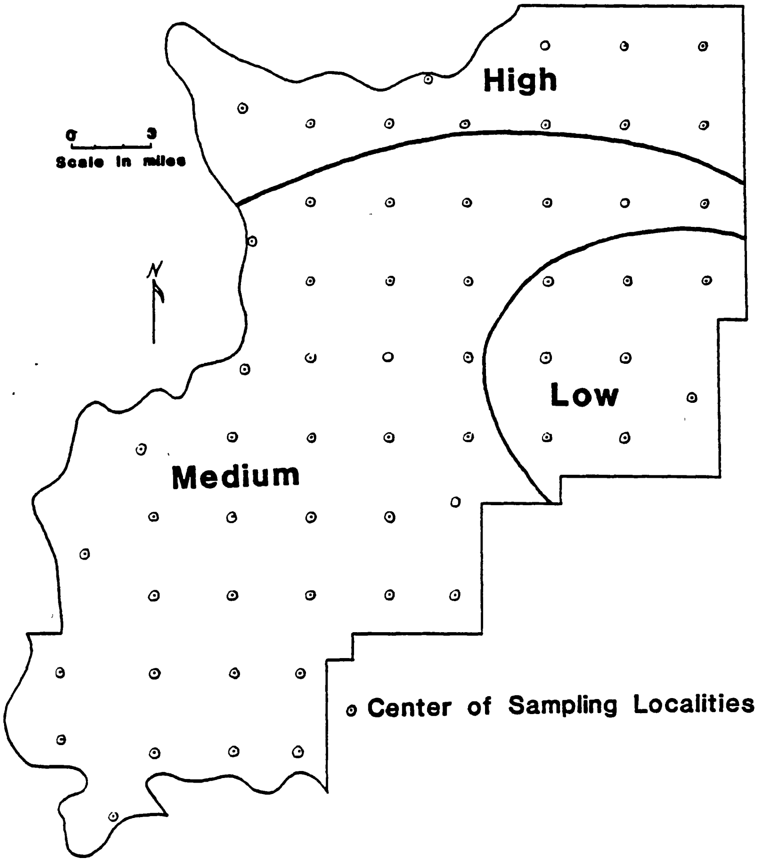


Figure 24. Relative SOM Concentrations Within the Williams Loam, Composite Map

organic matter concentrations within the unsaturated zone.

This map may be useful in land use planning under certain confining conditions. It must be understood that SOM only affects adsorption significantly in the unsaturated zone. As a result, this map is most useful in modeling the attenuation of contaminants in the unsaturated zone. Restrictions involving the types of organic chemicals that will be adsorbed onto SOM also exist. Hydrophobic, non-polar organic chemicals would have the greatest distribution coefficients. Retardation of these types of chemicals in unsaturated flow would be most significant. Adsorption on SOM occurs primarily because of its high CEC, but hydrophobic attachment of organics also occurs on SOM surfaces. In either case, there is a limited number of sites available for adsorption of organic chemicals. This restricts the use of the SOM map to the aerial spraying of low concentration wastes.

Suggestions for Further Research

SOM distributions in the C horizon of the Williams loam are most likely the result of changes in the physical and chemical characteristics of the glacial till upon which it developed. Measurements of till characteristics would clarify these relationships. A basinal biological assay would define the affect of biota on SOM distributions.

Adsorption studies should follow to determine aerial trends in distribution coefficient values. Likewise, bulk density and effective porosity measurements would be required to calculate retardation factors for unsaturated flow. As important as what reactions occur in the unsaturated zone is the quality of water entering the saturated zone.

This type of study can be applied to any area. The resolution of sampling required may be lower, but detailed tests in several other soil types should be completed to determine the confidence limits of various resolution sampling designs.

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APPENDIXES

APPENDIX A

PROC UNIVARIATE STATEMENTS

```
DATA APLCRK;

INFILE APPLCREK;

INPUT SOIL$ 1 LOCATION 2-3 HORIZON$ 4 X 7-9 Y 11-13
  SOM 15-18 CEC 20-23 CA 25-28 MG 30-33 K 35-38
  NA 40-43 CCC 45-48 EA 50-52;

PROC SORT; BY SOIL HORIZON;

PROC UNIVARIATE PLOT FREQ NORMAL;
  VAR SOM CEC CA MG K NA CCC EA; BY SOIL HORIZON;

PROC PRINT;

RUN;
```

APPENDIX B

PROC GLM STATEMENTS

```
100  DATA APLCRK;

200  INFILE APPLCREK;

300  INPUT SOIL$ 1 LOCATION 2-3 HORIZON$ 4 X 7-9 Y 11-13
       SOM 15-18 CEC 20-23 CA 25-28 MG 30-33 K 35-38
       NA 40-43 CCC 45-48 EA 50-52;

400  PROC SORT; BY SOIL HORIZON;

500  PROC GLM; MODEL SOM = X Y X*Y X*X Y*Y;
       OUTPUT OUT = PREDICT P = SOMPRDCT;
       BY SOIL HORIZON;

600  PROC PLOT DATA = PREDICT; BY SOIL HORIZON;
       PLOT Y*X = SOMPRDCT / CONTOUR = 4
       VAXIS = 0 TO 180 BY 20 HAXIS = 0 TO 140 BY 20
       VPOS = 45 HPOS = 45;

700  PROC PRINT; VAR X Y SOM SOMPRDCT;

800  RUN;
```

APPENDIX C

PROC CORR STATEMENTS

```
100  DATA APLCRK;

200  INFILE APPLCREK;

300  INPUT SOIL$ 1 LOCATION 2-3 HORIZON$ 4 X 7-9 Y 11-13
       SOM 15-18 CEC 20-23 CA 25-28 MG 30-33 K 35-38
       NA 40-43 CCC 45-48 EA 50-52;

400  PROC SORT; BY SOIL HORIZON;

500  PROC CORR; BY SOIL HORIZON;

600  PROC PRINT;

700  RUN;
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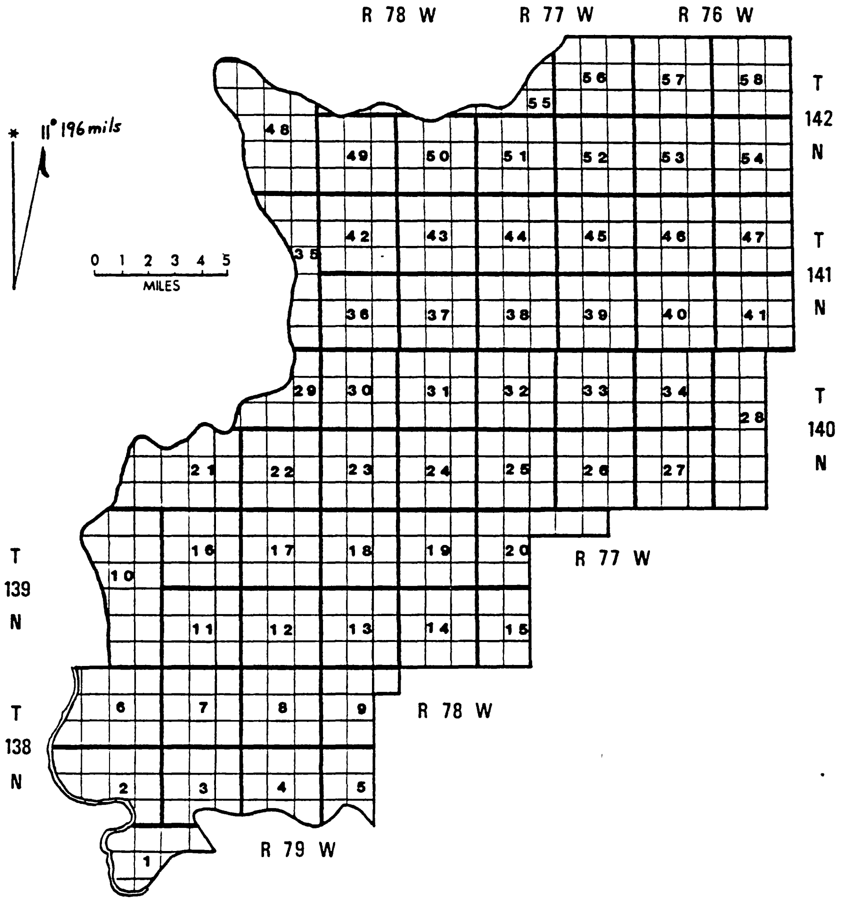
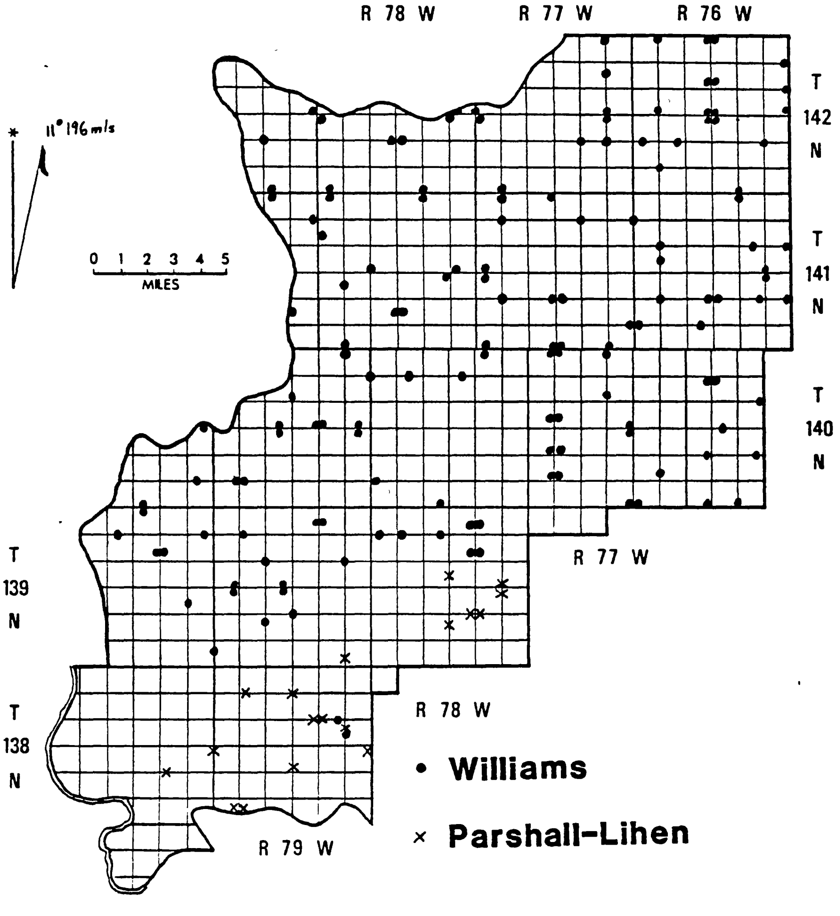
APPENDIX D

SAMPLING LOCALITY AND SAMPLE LOCATION MAPS



Regional Sampling Design


R 78 W
R 77 W
R 76 W
T 142 N
T 141 N
T 140 N
T 139 N
T 138 N
R 77 W
R 78 W
R 79 W
11° 196 mls
0 1 2 3 4 5
MILES
• Williams
× Parshall-Lihen

APPENDIX E

REGIONAL SOILS / ANALYTICAL VALUES

SOIL	LOCATION	HORIZON	X	Y	SOM	CEC	CA	MG	K	NA	CCC
P	20	A	83	66	2.700	21.70	17.80	2.01	1.650	0.284	3.94
P	19	A	69	63	3.590	27.30	21.10	3.35	2.520	0.282	6.15
P	15	A	83	46	3.750	23.10	17.10	3.31	2.200	0.477	5.99
P	14	A	69	46	2.890	22.70	17.20	3.04	2.230	0.214	5.48
P	13	A	53	46	3.230	24.70	19.20	3.04	2.190	0.230	5.46
P	9	A	50	30	2.330	16.70	12.10	2.28	1.910	0.387	4.58
P	8	A	36	30	2.610	19.20	14.80	2.44	1.600	0.370	4.41
P	5	A	50	14	1.970	11.40	7.75	2.10	1.190	0.371	3.66
P	4	A	36	14	3.180	22.50	17.40	3.28	1.470	0.398	5.15
P	3	A	20	14	2.750	18.30	14.50	1.93	1.390	0.437	3.76
P	20	B	83	66	1.310	23.00	19.20	2.51	0.967	0.365	3.84
P	19	B	69	63	1.320	18.10	13.40	2.70	1.730	0.306	4.74
P	15	B	83	46	1.110	54.30	47.10	5.26	1.160	0.773	7.19
P	14	B	69	46	1.060	51.70	43.40	6.44	0.990	0.843	8.27
P	13	B	53	46	1.330	19.10	14.40	3.17	1.060	0.433	4.66
P	9	B	50	30	1.180	13.40	9.66	2.14	0.931	0.685	3.76
P	8	B	36	30	0.974	10.70	7.30	2.04	0.561	0.332	2.93
P	5	B	50	14	0.970	8.25	5.18	1.45	1.020	0.598	3.07
P	4	B	36	14	1.570	23.50	19.40	3.19	0.573	0.382	4.15
P	3	B	20	14	0.869	18.40	16.00	1.19	0.575	0.626	2.39
P	20	C	83	66	0.441	77.20	72.70	3.57	0.356	0.587	4.51
P	19	C	69	63	0.664	125.00	120.00	4.08	0.693	0.501	5.27
P	15	C	83	46	0.442	162.00	154.00	5.62	1.180	1.330	8.13
P	14	C	69	46	0.667	301.00	279.00	19.10	0.852	3.260	23.20
P	13	C	53	46	1.210	163.00	155.00	5.28	0.763	0.662	6.71
P	9	C	50	30	0.552	26.70	22.50	2.98	0.571	0.673	4.22
P	8	C	36	30	0.551	54.20	50.40	2.58	0.565	0.660	3.81
P	5	C	50	14	0.741	9.95	6.00	2.43	0.690	0.834	3.95
P	4	C	36	14	0.509	56.40	52.50	2.99	0.413	0.513	3.92
P	3	C	20	14	0.339	20.40	18.10	1.63	0.260	0.432	2.32
W	59	A	135	162	6.530	25.60	19.30	3.64	2.050	0.582	6.27
W	57	A	118	162	6.520	22.90	17.40	3.06	1.870	0.611	5.54
W	56	A	102	162	5.260	22.30	16.30	3.60	1.630	0.773	6.00
W	55	A	77	155	6.150	23.30	17.20	3.50	2.090	0.513	6.10
W	54	A	135	145	6.970	26.10	19.80	3.69	1.900	0.752	6.34
W	53	A	118	145	9.700	31.30	24.30	4.14	2.250	0.589	6.98
W	52	A	102	145	5.550	28.90	21.60	4.31	2.210	0.733	7.25
W	51	A	85	145	6.610	27.20	20.70	3.71	2.040	0.709	6.46
W	50	A	69	145	4.050	20.40	15.00	3.49	1.470	0.473	5.43
W	49	A	53	145	4.560	19.60	14.20	3.01	1.680	0.665	5.36
W	48	A	38	148	5.540	23.60	18.00	3.65	1.380	0.579	5.62
W	47	A	135	129	5.830	25.60	19.40	3.68	1.840	0.645	6.17
W	46	A	118	129	6.560	26.80	19.40	4.32	2.410	0.664	7.39
W	45	A	102	129	6.130	25.00	18.90	3.21	2.370	0.542	6.12
W	44	A	85	129	5.590	22.30	17.40	3.55	1.260	0.571	5.38
W	43	A	69	129	4.740	18.70	14.30	2.77	1.140	0.535	4.45
W	42	A	53	129	5.120	22.00	17.20	2.89	1.290	0.597	4.78
W	41	A	135	113	5.800	25.00	20.60	3.32	1.890	0.203	5.41
W	40	A	118	113	4.780	19.70	14.50	2.86	1.720	0.618	5.20
W	39	A	102	113	6.030	23.10	17.00	3.41	2.020	0.678	6.11
W	38	A	85	113	5.130	37.70	28.80	5.23	3.190	0.478	8.90
W	37	A	69	113	5.190	23.20	15.90	4.35	2.630	0.364	7.34
W	36	A	53	113	5.200	28.30	22.90	3.59	1.930	0.359	5.88
W	35	A	40	121	4.320	27.10	21.10	3.84	1.910	0.245	6.00

SOIL	LOCATION	HORIZON	X	Y	SOM	CEC	CA	MG	K	NA	CCC
W	34	A	118	96	3.100	20.5	14.20	2.41	3.370	0.479	6.26
W	33	A	102	96	4.970	29.9	22.40	4.77	2.410	0.296	7.48
W	32	A	85	96	4.370	24.6	18.50	4.08	1.510	0.478	6.07
W	31	A	69	96	4.480	34.5	26.00	5.37	2.670	0.488	8.53
W	30	A	53	96	4.600	26.8	20.30	3.75	2.260	0.513	6.52
W	29	A	38	94	2.900	28.3	24.50	2.06	1.470	0.254	3.78
W	28	A	132	87	4.420	24.0	18.40	3.01	2.350	0.285	5.65
W	27	A	113	80	5.330	24.6	18.20	3.38	2.790	0.250	6.42
W	26	A	102	80	4.730	24.5	18.20	4.00	1.840	0.433	6.28
W	25	A	85	80	2.660	38.9	31.90	4.31	2.330	0.405	7.05
W	24	A	69	80	4.160	25.8	21.00	2.39	2.170	0.261	4.82
W	23	A	53	80	4.300	23.4	17.80	3.92	1.270	0.405	5.60
W	22	A	36	80	4.670	31.6	24.00	4.60	2.580	0.451	7.63
W	21	A	17	77	4.690	46.1	38.80	4.92	2.180	0.217	7.32
W	20	A	83	66	4.560	24.9	18.50	3.50	2.440	0.490	6.43
W	19	A	69	63	4.620	23.0	16.30	3.97	2.150	0.610	6.73
W	18	A	53	63	4.080	27.6	20.00	3.70	3.390	0.521	7.61
W	17	A	36	63	4.180	30.4	22.50	5.04	2.580	0.278	7.90
W	16	A	20	63	4.090	33.8	23.30	7.31	2.550	0.638	10.50
W	12	A	36	46	4.470	35.9	27.50	5.51	2.600	0.282	8.39
W	11	A	20	46	5.120	29.3	21.40	4.95	2.230	0.722	7.90
W	10	A	5	55	3.500	51.9	44.80	4.63	2.230	0.285	7.15
W	9	A	50	30	2.870	19.9	14.70	2.36	2.560	0.282	5.20
W	58	B	135	162	1.260	186.0	177.00	7.30	1.190	0.391	8.88
W	57	B	113	162	1.730	21.1	15.90	3.72	1.080	0.429	5.23
W	56	B	102	162	1.310	39.3	30.00	7.74	1.120	0.423	9.28
W	55	B	77	155	1.730	122.0	113.00	7.45	0.796	0.751	9.00
W	54	B	135	145	1.370	21.8	15.10	5.02	1.290	0.369	6.68
W	53	B	113	145	1.590	56.7	46.00	8.34	1.390	0.949	10.70
W	52	B	102	145	1.770	27.5	20.20	5.88	0.990	0.393	7.26
W	51	B	85	145	2.140	49.7	40.70	6.91	1.510	0.612	9.03
W	50	B	69	145	0.975	146.0	136.00	8.49	0.851	0.763	10.10
W	49	B	53	145	1.410	51.7	43.80	6.47	0.764	0.624	7.86
W	48	B	38	148	2.000	28.6	20.60	6.50	0.881	0.576	7.96
W	47	B	135	129	1.140	121.0	112.00	7.72	0.980	0.759	9.46
W	46	B	118	129	1.320	30.8	24.30	5.19	0.851	0.460	6.50
W	45	B	102	129	1.620	35.1	24.80	7.97	1.420	0.866	10.30
W	44	B	85	129	1.270	21.4	10.50	8.57	1.190	1.180	10.90
W	43	B	69	129	1.170	18.3	11.80	5.11	0.776	0.580	6.47
W	42	B	53	129	1.330	28.3	21.90	5.09	0.593	0.709	6.39
W	41	B	135	113	1.150	118.0	109.00	7.97	0.996	0.511	9.48
W	40	B	113	113	1.070	100.0	91.90	6.56	1.080	0.691	8.33
W	39	B	102	113	1.420	55.2	46.20	7.10	1.300	0.580	8.98
W	38	B	85	113	1.150	142.0	127.00	9.69	1.410	3.670	14.80
W	37	B	69	113	1.090	98.5	88.70	7.53	0.585	1.640	9.76
W	36	B	53	113	1.230	177.0	166.00	10.10	0.732	0.602	11.40
W	35	B	40	121	1.290	50.3	41.20	7.73	0.775	0.628	9.13
W	34	B	118	96	0.963	14.5	9.43	3.21	1.190	0.657	5.06
W	33	B	102	96	1.420	146.0	135.00	9.20	1.100	0.859	11.20
W	32	B	85	96	1.560	44.5	38.00	5.26	0.766	0.453	6.48
W	31	B	69	96	1.130	58.2	47.80	8.73	1.080	0.612	10.40
W	30	B	53	96	1.330	38.6	31.60	5.61	0.773	0.585	6.97
W	29	B	38	94	1.240	157.0	150.00	5.41	0.563	0.655	6.63
W	28	B	132	87	1.020	56.0	47.80	6.34	0.965	0.921	8.23

SOIL	LOCATION	HORIZON	X	Y	SOM	CEC	CA	MG	K	NA	CCC
W	27	B	116	80	1.090	38.0	29.3	6.96	1.090	0.615	8.67
W	26	B	102	80	1.110	84.3	75.9	7.34	0.750	0.323	8.41
W	25	B	85	80	0.608	27.2	20.5	5.59	0.836	0.319	6.75
W	24	B	69	80	1.450	184.0	178.0	5.08	0.767	0.389	6.24
W	23	B	53	80	1.510	22.9	15.7	5.83	0.900	0.445	7.18
W	22	B	36	80	1.740	61.3	52.4	7.31	0.858	0.685	8.85
W	21	B	17	77	1.490	91.5	79.7	9.69	0.881	1.180	11.80
W	20	B	85	66	1.390	35.2	29.2	4.79	0.812	0.375	5.98
W	19	B	69	63	1.430	53.1	45.3	6.30	1.110	0.406	7.82
W	18	B	53	63	1.370	85.5	68.8	7.68	1.030	8.030	15.70
W	17	B	36	63	1.730	107.0	95.7	9.16	1.070	0.580	10.80
W	15	B	20	63	1.360	125.0	99.8	20.80	0.951	3.840	25.60
W	12	B	36	45	1.650	37.4	29.1	6.96	0.893	0.484	8.34
W	11	B	20	46	1.330	135.0	113.0	19.50	1.140	1.010	21.70
W	10	B	[illegible]	55	1.850	128.0	121.0	6.03	0.730	0.518	7.28
W	9	B	50	30	1.590	15.7	11.4	2.65	1.010	0.595	4.26
W	58	C	135	162	0.574	164.0	150.0	11.30	1.010	1.350	13.70
W	57	C	118	162	0.650	53.1	52.0	5.06	0.388	0.649	6.10
W	56	C	102	162	0.799	77.9	67.7	8.37	0.846	1.020	10.20
W	55	C	77	155	0.628	192.0	175.0	13.90	0.795	1.800	16.50
W	54	C	135	145	0.811	106.0	93.6	8.74	0.774	0.997	10.50
W	53	C	118	145	0.571	114.0	99.4	11.30	0.744	2.730	14.80
W	52	C	102	145	0.531	146.0	132.0	11.50	0.795	1.350	13.60
W	51	C	85	145	0.661	127.0	110.0	15.60	0.725	0.947	17.30
W	50	C	69	145	0.475	237.0	182.0	52.60	0.620	1.370	55.10
W	49	C	53	145	0.561	153.0	134.0	16.90	0.466	1.220	18.60
W	48	C	38	145	0.691	150.0	137.0	11.60	0.558	1.130	13.30
W	47	C	135	120	0.639	120.0	104.0	12.70	0.884	2.480	16.10
W	46	C	118	120	0.578	81.7	72.7	7.32	0.651	1.030	9.00
W	45	C	102	120	0.492	112.0	101.0	8.39	0.818	1.430	10.60
W	44	C	85	120	0.491	135.0	120.0	11.90	0.891	2.500	15.30
W	43	C	69	120	0.422	40.1	33.6	5.33	0.347	0.859	6.54
W	42	C	53	120	0.503	113.0	101.0	14.50	0.541	1.580	16.60
W	41	C	135	113	0.454	123.0	103.0	16.10	1.350	2.920	20.40
W	40	C	118	113	0.538	156.0	142.0	9.71	1.260	2.540	13.50
W	39	C	102	113	0.565	153.0	143.0	12.70	0.663	1.310	14.70
W	38	C	85	113	0.535	95.0	72.9	14.70	0.639	6.730	22.10
W	37	C	69	113	0.417	74.0	46.2	18.50	0.575	8.760	27.80
W	36	C	53	113	0.433	106.0	85.3	16.30	0.548	3.390	20.20
W	35	C	40	121	0.554	119.0	104.0	12.70	0.267	1.300	16.40
W	34	C	118	95	0.746	19.1	12.8	4.80	0.732	0.722	6.25
W	33	C	102	96	0.549	118.0	101.0	14.10	0.489	2.000	16.60
W	32	C	85	95	0.584	140.0	129.0	9.52	0.351	1.190	11.10
W	31	C	69	96	0.600	71.0	53.2	14.70	0.591	2.530	17.80
W	30	C	53	95	0.477	42.5	34.3	7.21	0.291	0.703	8.21
W	29	C	38	94	0.655	88.1	78.5	8.13	0.538	0.925	9.59
W	28	C	132	87	0.600	85.9	72.1	12.10	0.605	1.050	13.80
W	27	C	118	80	0.609	156.0	141.0	13.00	0.607	1.570	15.20
W	26	C	102	80	0.630	163.0	156.0	5.28	0.753	1.430	7.47
W	25	C	85	80	0.367	23.6	16.5	5.13	0.819	1.150	7.10
W	24	C	69	80	0.923	89.8	82.9	5.41	0.643	0.329	6.38
W	23	C	53	80	0.562	154.0	142.0	10.50	0.384	0.776	11.70
W	22	C	36	80	0.837	121.0	104.0	15.00	0.436	1.610	17.00
W	21	C	17	77	0.608	83.3	61.5	14.90	0.621	6.320	21.80

SOIL	LOCATION	HORIZON	X	Y	SOM	CEC	CA	MG	K	NA	CCC
W	20	C	13	56	0.686	101.0	90.4	9.48	0.451	1.200	11.10
W	19	C	39	63	0.482	239.0	228.0	9.56	0.540	1.040	11.10
W	18	C	53	63	0.933	57.9	37.0	9.87	0.641	10.400	20.90
W	17	C	36	63	0.706	87.0	69.4	15.10	0.765	1.710	17.60
W	16	C	20	63	1.180	95.8	84.2	8.86	0.504	2.280	11.60
W	12	C	36	46	0.842	128.0	111.0	13.30	0.644	2.640	16.60
W	11	C	20	46	0.574	130.0	110.0	18.20	0.496	1.450	20.10
W	10	C	5	55	0.845	98.7	86.1	10.10	0.584	1.390	12.60
W	9	C	50	30	1.270	59.4	53.3	5.32	0.397	0.391	6.11

APPENDIX F

LOCAL SOILS / ANALYTICAL VALUES

SPACE	SOIL	LOCATION	HORIZON	X	Y	SOM
4	W	25	A	0	98	6.650
4	W	24	A	1	98	6.000
4	W	23	A	2	98	5.990
4	W	22	A	3	98	6.060
4	W	21	A	4	98	6.740
4	W	20	A	4	99	5.350
4	W	19	A	3	99	6.460
4	W	18	A	2	99	7.150
4	W	17	A	1	99	4.910
4	W	16	A	0	99	7.630
4	W	15	A	0	100	3.450
4	W	14	A	1	100	5.600
4	W	13	A	2	100	6.160
4	W	12	A	3	100	6.830
4	W	11	A	4	100	7.340
4	W	10	A	4	101	5.150
4	W	9	A	3	101	5.790
4	W	8	A	2	101	5.300
4	W	7	A	1	101	6.610
4	W	6	A	0	101	7.330
4	W	5	A	0	102	7.330
4	W	4	A	1	102	6.320
4	W	3	A	2	102	7.570
4	W	2	A	3	102	5.490
4	W	1	A	4	102	5.560
4	W	25	B	0	98	2.810
4	W	24	B	1	98	2.330
4	W	23	B	2	98	2.250
4	W	22	B	3	98	2.550
4	W	21	B	4	98	2.110
4	W	20	B	4	99	1.960
4	W	19	B	3	99	1.890
4	W	18	B	2	99	2.400
4	W	17	B	1	99	2.200
4	W	16	B	0	99	2.110
4	W	15	B	0	100	2.500
4	W	14	B	1	100	2.320
4	W	13	B	2	100	2.450
4	W	12	B	3	100	1.850
4	W	11	B	4	100	2.570
4	W	10	B	4	101	1.890
4	W	9	B	3	101	2.090
4	W	8	B	2	101	2.330
4	W	7	B	1	101	2.380
4	W	6	B	0	101	2.510
4	W	5	B	0	102	1.970
4	W	4	B	1	102	2.070
4	W	3	B	2	102	2.520
4	W	2	B	3	102	2.220
4	W	1	B	4	102	1.340
4	W	25	C	0	98	0.769
4	W	24	C	1	98	0.739
4	W	23	C	2	98	0.728
4	W	22	C	3	98	0.632

SPACE	SOIL	LOCATION	HORIZON	X	Y	SOM
4	W	21	C	4	98	0.627
4	W	20	C	4	99	0.556
4	W	19	C	3	99	0.609
4	W	18	C	2	99	0.595
4	W	17	C	1	99	0.740
4	W	16	C	0	99	0.743
4	W	15	C	0	100	0.824
4	W	14	C	1	100	0.590
4	W	13	C	2	100	0.679
4	W	12	C	3	100	0.572
4	W	11	C	4	100	0.580
4	W	10	C	4	101	0.677
4	W	9	C	3	101	0.615
4	W	8	C	2	101	0.795
4	W	7	C	1	101	0.991
4	W	6	C	0	101	0.599
4	W	5	C	0	102	0.565
4	W	4	C	1	102	0.854
4	W	3	C	2	102	0.752
4	W	2	C	3	102	0.915
4	W	1	C	4	102	0.664
200	W	25	A	2	0	5.470
200	W	24	A	52	0	5.770
200	W	23	A	102	0	6.410
200	W	22	A	152	0	6.140
200	W	21	A	202	0	6.220
200	W	20	A	202	50	6.460
200	W	19	A	152	50	5.020
200	W	18	A	102	50	5.040
200	W	17	A	52	50	5.650
200	W	16	A	2	50	5.610
200	W	15	A	2	100	6.150
200	W	14	A	52	100	5.730
200	W	13	A	102	100	5.980
200	W	12	A	152	100	6.080
200	W	11	A	202	100	3.910
200	W	10	A	202	150	5.410
200	W	9	A	152	150	6.410
200	W	8	A	102	150	5.750
200	W	7	A	52	150	6.600
200	W	6	A	2	150	5.740
200	W	5	A	2	200	4.720
200	W	4	A	52	200	5.010
200	W	3	A	102	200	5.070
200	W	2	A	152	200	5.900
200	W	1	A	202	200	5.020
200	W	25	B	2	0	2.430
200	W	24	B	52	0	1.890
200	W	23	B	102	0	2.160
200	W	22	B	152	0	1.900
200	W	21	B	202	0	2.020
200	W	20	B	202	50	2.520
200	W	19	B	152	50	2.280
200	W	18	B	102	50	2.370

SPACE	SOIL	LOCATION	HORIZON	X	Y	SOM
200	W	17	B	52	50	1.800
200	W	16	B	2	50	2.390
200	W	15	B	2	100	2.450
200	W	14	B	52	100	2.360
200	W	13	B	102	100	1.950
200	W	12	B	152	100	2.250
200	W	11	B	202	100	1.990
200	W	11	B	202	150	2.090
200	W	9	B	152	150	2.210
200	W	8	B	102	150	2.220
200	W	7	B	52	150	1.920
200	W	6	B	2	150	1.800
200	W	5	B	2	200	1.730
200	W	4	B	52	200	1.920
200	W	3	B	102	200	1.920
200	W	2	B	152	200	1.270
200	W	1	B	202	200	1.870
200	W	25	C	2	0	0.998
200	W	24	C	52	0	1.120
200	W	23	C	102	0	0.769
200	W	22	C	152	0	0.779
200	W	21	C	202	0	0.711
200	W	20	C	202	50	0.817
200	W	19	C	152	50	0.906
200	W	18	C	102	50	0.941
200	W	17	C	52	50	0.733
200	W	16	C	2	50	0.772
200	W	15	C	2	100	0.679
200	W	14	C	52	100	0.656
200	W	13	C	102	100	0.839
200	W	12	C	152	100	0.801
200	W	11	C	202	100	0.708
200	W	10	C	202	150	0.790
200	W	9	C	152	150	0.841
200	W	8	C	102	150	0.740
200	W	7	C	52	150	0.850
200	W	6	C	2	150	0.854
200	W	5	C	2	200	0.992
200	W	4	C	52	200	0.879
200	W	3	C	102	200	0.921
200	W	2	C	152	200	0.924
200	W	1	C	202	200	1.290

VITA

Duane Allen Wanty

Candidate for the Degree of

Master of Science

Thesis: THE SPATIAL VARIATION OF SEVERAL HYDROGEOCHEMICAL PARAMETERS WITHIN THE APPLE CREEK DRAINAGE BASIN, NORTH DAKOTA

Major Field: Geology

Biographical:

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