ORGANIC CARBON AND TRIHALOMETHANE FORMATION POTENTIAL IN GROUNDWATER AND SEDIMENT OF GLACIAL BURIED-VALLEY AQUIFERS IN NORTHEASTERN KANSAS

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My parents deserve a special thanks for always encouraging me to persevere and attain my goals.

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ABSTRACT

The primary purpose of this study was to examine the important groundwater quality and sediment parameters in glacial buried-valley aquifers and to then establish relationships between the groundwater quality and the characteristics of the surrounding sediments. This was accomplished by obtaining sediment cores and constructing monitoring wells at six sites in northeast Kansas. The sediment cores were analyzed for color, pH, moisture content, total organic carbon (TOC), extractable organic carbon (EOC), extractable trihalomethane formation potential (ETFP), and extractable ammonium (NH_4^+). The groundwater monitoring wells were sampled seasonally and analyzed for dissolved organic carbon (DOC), trihalomethane formation potential (TFP), NH_4^+, iron (Fe), manganese (Mn), pH, and major cation and anion species.

Many of the groundwater samples contained DOC concentrations of > 2.0 mg/L and produced TFP concentrations at or above the 100 ug/L primary drinking water standard. At all sites the NH_4^+ concentrations increased with depth. An association between DOC and NH_4^+, Fe, and Mn was evident. Generally the groundwater samples containing higher concentrations of DOC, NH_4^+, Fe, and Mn produced higher TFP concentrations and yields. The TOC content of the sediment cores varied widely with depth and was highly related to the color of the sediment. At the majority of the sites, the TOC content was found to be highest in the topsoil sample, although the TOC increased again in the darker gray sediments located at the mid-depths of the cores. The ETFP concentrations and yields produced by the sediments were generally higher in the sediments at the sites with high TOC and extractable NH_4^+ concentrations in the deeper sediments.

Comparing the groundwater and core sediment data revealed strong relationships between DOC and TOC, TFP and ETFP, and aqueous NH_4^+ and extractable NH_4^+. The sites with higher DOC and TOC concentrations had higher aqueous NH_4^+ and extractable NH_4^+ concentrations and generally produced higher TFP and ETFP concentrations and yields. Three sites (a cross-section from Nemaha County) were found to have the highest overall concentrations of all constituents examined and thus also the poorest groundwater quality. To obtain higher quality groundwater, wells drilled in the glacial buried-valley aquifers of northeastern Kansas should be located where the lighter colored sediments are thickest and screened in the lighter upper sediments. Wells drilled into the higher yielding aquifers in the darker glacial deposits should be expected to produce water of poorer quality.

Department of Civil Engineering
May, 1987

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INTRODUCTION

A. Background

Because of the increased demand for groundwater in many areas and the requirement that all water supplies meet increasingly stringent water quality standards, a need exists for more information on groundwater quality and its relationship to the geologic formations it is taken from. In northeastern Kansas, glacial buried-valley aquifers are the major source of groundwater for public water supplies. Surface water in the area is scarce, and its use is often imparied by various water quality problems such as excessive algal growths, high concentrations of organic matter, and taste and odor problems. Therefore, the demand for groundwater in northeast Kansas is increasing.

Many of the groundwater supplies in northeast Kansas have been found to have concentrations of nitrate above the 45 mg/L primary drinking water standard promulgated by the EPA. In other wells high concentrations (exceeding primary or secondary standards) of ammonia, iron, manganese, total dissolved solids, and sulfate occur. In addition, levels of TOC above 1.0 mg/L are common, and some water samples have been found to produce concentrations of trihalomethanes (THMs) just below the EPA standard of 100 ug/L (Denne *et al*., 1984).

Due to such water quality problems, several test wells must often be drilled before good quality water is found. From the data available for this area, it is not presently possible to predict where to drill a well to obtain water of good quality. Thus, research is needed to discover what factors influence the water quality in this and other glacial buried-valley aquifers.

B. Research Objectives

The primary purpose of this study was to examine the important groundwater quality and sediment parameters in glacial buried-valley aquifers and to then establish the relationships between the groundwater quality and the characteristics of the surrounding sediments. Important objectives of this study included the following:

1. To examine the spatial (horizontal and vertical), temporal and seasonal variations in the concentrations of organic carbon and THM precursors in the groundwater;
2. To identify the geological and geochemical factors influencing the concentrations of organic matter in the sediments and groundwater;
3. To ascertain whether there is a relationship between sediment TOC and groundwater DOC;
4. To provide guidance, with respect to well location and depth, to those seeking high quality groundwater in glacial buried-valley aquifers; and
5. To determine what relationships might exist between the inorganic chemical quality of the groundwater (particularly NH_4^+, Fe, and Mn) and sediment characteristics, depth, season, location, local geology, etc.

C. Research Approach

Six study sites were chosen in northeast Kansas: one in Marshall County and five in Nemaha County (see Figure 1). Sediment samples (cores) were obtained from each site and were analyzed for color, pH, moisture content, extractable ammonium ion, TOC, EOC, and ETFP. Wells, at multiple depths, were constructed at each site and were sampled seasonally for DOC, TFP, pH, NH_4^+, total Fe, total Mn, and principal inorganic chemical constituents.

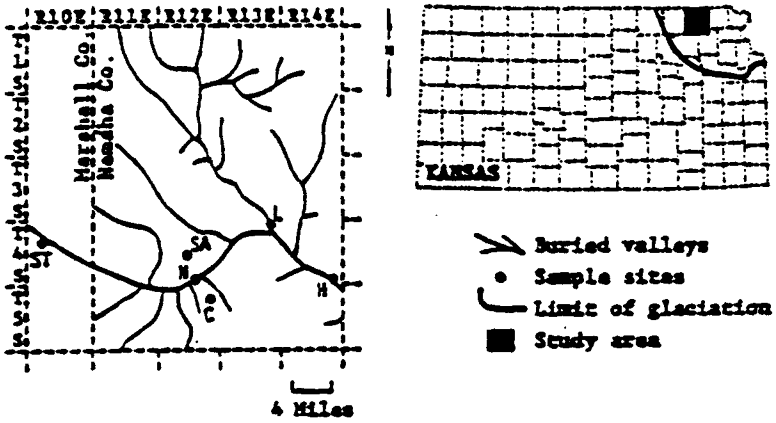

Figure 1: Study Site

RELATED RESEARCH

A. Organic Matter In Groundwater

Measurement

Dissolved organic carbon (DOC) and total organic carbon (TOC) are the parameters most often used to measure the natural organic carbon content found in groundwater. DOC is defined as the organic carbon passing through a 0.45 um membrane filter. DOC is a reliable measure of both the simple and complex organic molecules making up the dissolved organic load. Most of the DOC is smaller than the colloidal range of 0.001-0.45 um (Thurman, 1985a).

TOC is a measurement done without filtering the sample. It represents the sum of DOC and particulate organic carbon (POC). Groundwater samples taken from public and private water supply wells usually contain little particulate matter. Thus TOC and DOC values should be almost identical. In new wells set up for monitoring purposes and in wells that are infrequently pumped, large quantities of sediment are often brought up in the water. In such situations DOC is a more accurate measure of the organics actually present in the pore water. DOC is also more accurate because of the potential for incomplete combustion of particulate matter present during TOC analysis.

Concentration in Groundwater

DOC values for groundwater typically range from 0.2-15 mg/L (Leenheer _et al_., 1974; Maier _et al_., 1976; Spaulding _et al_., 1978; Barcelona, 1984). Exceptions to these values are found in the Southeastern U.S. and in semi-tropical regions where organic rich surface water recharges the groundwater. Here DOCs have been found to range from 6-15 mg/L (Thurman, 1985b). A comprehensive study done by Leenheer _et al_. (1974), which included 100 groundwater supplies in 27 states, including sandstone, gravel, limestone, and igneous aquifers, found the average and median DOCs for all aquifers but crystalline rock aquifers to be 1.2 mg/L and 0.7 mg/L respectively. The median value for crystalline rock was 0.5 mg/L. The DOC measurements were also found to be independent of the depth of the sample and its inorganic chemistry.

The 16 public groundwater supplies included in the study by Symons _et al_. (1975) had an average TOC of 1.85 mg/L (1.32 mg/L excluding one sample from Florida with a very high TOC). In a recent Kansas study, Miller _et al_. (1986) sampled 50 groundwater supplies representing most of the major aquifers in Kansas. The average TOC concentration (all samples were very clear except for two which were filtered) was 1.05 mg/L, ranging from 0.21 to 3.31 mg/L. Hence, TOC concentrations in Kansas groundwaters are similar to those found in other areas.

Trihalomethane Formation Potential

Natural organics in groundwater are in and of themselves rarely a serious contaminant problem. Rather, it is the THMs and other by-products formed by the reaction of free chlorine with natural organic matter present in the groundwater which are presently of greatest concern. Four THM species are formed: chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), chlorodibromomethane ($CHClBr_2$), and bromoform ($CHBr_3$). It has been documented that chloroform is an animal carcinogen and the other three species are suspected to be carcinogenic (NAS 1977, 1980, 1982). In addition to the formation of THMs, other organic halogen compounds are formed (Christman et al., 1983; Fleishacker and Randtke, 1983; Oliver, 1983). For the most part, the health effects of these other compounds are not known although some of these organic halogens have been shown to have mutanogenic effects (Kringstad et al., 1983). Because of the unknown nature of the public health risk posed by these compounds, in 1979 the EPA promulgated a National Primary Drinking Water Standard of 100 ug/L for total THM concentration for all drinking water supplies serving 10,000 people or more. Kansas extended this standard to include all new or modified water supplies regardless of size.

The important chemical reactions in THM formation, analytical techniques involved in measuring THMs, and treatment alternatives for controlling THM formation are discussed in Symons et al. (1981). The formation of THMs is a function of organic carbon (precursor concentration), pH, temperature, free chlorine dose, residual free chlorine concentration, and bromide ion concentration (Symons et al., 1975, 1981; Stevens and Symons, 1977; Amy et al., 1984).

Generally Kansas, as well as the rest of the U.S., has been more concerned with THM formation in surface water supplies because there have been few problems with groundwater supplies meeting the THM standard. The only exception to this is in the southeastern U.S. where, as was mentioned previously, the groundwater often contains larger quantities of organic carbon than are typically found in groundwater. Symons et al. (1975) found an average of 14.6 ug/L total THMs for 15 groundwater supplies, although one sample (the one from Florida) contained 427 ug/L THMs.

In the previously mentioned study done by Miller et al. (1986), only four of the 50 samples were found to have a total THM concentration above 100 ug/L, the highest being 178 ug/L. The average concentration was 45.4 ug/L. It must be noted however that the incubation period was four days at 25°C and the free chlorine dose was slightly higher than what would normally be used in the field. Therefore the THM concentrations reported maybe slightly higher than those that actually occur in the field. Nevertheless, it is logical to conclude that few groundwater supplies in Kansas are in danger of violating the 100 ug/L standard. However, if the standard is lowered to 10-25 ug/L, as is being discussed, then a number of groundwater supplies may be found in violation.

Origin

Since organics present in groundwater contribute to THM formation, understanding the origins of the organics in may help in the effort to control THM formation.

Groundwater is found in the saturated zone where all the pore spaces are filled with water. Directly above this saturated zone and extending to just below the land surface is the unsaturated zone. In this zone the pore spaces are filled with both water and air. The thickness of the unsaturated zone is variable and depends upon precipitation, evapotranspiration, and the underlying geology of a given area. This unsaturated zone contains soil moisture which acts as a barrier to incoming organic matter from the ground surface. The concentration of organic matter occurring in these shallow interstitial waters is also decreased by biological decay and adsorption on to the nearby sediments (Thurman, 1985b).

In temperate regions such as Kansas, spring runoff flushes organic matter from the soil and plant litter into the unsaturated zone. Summer and fall storms also flush the unsaturated zone (Thurman, 1985b). These events carry significant quantities of organic matter and humic substances to the saturated zone of groundwater.

It is also thought that some of the natural organics present in groundwater come from the surrounding sediments. Most organic matter in groundwaters having DOCs of 0.2-1.0 mg/L is thought to come from bacterial action on the kerogen present in the sediments. Groundwaters having higher concentrations of DOC probably are the result of direct contact of the water with sediments rich in kerogen, such as the 2-4 mg/L DOC average for groundwaters found in oil shale deposits (Thurman, 1985a and 1985b). Kerogen is fossilized organic matter present in the geologic material of the aquifer. It has a similar structure to humic acid, and is perhaps related to humic substances. It is hypothesized that kerogen is formed in part by the action of time and environmental conditions on the original humic (organic) input deposited during sedimentation (Huc and Durand, 1977).

However, since the concentration of organic matter (DOC) in groundwater is generally low, Thurman (1985a) gives several explanations as to why this is so:

1. The residence time of groundwater in an aquifer is in the range of hundreds to thousands of years. Organic carbon, being a food source for heterotrophic microbes present in the water, is converted to carbon dioxide (CO_2) contributing to alkalinity in aerobic conditions. Under anaerobic conditions a large fraction of the carbon becomes methane (CH_4).
2. Aquifer materials such as clays adsorb and bind organic matter, and it is chemically and biochemically degraded to CO_2.
3. Only trace amounts of water soluble organics leach from the sediments, making an insignificant contribution to groundwater DOC concentrations.

B. Sediment Organic Matter

Definitions

A review of the origins of organic carbon in sediments is relevant since organics present in sediment do contribute organics to groundwater. Before embarking on a review, the definitions of some basic terms (taken from Stevenson, 1982) are included to better clarify the discussion.

1. Soil Biomass: organic matter comprised of living microbial mass.
2. Humus or soil organic matter: the total amount of organics present in the soil, excluding undecomposed plant and animal tissues, partial decomposition products, and soil biomass.
3. Humic Substances: high molecular weight brown to black colored substances formed by secondary synthesis reactions. A generic term to describe colored material or its fractions based on solubility.
4. Non-humics: the part of humus consisting of biochemical molecules such as amino acids, carbohydrates, fats, waxes, resins, and organic acids, etc.
5. Humin: the alkali insoluble fraction of humus.
6. Humic Acid: dark colored organic material which can be extracted by various (usually alkaline) reagents, but is insoluble in dilute acid.
7. Fulvic Acid: lighter colored organic materials left in solution after acidification and removal of humic acid.

Origin

Plant organic matter is incorporated into soil by association with clays and metal ions. Soil organisms, such as fungi and bacteria, metabolize carbohydrates, cellulose, lignin, and simple organic molecules like amino acids, sugars, and fatty acids. The products, by-products, and remains of this biological activity build up in the soil (Thurman, 1985b). Organic material leaches down into the sediments through worm and root channels and coats the sediment particles. Organic material is also transported to depths by earth worms and burrowing animals which mix different soil layers (Stevenson, 1982 and 1985). Eventually the characteristic soil profile forms. Figure 2 illustrates the various soil horizons (based on Stevenson, 1982 and Thurman, 1985a).

Soil Horizon Formation

The O horizon contains the very youngest organic material consisting of partially decomposed fresh plants. Horizon A contains recent plant matter that is currently decomposing. The bottom half of horizon A, A_2, is lighter in color and contains more silicon (Si) and less iron (Fe) and aluminum (Al) than the upper part of horizon A, A_1. In addition, organic matter is also severely leached from A_2 where it is not in A_1. The organic material in horizon B consists mainly of transported humic and fulvic acids. The material in B is older than the material present in A. Much of the Fe, Al, and organics, which are lost from A_2, accumulate in horizon B. Therefore the color associated with the B horizon is darker than that of A_2. A secondary maximum of humus is often associated with accumulation of clay and sesquioxides (Fe and Al) and often occurs in horizon B (Stevenson, 1982 and 1985). Horizon C contains the oldest material in the soil profile and little organic carbon (Thurman, 1985a).

The fact that humus is often associated with clay has also been illustrated in a study done by Abdul et al. (1986). This study found that the largest fraction of organic carbon in three aquifer core

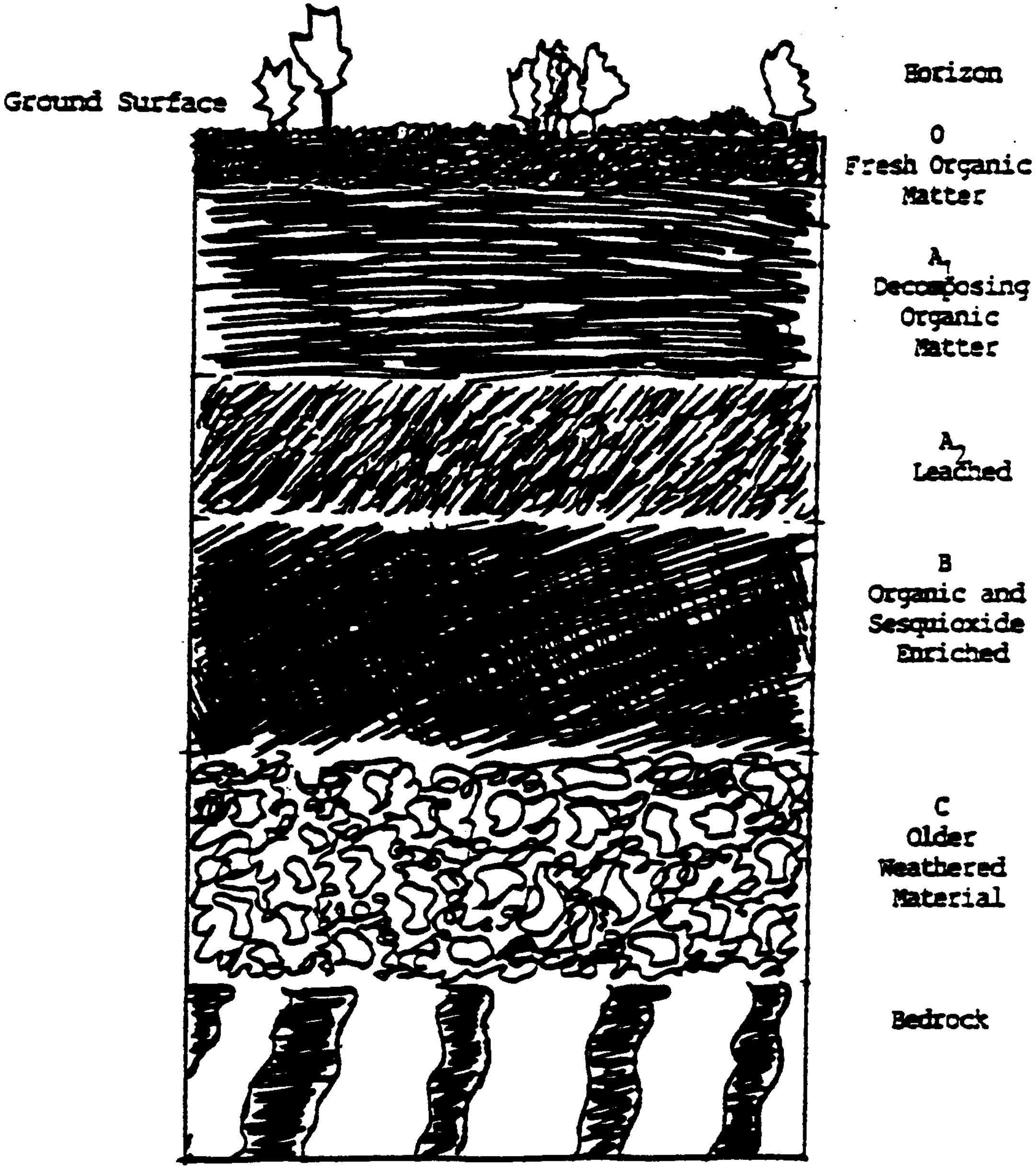

Figure 2: Generalized Soil Horizon Profile

sediments appeared in the 0-53 um particle range (fine clay to coarse silt, Wentworth particle size classification chart). However, the organic carbon associated with the 0-53 um partical range only comprised 23% of the total aquifer organic carbon.

Clay/Organic Matter Interactions

Several logical explanations exist as to why organic matter associates so strongly with sesquioxides and clays. There are four general ways in which humic substances are bound in sediments (Stevenson, 1982 and 1985):

1. As insoluble polymeric complexes of humic and fulvic acids. This mechanism is significant in organic rich sediments where the humus content is much larger than the content of clay and metal complexes.
2. As polymeric complexes of humic and fulvic acids bound together by divalent and trivalent cations (i.e. Ca^{2+}, Fe^{3+}, and Al^{3+}). This mechanism is most likely to occur in the B soil horizon where substantial amounts of Fe, Al, and organic matter accumulate. This can also occur in situations where clay minerals have become so coated with hydrous oxides that the oxides control the surface reactions.
3. By holding the organic substances in between layers of expanding type clay minerals. The only way to solubilze this organic material is to destroy the clay with hydrofluoric acid (HF).

4. By adsorption onto clays. Humic materials in most mineral soils are associated with clay by one of the following four adsorption mechanisms:
    a. Physical adsorption caused by van der Waals forces and dipole-dipole interactions.
    b. Electrostatic attraction/chemical adsorption, which is a cation exchange reaction. This occurs when a positively charged organic cation (i.e. R-NH^{3+}) replaces an inorganic cation in the clay matrix.
    c. Hydrogen bonding.
    d. Coordination complexes can form when a clay metal ion forms a bridge to an organic molecule. These clay-metal-humus complexes are the most common way that humic material is bound to clay. Again Ca^{2+}, Fe^{3+}, and Al^{3+} are the main ions responsible for forming the complexes. Humic substances bound as clay-Ca^{2+}-humic complexes can be easily displaced by a monovalent cation. The Fe^{3+} and Al^{3+} complexes, on the other hand, are very strongly bound and are not easily displaced.

C. Glacial Buried Valleys

Glaciated Central Region

The glaciated area of Northeastern Kansas is part of what is called the Glaciated Central Region. This region covers approximately 1,297,000 km^2 and extends from the Triassic Basin in

Connecticut and Massachusetts and the Catskill mountains of New York in the east to the northern great plains of Montana in the west (Graham et al. 1985).

The deposits are underlain by flat-lying consolidated sedimentary rocks of Paleozoic to Tertiary age. Glacial deposits of till and unsorted rock particles deposited directly by ice sheets lie above the bedrock. The till is interbedded and overlain by sand and gravel deposited by meltwater streams, silty clay deposits from glacial lakes, and in parts of the North Central States by loess. Loess is a well sorted silt thought to have been deposited by the wind (Graham et al., 1985).

The glacial deposits are thickest in buried valleys over bedrock surfaces. In the region westward from Ohio to the Dakotas, the thickness of the glacial deposits exceed the relief on the pre-glacial surface so the valleys are not evident by visual inspection of the present land surface. Till, lacustrine silts and clay, and large thicknesses of highly permeable sand and gravel make up the glacial deposits found in the buried valleys (Graham et al., 1985).

Groundwater is found in both the glacial deposits and the bedrock. Small to moderate amounts of groundwater can be found anywhere in the region. Sand and gravel, limestone, dolomites, and sandstone provide larger quantities of water. Because parts of the region are underlain by limestones and dolomites, the groundwater is often hard. In some areas Fe is a problem, and sulfates may exceed 250 mg/L in some sandstone aquifers (Graham et al., 1985).

Northeastern Kansas Area

The part of the glaciated central region lying in northeast Kansas was glaciated approximately 1-2 million years ago during the pre-Illinonian time. Surface deposits include till, outwash, and lacustrine deposits, loess, and alluvium. The deposits are from the Quaternary period. Pennsylvanian and Permian shale, limestone, and sandstone bedrock formations can be found near the land surface in some places or under the younger sediments. The main buried-valley aquifer now extends from Marshall to Atchinson County in Kansas and is a tributary of the ancestral Grand River in Missouri (Denne *et al*., 1986a).

Denne *et al*. (1986b) completed a study of 12 northeastern Kansas counties in which the locations of the buried channels were mapped and the nature of the sediments and water quality in the aquifers was described. The buried valleys were determined to be up to three miles wide, 400 feet deep, and 75 miles long. The valley deposits consist of basal gravel less than 20 feet thick under layers of clay, silt, sand, and/or gravel. The deposits vary both vertically and laterally, often within short distances (Denne *et al*., 1986a).

Local groundwater supplies come mainly from confined and unconfined sand and gravel aquifers which can yield up to 500 gallons per minute. Water levels range from 5 to 50 feet below the ground surface to as much as 100 feet or more. The construction of the wells is such that mixing of water from all aquifers occurs and therefore the water level measurements and groundwater samples from theses wells are representative of all the aquifers through which the wells are drilled (Denne *et al*., 1984).

The chemical quality of the groundwater is often fairly good, but there are instances of waters having levels of TDS, NO_3^-, SO_4^{2-}, Cl^-, Fe, and Mn that exceed the primary or secondary national drinking water standards. NH_4^+ concentrations of < 0.1-4.2 mg/L also have been measured. In deeper water samples taken from the southern part of the buried valley, NH_4^+ concentrations above 0.5 mg/L have been measured (Denne, 1983; Denne et al., 1986b).

Organic carbon data are lacking for the area, but in January 1984 seven previously existing wells sampled in Nemaha County were found to have 0.9-2.4 mg/L TOC with an average value of 1.4 mg/L. Six other wells sampled in northeast Kansas had measured TOC values of 0.1-2.4 mg/L with an average of 1.2 mg/L (Denne et al., 1984).

In 1982 and 1984 TFP was measured on water samples from four wells. Samples were chlorinated and then incubated for 7 days. Samples from three of the wells produced THM concentrations of 67-98 ug/L. The water from the fourth well produced a concentration of 25 ug/L. Three of the four samples were dominated by brominated haloforms. It is also interesting to note that the sample producing 25 ug/L of THMs contained a large amount of TOC, but had low concentrations of NH_4^+, Fe, and Mn (Hathaway et al., 1984; Denne et al., 1984). Since the samples producing higher amounts of THMs contained higher amounts of NH_4^+,Fe, and Mn, these results suggest that reducing conditions may favor THM production (Denne et al., 1986b).

Extractable NH_4^+ was measured in the sediments taken from three test cores drilled near one of the wells that had high NH_4^+ in the groundwater. The amount of extractable NH_4^+ increased with depth, from 2 mg/kg in the top soil to 74 mg/kg in grayish sediments and buried soil horizons (Denne et al., 1984). Wood fragments and a black "scum" were produced during drilling of some of the core holes and test holes. The black "scum" tested negative for oil and was thought to be comprised of buried humic substances (Hathaway et al., 1984; Denne et al., 1984).

SITE DESCRIPTION

Six sites were chosen to examine the sediments and water quality in the buried valley system, beginning with one site in southeastern Marshall County progressing eastward along the longitudinal axis of the system to southeastern Nemaha County. Table 1 shows the core zones, well depths, and well screen intervals. More complete descriptions are found in Denne et al. (1986b).

Site ST (4S-10E-17-ABD, Vermillion 7.4 Minute Quadrangle Map) is located in a pasture used for grazing cattle. (In fact the cattle were quite friendly during groundwater sample collection). The site is deep into the field, and there are farm buildings and a junk car pile located to the east of the wells. The surface elevation is 1240 feet. The wells lie about 185 feet from and 15 feet higher than two small farm ponds. The land slopes from the top of a hill (elevation 1295 feet) downward toward the northwest and the Black Vermillion River. The surface till contains boulders up to four feet in diameter. The site is also located near the well yielding the 25 ug/L THM concentration found by Denne et al. (1984).

Site SA (4S-12E-21AAB, Corning 7.5 Minute Quadrangle Map) lies in a planted field and is on an upland. The wells are located in the field directly next to a gravel road. The surface elevation is 1360 feet, 25 feet below the highest point of a hill lying 1000 feet to the south-southeast of the site. Plow guards were installed around the wells to keep the farmer from knocking over the well casings during plowing. The surficial deposits are glacial till.

Site N (4S-12E-34BCD, Corning 7.5 Minute Quadrangle Map) is located in a hay field just east of a farm house and garden and southeast of a pasture where cattle graze. The field is approximately 100 feet from a paved road. The surface elevation of the site is 1350 feet and roughly 35 feet below a hilltop 1000 feet to the west. As at site SA, the surface deposits are glacial till. The site is about 30 feet above a small intermittent stream that is about 400 feet east of the site. The stream is a tributary to Red Vermillion Creek.

Site C (5S-12E-12BBC, Corning 7.5 Minute Quadrangle Map) lies in a pasture which is sometimes used for cattle. Currently a horse grazes there. The surface elevation is approximately 1245 feet and the site is 100 feet from Red Vermillion Creek. The creek becomes perennial rather than intermittent a few hundred feet to the north (upgradient from the site. Deposits of alluvium occur along the creek. The city of Corning is now operating a sewage lagoon about a mile upstream from the site. The site is located upstream and across a highway (east) from a 60 foot deep well (5S-12E-11AAD) which previously had been used to supply Corning with water. This was the well that was previously found to have a THM concentration of 98 ug/L (Denne et al., 1984).

Site L (4S-12E-2ADD, Goff 7.5 Minute Quadrangle Map) lies on a slope and drains toward an intermittent drainageway. The drainageway is a tributary of Wolfley Creek. The wells are located deep in the field which is sometimes used to graze cattle. An abandoned barn is found to the northeast and planted fields lie to the northwest of the wells. The surface elevation is 1290 feet, 70 feet below the top of a hill to the northwest. Glacial till makes up the surface deposits at this site also.

Site H (4S-14E-35DDA, Wetmore 7.5 Minute Quadrangle Map) is found, right off a gravel road, in a field sometimes used for grazing cattle. The site lies at the north edge of somewhat flat alluvial deposits along Wolfley Creek. The drill site is located about 1000-2000 feet north of the creek. The surface elevation is 1090 feet, but the land slopes upward to the north. Within one mile the surface elevation becomes 1200 feet. Mud or standing water is usually found near the wells and is due to the seepage of groundwater.

Table 1
Core and Well Depths

Site/ Well*	Well Depth (ft.)	Well Screen Horizon (ft.)	Core Depths (ft.)	
ST-M	80	70-80	0-2	156-165
ST-D	175	171-175	14-16	165-174
			25-35	174-183
			78-87	183-192
			111-120	
SA-S#	45	41-45	0-2	127-136
SA-M	198	185-198	7-15	191-200
SA-D	285	277-285	37-45	250-259
			66-75	277-286
N-S	52	45-52	0-3	150-159
N-M1	164	154-164	10-15	159-168
N-M2	223	213-223	51-60	226-235
N-D	334	327-334	60-69	327-336
C-S	30	23-30	0-2	150-159
C-M	73	66-73	10-28	201-210
C-D	207	202-207	66-75	
L-S	30	20-30	0-2	186-195
L-M	145	139-145	14-16	256-265
			21-30	338-347
			59-68	361-370
			110-119	
H-S1	20	14-20	0-2	115-124
H-S2	35	28-35	10-35	146-155
H-D	154	135-154	76-85	

* S= shallow, M= middle, and D= deep

\# Well screen horizons are those of the original 5-inch wells. The 2-inch liners later installed in these wells are screened at 41-45, 181-194, and 276-284 feet.

SAMPLING PROCEDURES AND SAMPLE HANDLING

A. Well Drilling and Construction

The wells for this study were carefully constructed to avoid any extraneous groundwater contamination. The well casing materials were made out of polyvinylchloride (PVC) pipe. No drilling muds with organic additives were used, and all water used in drilling was chlorinated. A gravel pack was placed between the well casing and the drill hole wall for the entire depth of the well screen interval. To insure that no interconnections between aquifers occurred, cement was placed above the gravel pack all the way to the land surface. Most of the wells were developed by bailing or forced air lift pumping within one day of construction. More complete information on the well drilling and construction methods can be found in Denne _et al_., (1986a and 1987).

B. Groundwater Sample Collection

In this study all sampling equipment was made out of PVC. PVC was chosen because it had been shown to have a minimal contamination effect on well water samples, especially in regard to extraneous TOC addition. Four of the shallow wells were bailed (SA-S, N-S H-S1, and H-S2), and the rest of the wells were sampled using a PVC hose attached to an air compressor (Sears Craftsman 5-HP, 20 gal, Model #919.157140) to air lift water out of the well.

The bailed wells were bailed until the bailer (1 1/2" PVC) came up nearly empty. The wells were then allowed to recover anywhere from 1-24 hours before sample collection, depending upon recovery rate and the amount of silt contained in the water. The samples for determination of DOC and TFP were poured directly from the bailer through a thoroughly rinsed plastic funnel and into a 500-mL glass bottle with a polyethylene-lined screw cap. Another sample, to be analyzed for alkalinity, pH, and major cations and anions, was poured into a 500-mL polyethylene bottle. A third sample was taken for analysis of nitrogen species (NH_4^+ and NO_3^-) and trace metals. This sample was filtered in the field using a PVC filtering apparatus with brass fittings designed by the USGS. A vacuum was achieved by attaching a bicycle foot pump to the PVC filtering apparatus. The filters used were 0.45 um (Grade ME25, Schleicher & Schuell, Inc., Keene, N.H.). The 200-mL sample was filtered into a polyethylene bottle containing 2-mL of 6 M redistilled hydrochloric acid (HCl).

Developing time on the pumped wells was 30 minutes to 2 hours depending upon the pumping rate. Proper well purging is important in insuring unbiased samples (Barcelona and Helfrich, 1986; Dunbar et al., 1985). The stabilization of the solution chemistry parameters, pH (pHydrion pH paper) and specific conductance, were used as indicators of thorough well purging. Also several pump tests (staggered sample collection) were performed to insure that the DOC levels had stabilized. These pumped samples were collected directly into a rinsed plastic bucket as the water was being forced from the well. The procedures for transferring the water into the bottles and filtration were the same as for the bailed wells.

Four of the wells (N-M1, N-M2, N-D, and L-M) had initially high pH values($\geq$ 12). The other wells had stagnant water pH values of 6-7. However, within five minutes of pumping the pH values in the four wells decreased to and remained stable at 6. This phenomenon was probably due to minor grout contamination near the screens in the wells. A sampling bias due to extensive grout contamination generally is associated with continued high pH readings even after exhaustive pumping (Barcelona and Helfrich, 1986; Dunbar et al., 1985) and therefore should not have influenced the results of this study. Barcelona and Helfrich (1986) report having found pH values between 7 and 8 and stagnant water pH values in the 8-12 range in uncontaminated water samples, in good agreement with the results of this study. They also found that the alkalinity in grout contaminated well samples was mainly due to hydroxide ion (OH^-), and no such findings occurred in the inorganic analysis of the well samples taken in this study.

Another bias that can occur in groundwater sampling is caused by aeration of the sample while it is being collected. This can alter pH through the loss of CO_2, decrease calcium and bicarbonate ion concentrations through calcium carbonate precipitation, cause the oxidation of Fe^{2+}, and cause a loss of volatile organic chemicals (VOCs). Some aeration is introduced when bailing wells and much more occurs during forced air pumping. The purpose of this study was mainly to examine DOC and not VOCs. Since natural DOC is non-volatile, and since the method used to determine DOC involves aeration, the aeration of the samples should not have affected the DOC measurements or the study results (Nielsen and Yeats, 1985).

After the samples were collected, they were placed in coolers with blue ice and brought back to the lab for analysis. Once in the lab they were stored at 4°C until analysis could be completed, generally within 24 hours.

C. Core Sampling

The shallow cores at all sites were collected using an auger rig without the use of water or drilling mud. The deeper cores were collected using a hydraulic rotary rig. More complete details of the coring procedures and equipment are given in Denne et al. (1986a). Once collected, the core samples were cut into manageable lengths (1-2 feet), wrapped in plastic, labeled, stored in coolers with blue ice, brought back to the Kansas Geological Survey, and stored in a refrigerator at 4°C. Sub-samples were subsequently taken from various zones of the cores by cutting out pieces of previously undisturbed and unexposed material, placed in four-ounce glass bottles with teflon-lined screw caps, and stored at 4°C (if analysis could not be immediately undertaken). If more sample was desired than could fit into the four ounce bottle, an additional portion was placed in a polyethylene bag (Whirlpack, Fisher Scientific, St. Louis, MO) and stored at 4°C. Each sample to be analyzed for extractable NH_4^+ was obtained by cutting into the center of a core section and trimming away material near the outer edges of the core section to leave a rectangular sample approximately 2 X 1 X 1 inches in size. Each sample was then wrapped in plastic and aluminum foil and placed in a freezer to preserve it for later analysis. Samples were also taken for microbial analysis, as reported by Sinclair *et al*. (1987).

ANALYTICAL METHODS

A. Groundwater

Groundwater samples were analyzed for DOC, TFP, NH_4^+, dissolved Fe and Mn, pH, and major inorganic cations and anions. All the water samples for DOC and TFP analysis were filtered through glass fiber filters (Whatman 954-AH) prewashed with reagent grade deionized water (Milli Q, Millipore Corp., Bedford, MA).

DOC

DOC was determined by the UV-persulfate oxidation method (505 B) described in Standard Methods (APHA, 1985) for non-purgeable organic carbon. Samples were acidified to pH < 2 with concentrated H_3PO_4, purged for 5 minutes at 150 cc/min./10 mL at room temperature to remove CO_2, and were well shaken before injection. The analyzer used was a Dohrmann DC-80 Total Organic Carbon Analyzer (Xertex Corp., Santa Clara, CA) equipped with a sediment sampler.

TFP

The U.S. EPA developed a method for determining maximum TFP (Bellar et al., 1982), but it is expressly for regulatory purposes and not designed for comparing one sample to another. At this time The Joint Task Group on Trihalomethane Formation Potential, appointed to develop a TFP procedure to be included in the next addition of Standard Methods, is working on a method. However, they have not yet reached a consensus, and therefore no "standard" method exists.

Many difficulties arise in the determination of TFP. THM concentrations depend on pH, chlorine contact time, chlorine dose, chlorine residual, bromide ion concentration, temperature, and numerous other factors. TFP is a function not only of the intrinsic properties of a sample, but also of external factors. External conditions can be manipulated in the laboratory, but it is practically impossible to control all factors because not all factors work independently of one another. For example, two samples with the same concentration and type of organic matter contacted with the same chlorine dose can produce different chlorine residuals due to other constituents in the sample. If chlorine doses are such that the same residual concentration is produced, the sample with the higher chlorine dose will produce more THMs. The fact that laboratory conditions generally do not accurately reflect what might happen in the field also presents some difficulties. Often laboratory conditions produce a maximum concentration of THMs which is higher than what would be found in the field.

For these samples the TFP procedure was designed to produce the maximum concentration of THMs under conditions somewhat resembling those in the field and also allowing for comparable results between samples. The groundwater samples were buffered to pH 8.2 (the pH near most of the groundwater samples collected). A chlorine contact time of 4 days (96 hours) and a final chlorine residual of > 0.2 mg/L were used. The THM concentrations formed were probably greater than what would be found in the field, but a rough idea of the ability of the organic matter present to act as precursor material for TFP could be gained.

The procedure to determine TFP is as follows:

1. Reagents
   1. Purified water: Add 3 mL of household bleach to 18 liters of Milli Q water (giving about 10 mg/L of free chlorine), adjust the pH to > 10.0 by adding at least 1.8 mL of 1 N NaOH, and let stand at least overnight. Immediately prior to use, reduce the chlorine residual to < 0.1 mg/L by dropwise addition of Na_2SO_3 solution (90 g of Na_2SO_3 in 1 L of Milli Q water) to the desired quantity of water. Aerate the dechlorinated water for at least 30 minutes with 800 cc/min/L of high purity gas, and then adjust the pH to 8.2 with 0.1 N HNO_3. A reagent blank prepared with this water and incubated for 96 hours should produce no more than 5 ug/L of THMs.
   2. Chlorine solution: Prepare a concentrated chlorine solution by bubbling high purity chlorine gas into purified water and raising the pH to at least 9.5 with NaOH. Immediately prepare a working solution containing 305 mg/L of chlorine and adjust the pH of the working solution to 8.2. Store the working solution at 4^oC wrapped in aluminum foil. Immediately prior to use, check the titer of the working solution and vigorously aerate it for at least 20 minutes at room temperature to remove traces of chloroform.
2. Adjust the pH of each sample to 8.2 ± 0.1 using 0.1 N NaOH or HNO_3, and then add 50 mL to each of four 61 mL serum bottles. (Smaller volumes were sometimes used for

groundwater samples containing high concentrations of NH_4-N).

3. Chlorinate the samples by adding 1, 2, 3, 4, and 5 mL of chlorine solution to each bottle (giving free chlorine dosages of 5, 10, 15, 20, and 25 mg/L) and fill each bottle headspace free with purified water. Immediately seal the serum bottles with teflon-lined septa and aluminum seals, and then incubate them at $25^{o}C$ for 4 days (96 hours). (Higher chlorine dosages were required for a few of the groundwater samples containing NH_4-N. When the NH_4-N concentration was determined, the dosage of chlorine was increased stoichiometrically to remove the NH_4-N by breakpoint chlorination.)
4. Add 1 scoop (approx. 0.5 g) sodium sulfate (Na_2SO_4) and 4.00 mL of solvent (THM grade pentane, Burdick & Jackson, Muskegon, MI) to a 15-mL screw-cap extraction vial. Seal the vial tightly until ready for use (Step 7).
5. Uncap the serum bottle that received the lowest chlorine dosage and spot test for the presence of free chlorine by placing 9 mL of sample in DPD solution. If no free chlorine is present, go on to the next sample. If chlorine is present, go on to next step.
6. Open the extraction vial and add 2 drops of Na_2SO_3 and then 9 mL of sample. Measure the residual chlorine concentration by adding the remaining sample to the original 9 mL used for the spot test and using the DPD colorometric method (APHA, 1985). If the chlorine residual is less then 0.2 mg/L

discard the sample and return to step 5. If > 0.2 mg/L, go on to step 7.

7. Mix the contents of the extraction vial for 30 seconds using a vortex mixer. Then, using a disposable pipet, fill a 1-mL vial with the pregnant solvent and seal the the vial tightly with a teflon- lined aluminum seal. Store the vials in the dark at 4°C for THM analysis.
8. Repeat the procedure for the next two higher chlorine dosages of each sample (3 extracted samples for each groundwater sample).
9. Analyze the THM concentration in the solvent using gas chromatography. In computating the trihalomethane concentrations, take into consideration the volumes of dilution water and reagents used. Report the results in ug/L of TFP and yield of TFP in umoles per mg of carbon (DOC).

Solvent samples were analyzed for THMs using a Varian Model 2400 Gas Chromatograph (Varian Corp., Palo Alto, CA) equipped with a tritium/scandium electron capture detector and a 2m x 2mm I.D. glass column packed with 3% SP-1000 on 100/120 Supelcoport (Supelco, Inc., Bellefonte, PA). Reference standards obtained from the U.S. EPA and from an independent supplier (Supelco, Inc., Bellefonte, PA) were always within ± 3% of the in-house standards. The precision of the THM analysis is about ± 2%, but because of the difficulties discussed earlier, considerable caution must be exercised in comparing the TFP of one sample with another.

Ammonia measurements for TFP procedure

NH_4-N was determined (for the purposes of sample chlorination only) by the ammonia-selective electrode method (417 E in Standard Methods, APHA, 1985). The procedure was modified to use a small volume (10 mL), which was placed in a small test tube, adjusted to pH > 11 with 10 N NaOH, and mixed with a small magnetic stirring bar while the electrode (Model 9512, Orion Research, Inc., Cambridge, MA) was inserted into the sample. The reported NH_4^+ concentrations are those determined by the Analytical Services Section of the Kansas Geological Survey (KGS).

Inorganic Ions

All inorganic chemical analyses (NH_4^+, Fe, Mn, pH, and major cations and anions) were performed by the Analytical Services Section of KGS using methods described in Denne et al. (1987).

B. Sediments

Dry color, pH, percent moisture, TOC, EOC, ETFP, and extractable NH_4^+ were determined for each sediment sample.

Determination of Sediment Color

All sediment colors (as well as the colors of the filter papers used to filter the groundwater DOC samples) were determined using the Munsell soil chart. The four hue charts used were 7.5 YR, 10 YR, 2.5 Y and 5 Y; YR stands for yellow red; Y stands for yellow. The colors are given as, for example, 10 YR 5/1 gray. 10 YR is the hue chart, 5 is the value, 1 is the chroma, and gray is the designated color name. Hue indicates the color's relationship to red, yellow, green, blue, and purple. Value gives the lightness of the color (2 being darkest and 8 being lightest). Chroma is a color's departure from neutral (0 or 1 being neutral up to 8).

The 7.5 YR hue chart contains mostly reds and less yellow. The colors are clear pinky gray to brownish orange tones. Hue chart 10 YR ranges from brownish gray to brownish yellow. The colors contain less red than those found on chart 7.5 YR. 2.5 Y has olive greenish gray browns to olive yellow browns. The colors in chart 5 Y contain few brown tones. The colors range from olive grays to olive yellow grays.

Table 2 gives a list of all colors found in the sediments and on the groundwater filter papers. The Munsell soil chart number as well a named color are given. From this point on, however, the sediment and filter colors are referred to by Munsell color number only.

pH

The pH of a sediment water slurry of each sample was determined using the following technique:

1. Place 20-30 g of sample in a 75-100 mL test tube. Add an equal weight of Milli Q water. Vortex mix (Vortex Genie mixer, Scientific Products, McGaw, IL) until the sample disagregates, using a stirring rod or stainless steel spatula if necessary to break up the sample.
2. Vortex mix the sample every 10 minutes for 1 hour.

Table 2
Munsel Soil Chart Colors and Numbers

(Key to colors of sediments and groundwater filter papers)

Number	Color
* 7.5 YR 6/6	Reddish Yellow
* 7.5 YR 6/8	Reddish Yellow
* 7.5 YR 7/8	Reddish Yellow
10 YR 4/2	Dark Grayish Brown
10 YR 4/3	Dark Brown
10 YR 4/4	Dark Yellowish Brown
10 YR 5/2	Grayish Brown
* 10 YR 5/3	Brown
10 YR 5/1	Gray
10 YR 6/2	Light Brownish Gray
10 YR 6/4	Light Brownish Yellow
10 YR 6/6	Yellowish Brown
10 YR 7/1	Light Gray
10 YR 7/2	Light Gray
10 YR 7/3	Very Pale Brown
10 YR 7/4	Very Pale Brown
10 YR 8/2	White
* 10 YR 8/3	Very Pale Brown
* 10 YR 8/4	Very Pale Brown
2.5 Y 5/2	Grayish Brown
2.5 Y 5/4	Light Olive Brown
2.5 Y 6/2	Light Brownish Gray
2.5 Y 6/4	Light Brownish Yellow
2.5 Y 7/4	Pale Yellow
2.5 Y 7/6	Yellow
2.5 Y 8/2	White
2.5 Y 8/4	Pale Yellow
5 Y 5/1	Gray
5 Y 6/1	Gray
5 Y 7/1	Light Gray
5 Y 7/2	Light Gray
5 Y 8/1	White

* Indicates color only found on groundwater filter papers

3. After an hour, vortex mix the sample thoroughly and immerse a standardized pH electrode into the suspension.
4. Record the pH value to the nearest hundredth of a unit.

Moisture

So that results could be expressed on a dry-weight basis, the percentage of moisture in each sediment sample was determined by the following procedure:

1. Dry an aluminum dish in the oven at 105°C for at least 4 hours. Remove the dish from the oven and allow it to cool in a desiccator containing fresh calcium sulfate. After the dish cools, weigh it to the nearest 0.1 mg.
2. Weigh 10-15 g of sediment into the dish and place it in the 105°C oven for at least 24 hours.
3. Remove the dish from the oven and place it in the desiccator to cool. When the dish has cooled, weigh it to the nearest 0.1 mg.
4. Compute moisture content as the percentage of total wet weight of sample comprised of water:

$$\%\ \text{Moisture} = \frac{\text{wet weight} - \text{dry weight}}{\text{wet weight}} \times 100$$

Note: If a sample could not be analyzed immediately after it was received, it was stored at 4°C. Moisture would accumulate inside the container. Therefore, the containers were allowed to equilibrate at room temperature for 24 hours and large pieces of sample were weighed rather than small pieces.

Drying/ Milling Procedure

After completing pH and moisture analysis on a sample, the remainder was placed in a 105°C oven to dry for $\geq$ 48 hours. The dried sample was then milled in a Tekmar analytical mill (# A-10) and placed back into the glass bottle for TOC and EOC analysis.

Total Organic Carbon

Since a suitable method for determining TOC in the sediments could not be found, a procedure was developed to detect low levels of organic carbon in sediment without interference from large quantities of inorganic carbon (present in carbonate minerals found especially in the deeper sediments). Initially employing a method used by Froelich (1980) to determine TOC in marine sediments, numerous variations were tried, and eventually a suitable modified method was developed.

Due to the large amount of carbonate minerals present in the sediments, it was necessary to find an acid that would completely dissolve the carbonates without hampering the operation of the TOC analyzer. Initially H_3PO_4 was chosen because: 1) it was recommended by the manufacturer of the TOC analyzer; 2) it is relatively free of impurities; 3) it does not interfere in the analysis like HCl or HNO_3; 4)it would not be as likely to damage the TOC analyzer; 5) calcium phosphate precipitation should not retard dissolution of carbonate minerals to the same extent that calcium sulfate would if H_2SO_4 were used; and 6) Froelich (1980) found that H_3PO_4 was suitable for marine sediments containing substantial quantities of calcium carbonate.

Initially a comparison of TOC values using HCl and HNO_3 to those found with H_3PO_4 showed that the results were equivalent. However, it was later discovered that when a large quantity of calcium carbonate was present, it was not completely destroyed by H_3PO_4. This posed a significant problem in the deeper, highly calcareous sediments with low levels of TOC (Denne et al., 1986a). After discussing the effects of using HNO_3 with the TOC analyzer manufacturer and deciding that its use would not damage the analyzer, HNO_3 was selected for use in the sediment TOC analysis.

The procedure used to determine sediment TOC is as follows:

1. The amount of sample used depends on the dry color of the sample. For topsoils and all sediments in the dark brown to dark gray range use 1.0000 g of sample. For sediments in the medium gray (sometimes also light gray and yellow brown) range use 5.0000 g of sample. For light gray, pale brown, and yellow sediments use 10.0000-15.0000 g of sample. Weigh sample and place it in a 50-mL Nessler tube.
2. Slowly add 25 mL of 6 M HNO_3. For large sample amounts and highly calcareous samples adding 2-3 mL at a time is recommended to avoid allowing bubbling sample to escape from the test tube. After adding the acid, allow the sample to react approximately 5 min. or until most of the visible reaction is completed.
3. Vortex mix for 1 min.
4. Sonify the samples for 30 min. (Sonifier model B-221, Branson Cleaning Equipment, Shelton,Ct.).

5. After sonification, aerate (10 cc/min. of N_2 gas) the sample for 10 min. before measuring TOC.
6. Take a razor and cut off the end of the plastic pipette tip. (1/4-1/2") This insures that the pipette (40 uL automatic pipette, Eppendorf digital pippette 4210, Brinkman Instruments Co., Westbury, N.Y.) will not clog. Vortex mix the slurry well, take off vortex mixer, then immediately insert the pipette and slowly draw up sample. Immediately inject the sample into the boat.
7. Keep track of the number of injections made, including any rinses of the pipette. After sample analysis is completed, use a graduated volumetric pipette to fill the tube with water up to the 50 mL mark. Keep track of the mL of water added to the nearest 0.1 mL.

$$\text{Sample vol., L} = \frac{[50 - \text{mL added} + (0.04\ \text{mL} \times \text{no. of inj.})]}{1000}$$

$$\text{TOC, mg/g of sample} = \frac{\text{TOC} \times (\text{Sample Vol., L})}{\text{grams of sample}}$$

After preliminary analysis of the N and SA cores, it was evident that some of the lighter sediments had very low TOC concentrations. Since the sediment sampler of the TOC analyzer has a blank value of 5-15 mg/L, it was deemed necessary to have a slurry TOC of at least 100 mg/L and preferably above 400 mg/L to obtain accurate results. Since sediment TOC appeared to be correlated to sediment color, more sediment was used when measuring the TOC of the lighter sediments. However, some sediment samples were quite low in TOC so that using as much as 15 g of sediment did not give a TOC above 100 mg/L. In such cases, concentrations are reported as < 0.16 mg/g.

$$\text{Accurate Quantification Limit} = 100\ \text{mg/L} \times 0.025\ \text{L/15g}$$
$$= 0.16\ \text{mg/g.}$$

EOC

Although there are numerous procedures described in the scientific literature for extracting organic matter from soils (e.g., Stevenson, 1982), few (if any) can be considered as "standard" procedures. Furthermore, there appeared to be no information available regarding the ability of such procedures to extract organic matter from deep core samples. Therefore, a great many experiments were conducted to develop a method that would extract as much organic matter as possible from the core samples using the fewest number of steps. Since it was reasonable to assume that the organic matter present in the core samples would be quite similar to humic substances found in soil, the literature on humic substances was reviewed to provide guidance in developing a suitable extraction procedure for the core samples. According to Stevenson (1982), reagents that have been used to extract humic substances from soil include strong bases (sodium hydroxide and sodium carbonate), neutral salts (sodium pyrophosphate, sodium fluoride, and organic acid salts), organic chelates (e.g., 8-hydroxy- quinoline), formic acid, and an acetone-water-HCl mixture. Of these, sodium hydroxide generally extracts the greatest percentage of organic matter, but it also has the greatest potential for hydrolyzing or oxidizing (in the presence of oxygen) the organic matter. To avoid altering the organic matter, many investigators have used a solution of sodium pyrophosphate adjusted to a pH of 7-9. Stevenson (1982) also reported that pretreatment of soil samples with hydrochloric or hydrofluoric acid has been found to increase the efficiency of alkaline extraction, presumably by removing calcium and other multivalent cations that help bind the organic matter to the soil.

Since sodium hydroxide had previously been found to be the most effective extractant, and since acid pretreatment had been reported to increase the extraction efficiency in some cases, experimentation began with the development of a method employing sequential extractions with acid and sodium hydroxide. After some preliminary experiments, 0.5 M sodium hydroxide (NaOH) and 0.5 M nitric acid (HNO_3) were selected as the extractants. Other concentrations of NaOH gave poorer or equivalent results. Other acids (including hydrofluoric, hydrochloric, and phosphoric) were no more effective than HNO_3 in enhancing the alkaline extraction, and they each introduced procedural complications. The acid pretreatment increased extraction efficiency by only a small percentage.

The next step was to examine several other extractants, including distilled water, borate buffer (pH 8.0), and sodium tripolyphosphate (STP). Distilled water was a very poor extractant, and the borate buffer was somewhat effective. The STP was nearly as effective as the acid/base combination, and offered several important advantages: 1) the extraction could be done in a single step; 2) the extract was already buffered for the ETFP analysis; 3) no precipitation of organic matter, which would interfere with both the EOC and ETFP analysis, occurred following extraction (when the acid and base extracts were combined, the cations in the acid extract precipitated a substantial amount of the organic matter in the base extract); 4) acid pretreatment was not necessary (since the STP effectively bound the multivalent cations, acid pretreatment did not substantially improve extraction efficiency); and 5) the pH of the extractant (about 9.1) was very close to the pH of the ground water flowing through the material in its natural state, so the extracted organic matter could be viewed as material that might potentially leach into the water over a long period of time.

Because the sediments had a wide range of TOC contents, it was necessary to extract different weights of sediment to achieve the 5.00 mg/L EOC for chlorination. For top soil, and other sediments with a TOC $\geq$ 6.0 mg/g, 2.0000 g of sample was used. For lower TOC sediments more sample was needed. It was discovered that the most efficient extraction occurred using not more than 1-2 g/30 mL of STP. Therefore in the lower TOC sediments more test tubes were used, each containing 2.0000 g of sediment, to achieve the 5.0 mg/L EOC concentration.

The procedure used for sediment EOC determination is as follows:

1. Make up a 0.25 M STP solution (91.9825 g in 1 L of Milli Q) prior to the extraction procedure. Add 50 mg/L of Cl_2 to the solution by adding 1 mL of Chlorox bleach. When ready to perform extractions, make 10 mM STP from the 0.25 M solution by diluting 40 mL of the 0.25 M STP to one liter with purified Milli Q water (refer to TFP procedure for purification procedure). Dechlorinate the 10 mM STP to < 0.1 mg/L Cl_2 by adding Na_2SO_3 dropwise (90 g/L Na_2SO_3 prepared with Milli Q). Aerate the STP for 30 minutes with 800 cc/min/L of high purity N_2 gas.

2. Weigh 2.0000 g of dried and milled sediment into a 50 mL polyethylene test tube.
3. Add 30 mL of 10 mM STP to the test tube.
4. Vortex mix 1 minute.
5. Sonify for 15 minutes.
6. Vortex mix 30 seconds.
7. Centrifuge 10 minutes (at ~ 2500 rpm).
8. Decant or pipet off the supernatant into a 250 mL volumetric flask.
9. Dilute the extract to 250 mL with purified STP.
10. Determine EOC using the same method as was used for DOC.

$$\text{EOC mg/g} = \frac{\text{EOC of sample, mg/L} \times 0.250\ \text{L}}{\text{g of sample extracted}}$$

$$\%\ \text{Extractable} = \frac{\text{EOC mg/g}}{\text{TOC mg/g}} \times 100$$

ETFP

The same procedure was followed for the sediment extracts as was used to determine the TFP of the groundwater samples. After EOC determination and dilution to $\leq$ 5.7 mg/L EOC, the extracts were buffered to pH 8.2, and an STP blank was also chlorinated along with the sediment extracts. The solvent used was THM grade iso-octane (Burdick & Jackson, Muskegon, MI). Results are reported as ETFP in ug/L and ETFP yield in umoles/mg carbon (EOC). The procedure for EOC determination and dilution for ETFP is as follows:

1. If the EOC is $\leq$ 5.0-5.7 mg/L, do not dilute. If the EOC is > 5.7 mg/L, dilute to approximately 5.0 mg/L.

2. Compute the volume of sample taken for dilution:

   $$\text{mL of sample} = \frac{250\text{ mL} \times 5.0\text{ mg/L}}{\text{EOC of sample, mg/L}}$$

   Round this volume up to the next whole number and dilute to 250 mL.

3. Calculate the EOC of the diluted sample:

   $$\text{New calculated EOC, mg/L} = \frac{\text{mL of sample} \times \text{EOC of undiluted sample mg/L}}{250\text{ mL}}$$

4. It is best, however, to verify the exact EOC by analyzing the diluted sample for EOC, since the purified STP usually has a TOC of 0.300-0.500 mg/L. In this study, the diluted EOC values were only verified for sites ST, L, and H. Although none of the values were corrected for the STP blank, all diluted samples contained the same concentration of STP and therefore the blank does not influence comparisons made among samples.

5. Because the dilution of the extract was to 250 mL, the maximum number of tubes was 8 (8 x 30 = 240 mL) which corresponds to 8 x 2 = 16 g of sediment. However, even at 16 g some low TOC sediments did not reach the targeted EOC of 5.0 mg/L.

Extractable NH_4^+

Frozen core sections were thawed and approximately 2 g of sediment were removed from the interior portion, weighed, and suspended in 25 mL of a 3 M KCl solution in 100 mL centrifuge tubes. These mixtures were placed in an ultrasonic bath for 10 minutes.

Upon removal from the bath, the mixtures were redispersed with the aid of a micromixer and allowed to stand 45 minutes, with resuspension at 15 minute intervals. Mixtures were then centrifuged at 2,200 rpm for 20 minutes, and the clear supernatants were drawn off using disposable Pasteur pipets. The NH_4^+ in the extracts was determined by the automated indophenol method (Technicon Auto-Analyzer II). Calibration standards were made up in 3 M KCl, and a 3 M KCl rinse solution was also employed with the auto sampler.

RESULTS AND DISSUCUSSION

A. Groundwater Samples

DOC

Groundwater samples were collected four times throughout the duration of this study. Summer samples were taken in August, fall samples in November, winter samples in January, and spring samples in March. Due to the fact that some wells had not been constructed at the time of the summer and fall sampling, no DOC values are available for those wells. Table 3 gives the compilation of all the DOC values measured.

As was mentioned earlier (in Sampling Procedures and Sample Handling), pump tests were performed on several wells to insure that thorough well purging was occurring. During the fall sampling, a pump test was performed on well N-M2. An initial sample was taken from the stagnant water, and then samples were taken every 30 minutes for an hour and a half. It can be seen that the DOC decreased rapidly from 6.19 mg/L to 2.38 mg/L in the first thirty minutes and then decreased slowly, almost negligibly, for the next hour. Because it appeared from the fall pump test that perhaps the DOC was still decreasing in N-M2, another pump test was performed on N-M2 during the winter sampling. As can be seen from the pump test data, the DOC in N-M2 appeared to be still decreasing slightly at the end of the test, from 1.63 mg/L at 1 hour to 1.44 mg/L at 1.5 hours.

Table 3
Groundwater DOC Concentrations#

Well	Summer	Fall	Winter	Spring	Avg.
ST-M	1.45	1.16	1.19	1.16	1.24
ST-D	1.16	1.31	0.67	1.02	1.04
SA-S		3.43	2.90	1.53	2.62
SA-M		2.97	1.96	2.80	2.58
SA-D		3.08	2.99	3.46	3.15
N-S		6.23	5.19	3.23	4.88
N-M1		2.12	1.82	1.77	1.90
N-M2		*6.19 *2.38 *2.17 2.08	*1.63 1.44	4.24	2.58
N-D	3.28	2.58	*2.49 2.79	3.07	2.93
C-S	3.80	2.85	*2.63 2.70	2.77	3.03
C-M	5.56	3.49	3.56	3.52	4.03
C-D	6.72	5.94	4.89	5.26	5.70
L-S		1.46	1.20	1.66	1.44
L-M			1.02	1.03	1.02
H-S1		4.74	2.09	1.96	2.93
H-S2		4.86	2.29	3.01	3.39
H-D			1.08	1.02	1.05
Average	3.66	3.22	2.34	2.47	2.64

Concentrations given in mg/L.

* Pump tests value, excluded from averages.

Pump tests were also performed during the winter sampling on N-D and C-S. N-M2 was a slowly producing well. N-D and C-S pumped much faster. Looking at the DOC values for N-D of 2.49 mg/L found after 30 minutes of pumping and 2.79 mg/L found at 45 minutes, it appeared that the DOC was increasing. The pump test DOC values for C-S of 2.63 mg/L and 2.70 mg/L at 30 minutes and 1 hour, respectively, were fairly constant. The two values agreed to within ± 1.8%, which is within the ± 2.0% error present in the TOC analysis. Based upon an evaluation of all of the pump test data, it is concluded that the wells were being purged adequately and that the water samples were reasonably representative of the aquifers from which they were drawn.

There are several possible causes of the inconsistency of the values found for N-M2 and N-D: 1) errors associated with the sampling technique itself (perhaps a very small amount of contamination present in the bucket, funnel or sampling device contributed a DOC of 0.2-0.3 mg/L); 2) variable pumping rates resulting in variations in the amount of organic matter dislodged from the gravel pack, screen, and well casing; 3) the mixing of different amounts of water from different sediment layers; 4) analytical error ; 5) since N-M2 did pump so slowly, the DOC could truly have been decreasing; and 6) N-M2 and N-D were two of the wells that had high pH values in the stagnant water. Even though the pH decreased to 6.0 within five minutes of pumping, some leaching of organics and disruption of normal purging might have occurred, although this seemed unlikely in the case of well N-D because it pumped so well.

No pump tests were performed during the March sampling. N-M2 was pumped for 2 hours instead of 1.5 hours, but the DOC value of 4.24 mg/L seemed unreasonably high. The well produced even slower than it had during the two previous samplings. More sediment was also present in the water. This led to the conclusion that the well may have been insufficiently developed or that the aquifer penetrated may not produce large quantities of water. Since it could not be proven that the 4.24 mg/L value was anomalous, it was included as measured.

No clear seasonal trends could be detected from the DOC values, and only the shallow wells would be expected to show seasonal changes. The two pumped shallow wells, C-S and L-S, showed relatively stable DOC values throughout the sampling. However, the four shallow bailed wells, N-S, SA-S, H-S1, and H-S2 seemed not to be so stable, although the instability could be attributed to the sampling technique rather than seasonal change. Bailing did not adequately develop the wells, as evidenced by the fact that more sediment was present in the bailed samples than was present in the pumped samples. The overall decreasing trend in DOC found in the bailed wells may be attributable to the increased development which resulted from each sampling. However, the investigation by Junk et al., (1980) into differences in DOC concentrations of groundwaters next to the Platte River in Iowa found that groundwater DOC concentrations in shallow wells were highest in September. Therefore, more seasonal DOC data is needed for wells SA-S, N-S, H-S1, and H-S2 before any definitive conclusions as to poor well development problems or seasonal trends can be made. As for the other wells, some had stable DOC values while others did not.

Evaluation of the DOC values on a site by site basis led to some interesting observations. All the DOC values at Site N were relatively high, generally > 2.0 mg/L. N-M1 seemed to stabilize at 1.90 mg/L, and N-D appeared to have a stable DOC of around 2.93 mg/L. The DOC concentrations in wells N-S and N-M2 never stabilized, possibly for the reasons discussed previously.

At site SA the DOC values again were generally near or above 2.0 mg/L. SA-S showed the decreasing trend of the bailed wells. SA-M dropped to 1.96 at the winter sampling but was back up to 2.80 mg/L in the spring. SA-D was stable at about 3.15 mg/L.

Site C had by far the most consistently high DOC values. Disregarding the summer measurements, the DOC values in all three wells were fairly constant throughout the entire sampling period. This site also showed a general trend of increasing DOC with depth. No other site exhibited a consistent increasing or decreasing trend in DOC values with depth. C-S was consistent at around 2.77 mg/L, C-M at 3.52 mg/L, and C-D at about 5.36 mg/L. The higher values found during the summer sampling were probably due to a lack of well development. Another explanation could be that the microbial populations in the sediments were more active during the warmer summer months breaking down more of the organic material present in the sediments and thus increasing the DOC. This is possible, but it is not as plausible as the poor well development explanation since seasonal changes should only affect the shallow wells and since the temperature at these deeper depths is expected to show little seasonal variation.

Site ST had very low concentrations of DOC in both the mid and the deep wells. The average DOC concentration was around 1.0 mg/L for both wells. ST-M seemed to stabilize after the summer sampling. ST-D never did stabilize completely, but the DOC was always low. Both ST-M, and ST-D pumped relatively well.

The wells at sites L and H were the last to be completed. Only fall sampling took place on L-S, H-S1, and H-S2. L-M and H-D were not completed in time for the fall sampling.

The DOC values at site L were also fairly low, and both wells pumped well. L-S had fairly stable DOC values and the average of the three samples was 1.44 mg/L. The mid-depth well, although it was only sampled twice and had a stagnant water pH $\geq$ 12, produced DOC values within ± 0.7 mg/L.

At site H, H-S1 and H-S2 were bailed wells, subject to problems associated with the lack of development. Both wells had very high DOC values of > 4.0 mg/L in the fall sampling, but the values decreased in the winter sampling. The spring DOC value for H-S1 of 1.96 mg/L was close to that of 2.09 mg/L found in the winter, indicating that perhaps the well was reaching full development. The DOC values in H-S2 increased from 2.27 mg/L in the winter to 3.01 mg/L in the spring. It was interesting to note that even after filtration H-S2 was still somewhat cloudy. Perhaps some of the colloidal organic matter present in H-S2 was smaller than 0.45 um and therefore not removable by filtration. This would explain the higher DOC found in H-S2 as compared to H-S1. H-D pumped wonderfully. Like

L-M, it was only sampled twice but had stable DOC values, averaging 1.05 mg/L. This value was considerably less than the DOC values found in H-S1 and H-S2.

The average DOC for each seasonal sampling and an overall average (excluding pump test data) are also given in Table 3. The average DOCs found for the winter and spring samplings were close at 2.34 mg/L and 2.47 mg/L. These averages compare favorably with the overall average DOC of 2.64 mg/L. These average DOC values are somewhat higher than those found in previous studies (Miller _et al_., 1986; Denne _et al_., 1984), but they may have been somewhat skewed due to poor well development.

TFP

Table 4 is a compilation of the TFP data. The three data points for each sample (according to the procedure outlined in Analytical Methods) were converted into one point by performing linear regression and interpolating to a 3.0 mg/L Cl_2 residual. This was done to allow a more accurate comparison between the different samples, since TFP is a function of Cl_2 residual. The TFP and yield data then reflect the values that would be expected for each sample at a Cl_2 residual concentration of 3.0 mg/L. Generally, all three data points were used in the regression analysis; however, in some cases the curves were very non-linear and the regression coefficient was less that 0.96. In such situations the dosage providing a Cl_2 residual closest to 3.0 mg/L and the next highest dosage were used in the computation. If a Cl_2 residual was exactly 3.0 mg/L, it was used as the data point.

Table 4
Groundwater TFP Concentrations and Yields#
(At 3.0 mg/L Cl_2 Residual)

Well	Summer		Fall		Winter		Spring		Avg.	
	TFP	Yield	TFP	Yield	TFP	Yield	TFP	Yield	TFP	Yield
ST-M	55.2	0.23	36.9	0.20	27.6	0.14	35.9	0.19	38.9	0.19
ST-D	43.4	0.22	24.1	0.12	17.2	0.17	22.8	0.14	26.9	0.16
SA-S			178.6	0.38	124.0	0.29	67.6	0.30	123.4	0.32
SA-M			126.7	0.32	125.1	0.47	127.4	0.34	126.4	0.38
SA-D			161.6	0.34	163.8	0.34	150.1	0.27	158.5	0.32
N-S			270.0	0.34	264.9	0.39	161.3	0.39	232.1	0.37
N-M1			86.2	0.30	79.6	0.33	74.8	0.32	80.2	0.32
N-M2			98.4	0.35	92.8	0.48	96.6	0.17	95.9	0.33
N-D	172.4	0.34	149.2	0.36	153.8	0.35	149.9	0.31	156.3	0.34
C-S	*	*	160.8	0.32	201.8	0.42	157.2	0.31	173.3	0.35
C-M	*	*	184.6	0.35	182.7	0.33	165.7	0.31	177.7	0.33
C-D	395.4	0.37	275.3	0.35	292.2	0.37	259.2	0.31	305.5	0.35
L-S			41.2	0.19	26.3	0.14	30.5	0.12	32.7	0.15
L-M					31.9	0.24	31.4	0.23	31.6	0.24
H-S1			197.0	0.37	61.2	0.22	65.1	0.25	107.8	0.28
H-S2			217.5	0.40	122.9	0.42	95.1	0.24	145.2	0.35
H-D					57.9	0.27	56.7	0.29	57.3	0.28
								Average of:	125.0	0.30

TFP concentrations are given in ug/L and yields in umoles/mg DOC.

* No TFP Data was available for the summer samples of C-S or C-M. The high concentrations of ammonia contained in the samples were unknown until analysis of the first TFP results. Not enough sample was left to rechlorinate to the breakpoint.

The TFP concentrations and yields generally increased with increasing Cl_2 dose and residual. At 3.0 mg/L Cl_2 residual, the average yield was 0.30 umoles/mg DOC and the average TFP was 125 ug/L. The average TFP of 125 ug/L is above the EPA limit of 100 ug/L. Although these TFP values are probably somewhat higher than what might be found in the field, they do indicate that a THM problem may exist if some of these aquifers are used as a source of drinking water. The average TFP yield (0.30 umoles/mg DOC) is comparable to the value of 0.24 umoles/mg TOC found by Miller _et_ _al_. (1986).

The highest TFP concentrations and the greatest yields occurred at sites SA, N, and C with the values being at or above average. These were also the sites which had the highest DOC values. At site H, TFP concentrations and yields were quite variable, but generally corresponded to the variance in the DOC concentration. Sites ST and L had the lowest TFP concentrations and yields, and the TFP concentrations at a 3.0 mg/L Cl_2 residual were all much below the 100 ug/L primary standard. The yields at site ST and L were also well below the average for all sites of 0.30 umoles/mg DOC with the highest yield being 0.24 for the winter sampling of well L-M.

The concentrations of the individual THM species differed from sample to sample. Table 5 gives the %Cl values (the percentage of the halogen atoms in the THMs that are chlorine with the balance being bromine) at 3.0 mg/L Cl_2 residual for all the groundwater samples. Seven of the wells (SA-S, N-S, N-M1, N-M2, L-M, H-S1, and H-S1) produced TFP concentrations that were dominated by $CHCl_3$. The %Cl values for these samples were between 86.2 and 95.9. SA-S always produced some of all four THM species with $CHCl_3$ being the greatest

Table 5
Percentage of Halogen Atoms in the Form of Chlorine in the Groundwater THMs
(at 3.0 mg/L Cl_2 residual)

Well	Summer	Fall	Winter	Spring	Avg.
ST-M	68.1	69.7	64.1	67.7	67.3
ST-D	63.1	77.8	73.4	74.6	72.2
SA-S		87.2	84.1	75.4	82.2
SA-M		90.4	89.0	89.6	89.7
SA-D		72.6	70.1	69.6	70.8
N-S		93.5	91.6	93.4	92.8
N-M1		86.2	88.3	87.8	87.4
N-M2		88.0	89.6	90.0	88.0
N-D	72.4	69.6	72.5	72.3	71.7
C-S		56.2	56.7	58.5	57.1
C-M		75.8	74.1	75.0	75.0
C-D	72.2	69.0	68.7	68.2	69.5
L-S		77.5	70.9	71.1	73.2
L-M			91.4	91.0	91.2
H-S1		95.4	89.7	91.4	92.2
H-S2		95.9	93.2	91.5	93.5
H-D			41.5	46.0	43.8

in concentration (%Cl=75.4-87.2). ST-M, SA-D, N-D, C-M, and C-D produced fairly equal concentrations of $CHCl_3$, $CHCl_2Br$, and $CHClBr_2$ but very little $CHBr_3$ (%Cl=64.1-75.8). C-S and H-D were always dominated by the three bromine containing species. Their corresponding %Cl values were the lowest of all the samples, varying from 41.5-58.5. ST-D had fairly equal concentrations of all species in the summer sampling (%Cl=63.1) and then produced little $CHBr_3$ in the fall, winter, and spring (%Cl=73.4-77.8). L-S produced some of all the species in the fall (%Cl=77.5) but was dominated fairly equally by the three chlorine species in the winter and spring (%Cl=~71). Despite the obvious differences in types of species produced in different samples at the same site and also between the same wells sampled during different seasons, %Cl could not be correlated to the site, DOC, or depth of the groundwater samples. The single most important factor influencing %Cl is undoubtedly the bromide ion concentration, but bromide ion concentrations were not measured, and no relationship was found to exist between chloride ion concentration and %Cl.

Some interesting correlations were observed between TFP and DOC. Figure 3 shows a plot of DOC versus TFP. It can be seen, despite the variability of the data, that there was a strong positive correlation between DOC and TFP ($r = 0.937$). Miller et al. (1986) also found a positive correlation of increasing TFP concentration with increasing DOC concentration. The y-intercept of the regression line is a negative value (-17.5) which indicates that there is a fraction of the DOC which does not act as precursor material. In this case the unreactive DOC concentration is ~0.33 mg/L DOC.

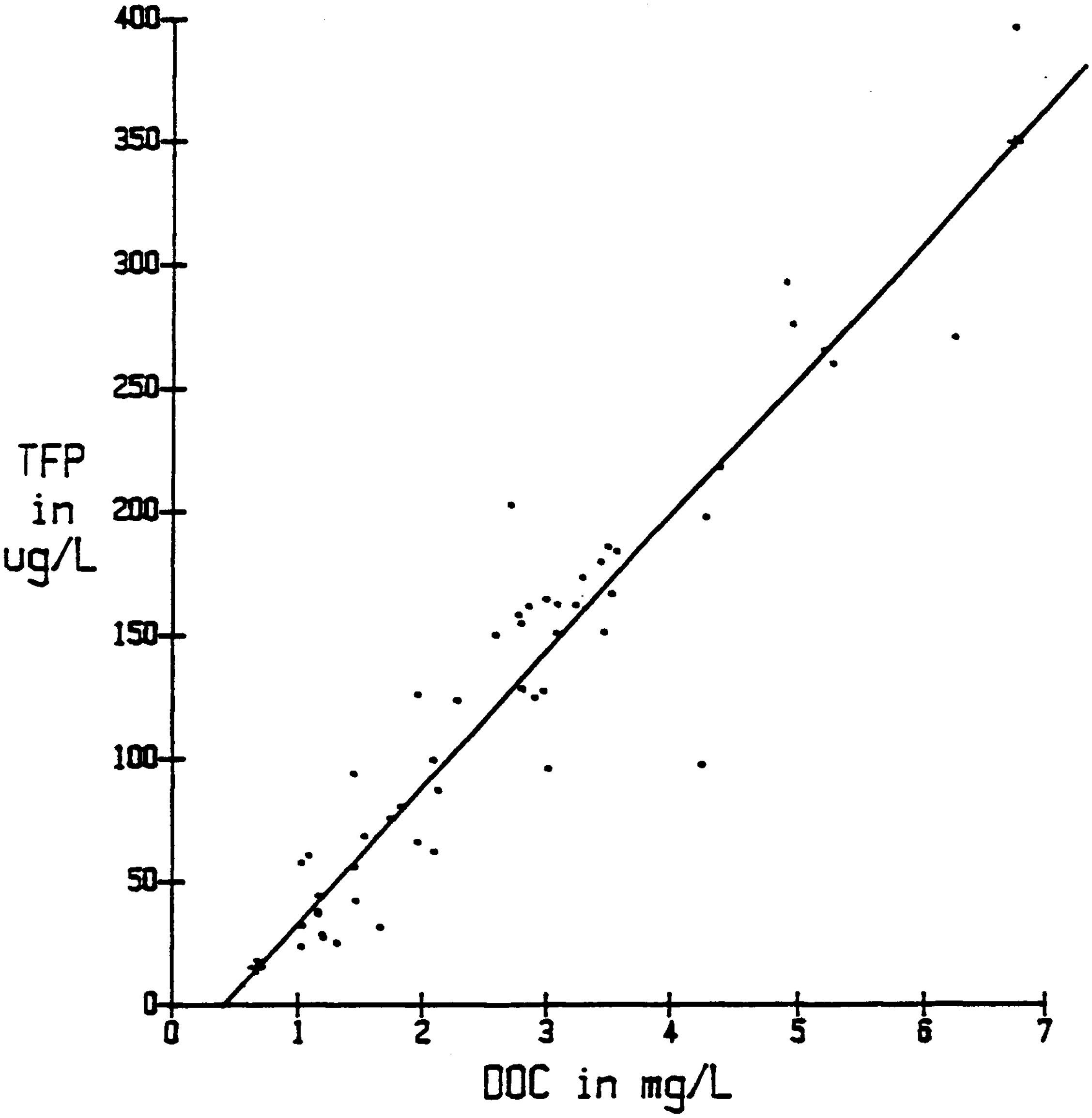

Figure 3: DOC vs TFP

Figure 4 is a plot of DOC versus TFP yield. These data are somewhat more sporadic than those in Figure 3, but again there is a positive correlation ($r=0.494$) significant at the 99% confidence level indicating that TFP yield increased with increasing DOC.

It appeared that the organic precursor material present in the groundwater with DOC values of $\geq$ 2.0 mg/L (avg. yield 0.33 umoles/mg DOC) was different from that found in the groundwater with DOC values below 2.0 mg/L (avg. yield 0.24 umoles/mg DOC). However, this was not always true. For instance, a comparison of the DOC values (Table 3) and yields (Table 4) for the spring samples of N-M1 and L-S revealed that although their DOC values of 1.77 mg/L and 1.66 mg/L were relatively comparable, the yield values of 0.32 and 0.12 umoles/mg DOC were not even close. Winter samples SA-M, N-M1, and N-M2 and spring sample SA-S also had yields above the average 0.24 umoles/mg DOC of the samples having $\leq$ 2.0 mg/L. Obviously a DOC below 2.0 mg/L does not necessarily indicate that the TFP yield will also be low.

A statistical analysis of the DOC, TFP concentration, and TFP yield data is given in Table 6. The strong correlations between DOC vs TFP and DOC vs TFP yield shown by the r values indicate that DOC, TFP concentration, and yield are related by site. The average DOC concentrations above 2.0 mg/L and the relatively higher TFP concentrations and yields at sites SA, N, C, and H again indicate that the precursor material present in DOC concentrations $\geq$ 2.0 mg/L is different from the material present in low DOC concentrations $\leq$ 2.0 mg/L. The samples cited as exceptions to this in the previous paragraph (SA-M, N-M1, N-M2 winter, SA-S and N-M1 spring)

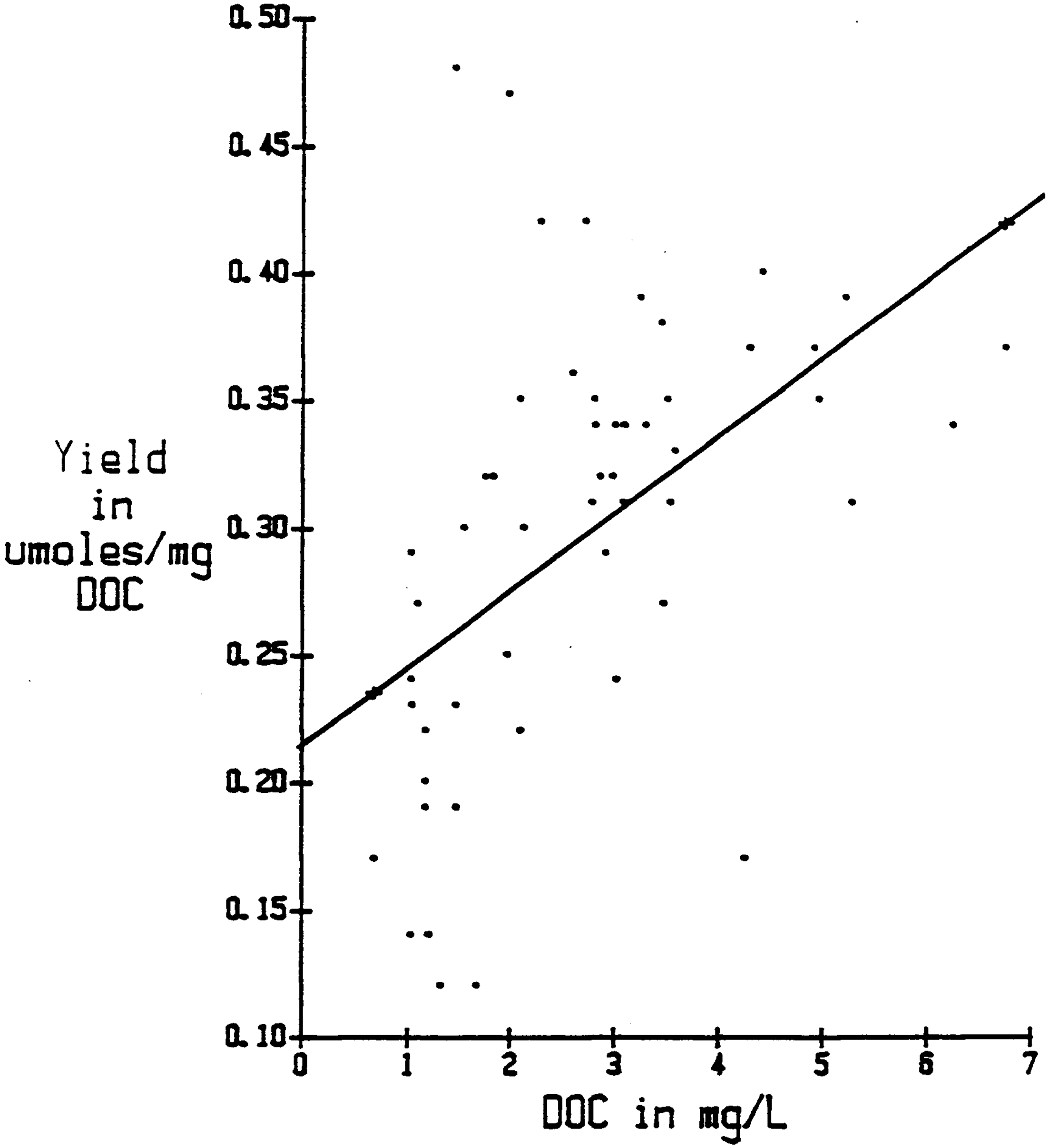

Figure 4: DOC vs Yield

are from sites SA and N. It is possible that these exceptions are due to diffferences in the overall groundwater chemistry in these 5 samples as compared to other samples having DOC concentrations below 2.0 mg/L.

Table 6
Statistical Analysis of DOC and TFP Data

Site	Avg. DOC (mg/L)	Avg. TFP (ug/L)	Avg. Yield (umoles/mg DOC)
ST	1.14	32.9	0.18
SA	2.79	136.1	0 34
N	3.06	142.3	0.34
C	4.26	222.7	0.34
L	1.27	32.3	0.18
H	2.63	109.2	0.31

Correlation	(r)
Avg. DOC vs Avg. TFP	0.995
Avg. DOC vs Avg. Yield	0.899

Six of the samples, N-M1, N-D, C-M, C-D, L-M, and H-D could be said to have behaved "ideally" in that they had fairly constant DOC, TFP, and yield values. Using C-M as an example (and disregarding the summer sampling), the DOC values were 3.49, 3.56, and 3.52 mg/L, the corresponding TFP values were 184.6, 182.7, and 165.7 ug/L and the yields were 0.35, 0.33, and 0.32 umoles/mg DOC. This would seem to indicate that the precursor materials and other factors contributing to THM formation remained fairly consistent from season to season. It should also be noted that these samples were all from mid or deep wells that produced water readily.

The rest of the samples (the majority) either maintained constant TFP concentrations or yields with variable DOC or had constant DOC values and changing TFP concentrations or yields. The most striking example of changing DOC and yield with constant TFP was

N-M2. The DOC and yield values were widely variable: DOCs of 2.08, 1.44, and 4.24 mg/L and yields of 0.35, 0.48, and 0.17 umoles/mg DOC. The corresponding TFP values produced were 98.4, 92.8, and 96.6 ug/L. Perhaps the DOC concentrations measured may have been in error with the true DOC concentration being near 2.0 mg/L. SA-M also produced constant concentrations of TFP with changing DOC concentration and TFP yield. N-S had fairly constant TFP yields of 0.34, 0.39, and 0.39 umoles/mg DOC while the DOC and TFP concentrations decreased. This was just the opposite of the trend in N-M2 and SA-M. For N-S, it appeared that the changing DOC did affect the TFP concentrations produced, but not the average potency of the precursor material contained in the DOC. Wells ST-M, SA-D, C-S, and L-S all had relatively stable DOC concentrations, but the TFP concentrations and yields produced were moderately variable. The four wells ST-D SA-S, H-S1, and H-S2 could only be described as variable on all counts. H-S1 did appear to be reaching steady values between the winter and spring sampling, but this was not true of any of the other three wells.

It could be the poor well development problems discussed earlier which caused the inconsistencies in the data in the four bailed wells, SA-S,N-S, H-S1, and H-S2. As for the consistencies of the "ideal" well samples, they could be explained by good well development and perhaps by the deepness from which the samples were taken since the deep wells would be the least likely to be affected by seasonal change. The inconsistencies in the rest of the wells might have been due to seasonal changes in precursor material, changes in inorganic chemistry, or errors associated with sampling and analysis.

Inorganic Chemistry

Miller et al. (1986) found that DOC and TFP concentrations were not associated with the concentrations of the major cations and anions, but there appeared to be a significant relationship between NH_4^+, Fe, and Mn concentrations and the concentrations of DOC and TFP. However, it was concluded that perhaps this relationship was due to the close association of all of theses variables with alluvial aquifers and was not a causal relationship. Therefore, this study examined only the concentrations of NH_4^+, Fe, and Mn in relation to DOC and TFP. Tables 7-9 list the concentrations of each constituent measured in the samples. It must be noted that sediment was present in all fall samples and in the C-M summer sample. The presence of the sediment most likely caused the Fe and Mn concentrations in these samples to be artificially high but probably had little or no influence on the concentrations of NH_4^+.

The NH_4^+ measurements were fairly consistent between each sampling and thus appeared to be unaffected by the presence of sediment in some of the samples. There was a definite trend of increasing NH_4^+ concentration with depth. This was true for all sites. Sites SA, N, and C had considerable concentrations of NH_4^+ in all the samples and especially in the deepest samples. All the samples at sites ST, L, and H contained $\leq$ 0.9 mg/L NH_4^+ except the H-D spring sample which had 1.1 mg/L.

Table 7

Groundwater NH_4^+ Concentrations#

Well	Summer	Fall	Winter	Spring	Avg.
ST-M	0.1	0.1*	< 0.1	0.1	0.1
ST-D	0.2	0.2*	0.1	0.2	0.2
SA-S		0.4*	0.2	0.1	0.2
SA-M		2.3*	2.6	2.9	2.6
SA-D		5.4*	5.2	5.4	5.3
N-S		0.6*	0.5	0.4	0.5
N-M1		2.0*	1.7	1.9	1.9
N-M2		2.6*	2.9	3.2	2.9
N-D	9.8	8.8*	8.9	9.4	9.2
C-S	0.9	1.0*	0.9	0.9	0.9
C-M	4.8*	4.2*	4.3	4.1	4.4
C-D	7.7	7.0*	6.7	6.7	7.0
L-S		0.2*	0.3	0.1	0.2
L-D			0.8	0.9	0.8
H-S1		0.1*	0.1	0.1	0.1
H-S2		0.3*	0.2	0.2	0.2
H-D			0.9	1.1	1.0
Average	3.9	2.2	2.1	2.2	2.4

Concentrations are given in mg/L.

* Sediment was present in the C-M summer sample and all the fall samples which could have caused the NH_4^+ concentrations to be artificially high in these samples.

Table 8
Groundwater Fe Concentration@

Well	Summer	Fall	Winter	Spring	Avg.#
ST-M	292	30*	< 22	< 22	112
ST-D	< 22	156*	137	105	55
SA-S		4,360*	26	28	27
SA-M		64*	61	< 22	42
SA-D		425*	826	1,040	933
N-S		9,140*	32	42	37
N-M1		21*	< 21	28	24
N-M2		1,190*	68	61	64
N-D	33	252*	885	906	608
C-S	8,660	2,590*	2,124	751	3,845
C-M	7,380*	2,190*	1,120	38	579
C-D	2,240	2,040*	50	41	698
L-S		3,370*	312	34	173
L-M			32	132	82
H-S1		2,020*	206	79	142
H-S2		8,450*	368	33	200
H-D			306	385	346

@ Concentrations given in ug/L.

Calculated with sediment-free samples only

* Sediment was present in the C-M summer sample and all the fall samples which could have caused the Fe concentrations to be artificially high in these samples.

Table 9
Groundwater Mn Concentrations@

Well	Summer	Fall	Winter	Spring	Avg.#
ST-M	22	4.9*	4	< 4	10
ST-D	206	224*	212	212	210
SA-S		778*	115	149	132
SA-M		683*	890	1,010	950
SA-D		758*	771	793	782
N-S		3,220*	55	24	40
N-M1		263*	146	177	162
N-M2		475*	133	139	136
N-D	428	399*	444	459	444
C-S	1,750	1,720*	1,680	1,610	1,680
C-M	1,100*	556*	458	314	386
C-D	325	351*	305	295	380
L-S		344*	32	7	20
L-M			71	71	71
H-S1		250*	32	26	29
H-S2		905*	110	58	84
H-D			201	196	198

@ Concentrations given in ug/L.

Calculated with sediment-free samples only.

* Sediment was present in the C-M summer sample and all the fall samples which could have caused the Mn values to be artificially high in these samples.

The Fe concentrations in the samples appeared to be affected by the sediment present in some of the analyses. However, the Fe concentrations in the sediment-free samples were still quite variable within in the same sample from season to season and from well to well at the same site. Samples SA-D, C-S, C-M, and H-D always contained Fe concentrations above the 300 ug/L standard. N-D, C-M, C-D, L-S and H-S2 had concentrations which exceeded the standard at least once in the four sampling periods. All the sites with the exception of site ST had at least one well above 300 ug/L at some point in the sampling. Generally it was the deepest well that contained the highest Fe concentrations at each site, although the reverse trend was observed at site C. C was the only site to have had some very high concentrations of Fe that appeared not to have been caused by the presence of sediment. The high concentration did decrease in the spring samples to a level more closely resembling the concentrations of Fe found at the other sites.

The Mn concentrations also apppeared to be somewhat affected by the sediment present in some of the samples. The Mn concentrations were still variable, even in samples without sediment, although they were not as inconsistent as the Fe concentrations. Disregarding the samples obviously anomalous due to the presence of sediment, only wells ST-M, L-S, and H-S1 were consistently below the 50 ug/L national secondary standard for Mn. Again the deepest samples at all sites generally had the highest Mn concentrations with the exception of site C. Site C again seemed to have the most consistently high Mn values, but sites N and SA also had fairly high concentrations in the deeper wells compared with the other sites.

None of the inconsistencies in TFP yields in the individual wells appeared to be correlated with changes in inorganic chemistry. NH_4^+ concentrations in well N-M2 increased from fall to spring, while the concentrations of Fe and Mn (disregarding the fall sample) remained fairly constant. The inconsistent TFP yields for this well were probably due to differences in DOC concentrations. Conversely, The TFP yields in well C-D were relatively constant despite the small changes in NH_4^+ concentration and the drastic changes in Fe concentration. Thus it seemed that changes in NH_4^+, Fe, and Mn concentration in the wells were not associated with the individual changes in TFP yields.

Although the inorganic chemistry of the well samples did not explain the inconsistencies in TFP yield, it did corrrelate in another way to the groundwater data. Table 10 shows a statistical analysis of the inorganic chemistry as it relates to the groundwater DOC concentration. The DOC concentration was strongly correlated to NH_4^+ ($r=0.848$), Fe ($r=0.792$), and Mn ($r=0.804$). These values are all close to the 95% confidence level ($r=0.811$). The average NH_4^+, Fe, and Mn concentrations were highest at sites SA, N, and C which were the sites having the highest average DOC and TFP concentrations and yields. Table 10 also shows a statistical analysis for TFP concentration and yield versus inorganic chemistry using Spearman's rank order correlation coefficient (r_s). TFP concentration was strongly correlated with NH_4^+ ($r_s=0.828$), Fe ($r_s=0.886$), and Mn ($r_s=0.886$). Strong correlations also were present for TFP yield and NH_4^+ ($r_s=0.943$), Fe ($r_s=0.943$), and Mn ($r_s=0.771$). These correlations show that differences in TFP concentrations and yields

Table 10
Statistical Analysis of DOC, TFP, NH_4^+, Fe, and Mn

Site	Avg. DOC (mg/L)	Avg. NH_4^+ (mg/L)	Avg. Fe (ug/L)	Avg.Mn (ug/L)
ST	1.14	0.1	100	110
SA	2.79	2.7	334	621
N	3.06	4.0	231	223
C	4.26	4.1	1,878	842
L	1.27	0.5	128	45
H	2.63	0.4	230	104

Site	Avg. TFP (ug/L)	Avg. TFP Yield (umoles/mg DOC)
ST	32.9	0.18
SA	136.1	0.34
N	142.3	0.34
C	222.7	0.34
L	32.3	0.18
H	109.2	0.31

Correlation	(r)
Avg. DOC vs Avg. NH_4^+	0.848
Avg. DOC vs Avg. Fe	0.792
Avg. DOC vs Avg. Mn	0.804

Correlation	(r_s)
Avg. TFP vs Avg. NH_4^+	0.828
Avg. TFP vs Avg. Fe	0.886
Avg. TFP vs Avg. Mn	0.886
Avg. yield vs Avg. NH_4^+	0.943
Avg. yield vs Avg. Fe	0.943
Avg. yield vs Avg. Mn	0.771

The average concentrations for Fe and Mn were computed without the sediment contaminated values.

were not only related to DOC concentration and site but also to concentrations of NH_4^+, Fe, and Mn.

Pulling these correlations together, it seems apparent that high DOC, TFP concentration, TFP yield, and reducing conditions in these groundwater samples go hand in hand on a site specific basis. Samples containing $\geq$ 2.0 mg/L DOC generally had higher TFP yields than samples containing $\leq$ 2.0 mg/L DOC. The only exceptions were found at sites SA and N. Sites SA and N had high concentrations of NH_4^+, Fe, and Mn which were shown to be correlated with high TFP yield. Again using the spring samples of N-M1 and L-S as examples, the DOC concentrations (Table 3) were comparable at 1.77 mg/L and 1.66 mg/L. However, the concentrations of NH_4^+, Fe, and Mn in the samples were very different (Tables 7-9), being much higher in N-M1 than in L-S (except for iron which was nearly equal in both samples). The TFP concentrations and yields (Table 4) for N-M1 (74.8 ug/L, and 0.32 umoles/mg DOC) were much higher than those for L-S (30.5 ug/L and 0.12 umoles/mg DOC). Thus, it also appears that the conclusion reached by Denne _et_ _al_. (1986b) and Miller _et_ _al_. (1986) that reducing conditions in the aquifer favor THM production is supported by this data.

B. Sediments

Tables 11-16 give a summary of the experimental results for the sediment cores.

Table 11
Experimental Results for Site ST Sediment Samples

DEPTH (ft.)	COLOR	pH	% H_2O	TOC (mg/g)	EOC (mg/g)	%EOC	NH_4^+ (mg/kg)	EIFP (µmoles/g)	Yield (µmoles/mg EOC)
1.00	10 YR 4/4	6.11	9	8.29	5.40	65	3.1	1.566	0.29
14.50	2.5 Y 7/4	6.61	3	< 0.16	0.02*	27*		0.008	0.36
29.00	10 YR 7/1	7.39	6	< 0.16	0.02*	42*		0.006	0.31
31.50	10 YR 7/2	7.48	10	< 0.16	0.03*	52*	1.0	0.008	0.24
34.00	10 YR 7/2	6.96	11	< 0.16	0.03*	51*		0.008	0.22
85.50	10 YR 7/2	8.38	20	< 0.16	0.03*	23*	0.9	0.006	0.18
87.50	10 YR 7/2	8.58	17	< 0.16	0.03*	24*		0.006	0.18
117.50	10 YR 7/2	8.19	23	0.21	0.05	26	0.7	0.010	0.18
160.25	10 YR 7/2	8.49	18	0.46	0.18	38	1.6	0.042	0.23
160.50	10 YR 7/2	8.44	10	0.60	0.20	34	4.6	0.041	0.20
178.00	10 YR 6/2	9.33	19	0.72	0.41	57		0.090	0.22
186.75	10 YR 6/2	9.62	17	0.86	0.55	65	3.8	0.110	0.20
188.00	10 YR 6/2	9.54	18	0.99	0.50	51		0.106	0.21
190.50	10 YR 6/2	9.39	20	3.76	1.12	30		0.348	0.31
191.00	2.5 Y 6/2	9.20	18	1.78	0.78	44	5.6	0.265	0.34

* Calculated using actual (inaccurate) TOC data

Table 12
Experimental Results for Site SA Sediment Samples

DEPTH (ft.)	COLOR	pH	% H_2O	TOC (mg/g)	EOC (mg/g)	%EOC	NH_4^+ (mg/kg)	EIFP (µmoles/g)	Yield (µmoles/mg EOC)
1.00	10 YR 4/2	5.74	17	20.28	7.27	36	3.2	2.617	0.36
7.00	10 YR 7/3	8.24	20	0.80	0.13	16		0.031	0.24
15.00	10 YR 8/2	8.52	18	0.49	0.06	12		0.012	0.22
44.00	2.5 Y 8/4	8.62	20	0.68	0.10	15	1.3	0.023	0.22
45.00	2.5 Y 8/4	8.31	19	1.18	0.28	24		0.135	0.48
70.50	2.5 Y 7/6	8.63	17	1.14	0.27	24		0.081	0.30
72.00	5 Y 5/1	8.39	16	11.58	0.76	7	6.0	0.319	0.42
130.00	5 Y 5/1	8.13	15	11.57	0.67	6		0.274	0.41
195.00S	5 Y 5/1	9.17	19	8.68	0.50	6		0.145	0.29
195.00C	5 Y 5/1	8.94	14	7.36	0.86	12	72.0	0.372	0.43
254.00	5 Y 7/2	9.12	18	1.89	0.49	26	99.0	0.132	0.27
259.00	5 Y 8/1	9.30	23	0.67	0.16	23		0.032	0.21*
259.75	5 Y 8/1	9.32	24	0.45	0.09	19	78.0	0.025	0.29
277.00	2.5 Y 8/2	9.32	19	0.46	0.13	28		0.024	0.19
279.00	2.5 Y 8/2	9.38	16	0.16	0.06	41		0.012	0.18
280.00	5 Y 8/1	9.30	20	0.36	0.08	21		0.018	0.24
281.00	5 Y 8/1	9.30	19	0.29	0.08	27	46.0	0.012	0.15

S= sand, C= clay

* SA 259.00 only had a Cl_2 residual of 0.15 mg/L

Table 13
Experimental Results for Site N Sediment Samples

DEPTH (ft.)	COLOR	pH	%H_2O	TOC (mg/g)	EOC (mg/g)	%EOC	NH_4^+ (mg/kg)	ETTP (umoles/g)	Yield (umoles/mg EOC)
1.00	10 YR 4/2	7.72	20	14.77	8.27	56	2.7	2.481	0.30
14.50	10 YR 8/2	8.62	18	0.43	0.10	23		0.025	0.25
52.75	2.5 Y 8/4	8.12	17	0.54	0.18	33		0.050	0.28
54.00	10 YR 6/1	8.22	18	11.01	1.12	10	3.5	0.493	0.44
58.00	2.5 Y 7/6	8.38	20	0.45	0.17	38		0.042	0.25
59.00	10 YR 6/1	8.13	16	11.97	0.88	7	5.3	0.325	0.37
158.00	2.5 Y 5/2	8.41	20	14.53	0.56	4	23.0	0.228	0.41
165.50	2.5 Y 5/2	8.02	20	14.52	0.87	6	20.0	0.422	0.48
168.00	2.5 Y 5/2	8.26	13	13.19	0.92	7		0.388	0.44
233.00	2.5 Y 5/2	8.81	17	7.75	0.74	10	35.0	0.273	0.37
324.50	10 YR 7/2	8.79	18	1.62	0.32	20		0.115	0.36
330.00S	10 YR 7/1	8.50	17	1.08	0.33	31		0.088	0.29
330.00C	10 YR 7/1	8.83	23	8.51	1.07	13	74.0	0.417	0.39

S= sand, C= clay

Table 14
Experimental Results for SITE C Sediment Samples

DEPTH (ft.)	COLOR	pH	% H_2O	TOC (mg/g)	EOC (mg/g)	%EOC	NH_4^+ (mg/kg)	ETTP (umoles/g)	Yield (umoles/mg EOC)
1.0	10 YR 5/2	8.01	17	20.89	5.84	28	1.4	2.511	0.43
11.5	10 YR 4/2	7.30	30	20.67	6.37	31		3.695	0.58
12.5	10 YR 4/1	7.33	29	15.83	5.61	35		2.356	0.42
15.0	2.5 Y 5/2	7.72	31	10.44	3.41	33	37.0	1.500	0.44
17.5	2.5 Y 6/4	8.38	23	2.60	1.19	46	9.2	0.321	0.27
23.5	2.5 Y 7/4	8.29	18	0.95	0.35	37	5.8	0.090	0.26
27.0	10 YR 6/1	8.20	17	9.00	0.66	7		0.278	0.42
29.5	10 YR 6/1	8.21	14	9.15	0.67	7	11.0	0.255	0.38
31.5	10 YR 6/1	8.22	19	10.15	0.77	8		0.302	0.39
67.0	10 YR 6/1	8.41	16	9.18	0.62	7	25.0	0.244	0.39
72.0	5 Y 6/1	8.50	16	7.94	0.66	8		0.232	0.35
152.5	5 Y 7/1	8.91	18	2.70	0.50	19	69.0	0.181	0.36
207.5	5 Y 6/1	9.12	22	4.18	0.83	20	67.0	0.282	0.34
208.0	5 Y 6/1	9.20	19	2.76	0.49	18		0.175	0.36
209.5	5 Y 6/1	9.19	24	10.16	1.28	13	129.0	0.448	0.35

Table 15
Experimental Results for SITE L Sediment Samples

DEPTH (ft.)	COLOR	pH	% H_2O	TOC (mg/g)	EOC (mg/g)	%EOC	NH_4^+ (mg/kg)	EDTP (umoles/g)	Yield (umoles/mg EOC)
1.0	10 YR 4/3	5.84	16	15.81	9.36	59	2.9	2.522	0.28
15.0	10 YR 7/4	7.71	17	0.26	0.08	30		0.024	0.32
24.5	10 YR 6/4	8.62	22	0.27	0.08	31		0.021	0.25
25.0	10 YR 6/6	7.71	19	< 0.16	0.03	25	0.7	0.011	0.38
61.0y	2.5 Y 5/4	8.80	26	2.38	0.45	19		0.014	0.32
61.0g	2.5 Y 6/2	8.92	25	9.59	0.83	9	1.2*	0.299	0.36
61.5	2.5 Y 6/4	9.00	22	3.40	0.30	9	1.0	0.086	0.29
65.0	10 YR 6/1	8.85	24	17.33	0.51	3		0.197	0.39
68.0	10 YR 6/1	8.80	23	13.29	0.67	5		0.022	0.32
110.5	2.5 Y 6/2	8.90	10	1.04	0.26	25	3.7	0.008	0.33
137.0	10 YR 6/1	9.20	20	10.12	0.66	7		0.205	0.31
138.0	10 YR 6/1	8.80	14	3.73	0.39	10		0.174	0.45
193.0	10 YR 6/1	8.80	15	8.15	0.64	8	29.0	0.328	0.51
258.5	2.5 Y 6/2	9.37	17	4.07	1.15	28		0.621	0.54
261.5	2.5 Y 6/2	9.42	18	2.97	0.75	26	37.0	0.041	0.54

y= yellow, g= gray

* yellow/gray composite

Table 16
Experimental Results for SITE H Sediment Samples

DEPTH (ft.)	COLOR	pH	% H_2O	TOC (mg/g)	EOC (mg/g)	%EOC	NH_4^+ (mg/kg)	EDTP (umoles/g)	Yield (umoles/mg EOC)
1.0	10 YR 4/2	6.92	14	10.37	5.56	54	3.3	1.333	0.24
14.5	10 YR 7/3	6.82	22	1.51	0.54	36	1.0	0.103	0.19
20.0	10 YR 7/3	7.52	15	0.50	0.17	34		0.036	0.21
24.5	10 YR 7/4	8.11	20	2.22	0.77	35	5.1	0.223	0.29
25.0	10 YR 7/1	8.21	15	5.78	0.80	14		0.297	0.37
27.5	2.5 Y 6/2	8.12	17	4.45	0.71	16	6.2	0.291	0.41
35.0	10 YR 6/1	8.78	16	6.71	0.49	7	6.3	0.157	0.32
79.0	10 YR 7/1	9.23	15	4.44	0.48	11	16.0	0.165	0.34
121.0	10 YR 7/1	8.91	22	0.98	0.13	13	16.0	0.041	0.31
152.5	10 YR 7/2	9.10	21	1.98	0.23	12	13.0	0.068	0.29
153.5	10 YR 7/1	9.01	15	0.58	0.07	12		0.015	0.23

pH

At all sites there was a trend of increasing pH with increasing depth. Some of the topsoil samples had acidic pH values (ST, SA, L, and H). Many of the deep sediments had very high pH values in the range of 8.50 to around 9.40, indicating that the samples were highly calcareous. Upon the addition of acid during the TOC analysis, many of these samples reacted violently. It was the presence of large quantities of carbonate minerals that led to the choice of HNO_3 as the acid for the TOC analysis.

Moisture

The moisture content of the sediments was variable, ranging from about 3-30% with most of the values falling between 10-20%. Since the core samples were taken from the different sites during different seasons (when the ground was not too muddy or frozen to drill), the moisture contents of unsaturated samples from the various sites are not comparable. No correlation appeared to exist between sediment moisture content and any of the other parameters measured.

Color, TOC, EOC and %EOC

The most interesting relationships were found among color, TOC, EOC, and %EOC. The TOC values ranged from a high of 20.80 mg/g in the top soil at site C to below the quantification limit of 0.16 mg/g, which occurred often at site ST. Generally, the highest sediment TOC value was found in the topsoil at each site although, at every site there were depths at which the TOC increased again. Site L was the only site which had a greater TOC at depth than in the topsoil. Figures 5-10 show graphically the relationship between TOC and depth for each site. The sites generally showed obvious increases in TOC at mid depth and a decrease in TOC again in the deepest sediments. The deepest samples at sites N and C, however, had TOC contents considerably higher than the samples directly above. The TOC values at site ST were very low, and the trend of a decrease in TOC in the deepest sediments did not appear. At site L there was quite a lot of variation in the TOC content in the samples. There was an immediate decrease from L 1.0 to L 15.0, but from 61 to 261.5 feet the TOC concentrations appeared to vary randomly from moderate to high concentrations. Also, the TOC concentrations varied greatly over very short distances (e.g. L 61y, L 61g, and L 61.5 had values of 2.38, 9.49, and 3.40 mg/g).

The amount of TOC present correlated well with the color of the sediment. The darker gray and brownish gray sediments (Munsell colors 10 YR 4,5,6/1 and 4,5,6/2; 2.5 Y 5,6/2; 5 Y 5,6/1) had the highest TOC values. Lower values and those values below the limit of accurate detection tended to be associated with the light gray, light brownish gray, and yellowish sediments (Munsell colors with values of 7 and 8 and chromas 1-8 e.g. 10 YR 8/2). The differences in TOC and color within short distances can be illustrated well by looking at N 58 and N 59. The Munsell soil colors were 2.5 Y 7/6 yellow and 10 YR 6/1 gray respectively. The corresponding TOC values were 0.45 and 11.97 mg/g. Although these samples were found within one foot of each other, they had very different TOC contents and colors. Table 17 gives the correlation coefficients for TOC vs color at each site. The sediment color number was selected by using its Munsell color

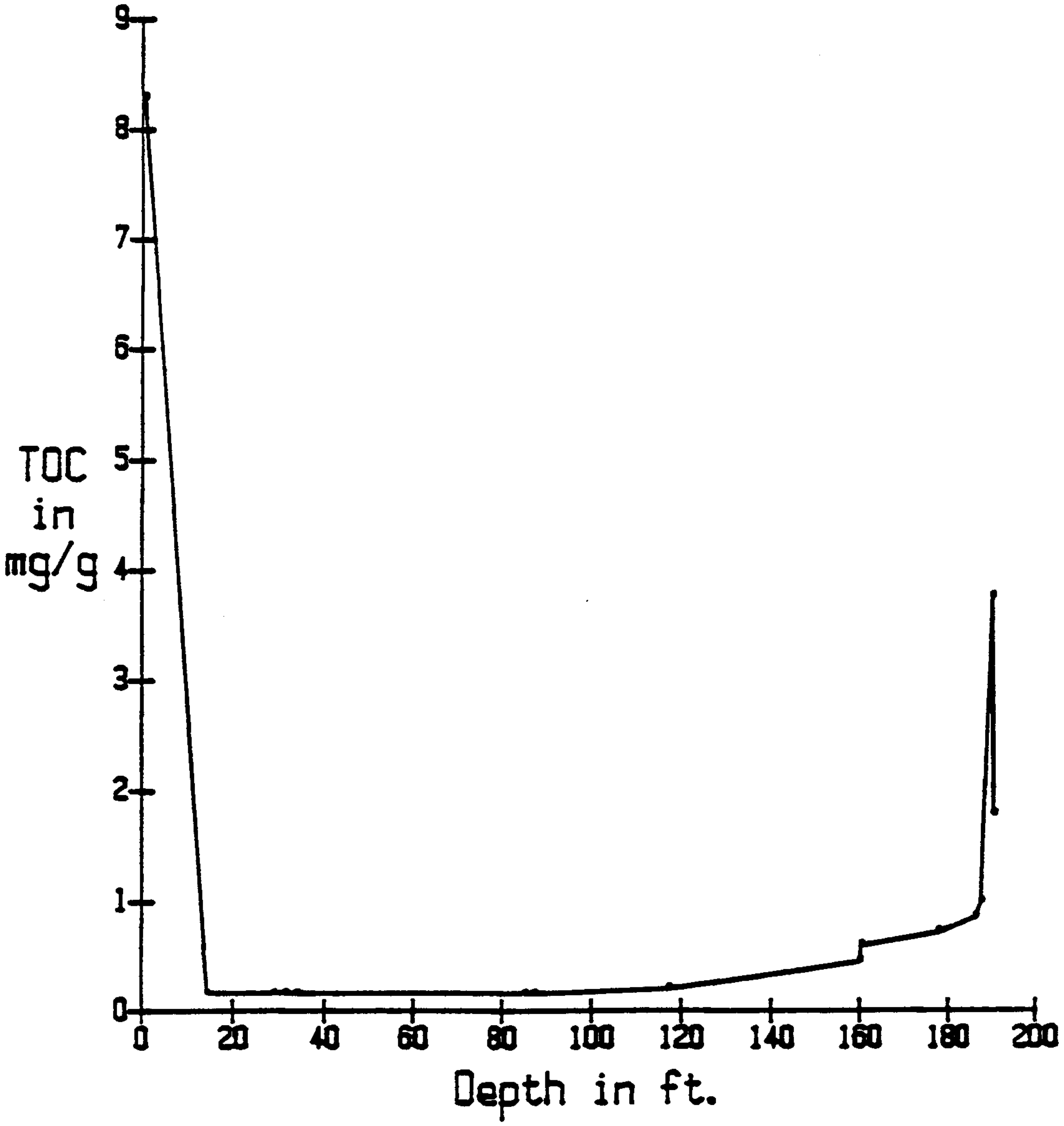

Figure 5: Depth vs TOC for Site ST

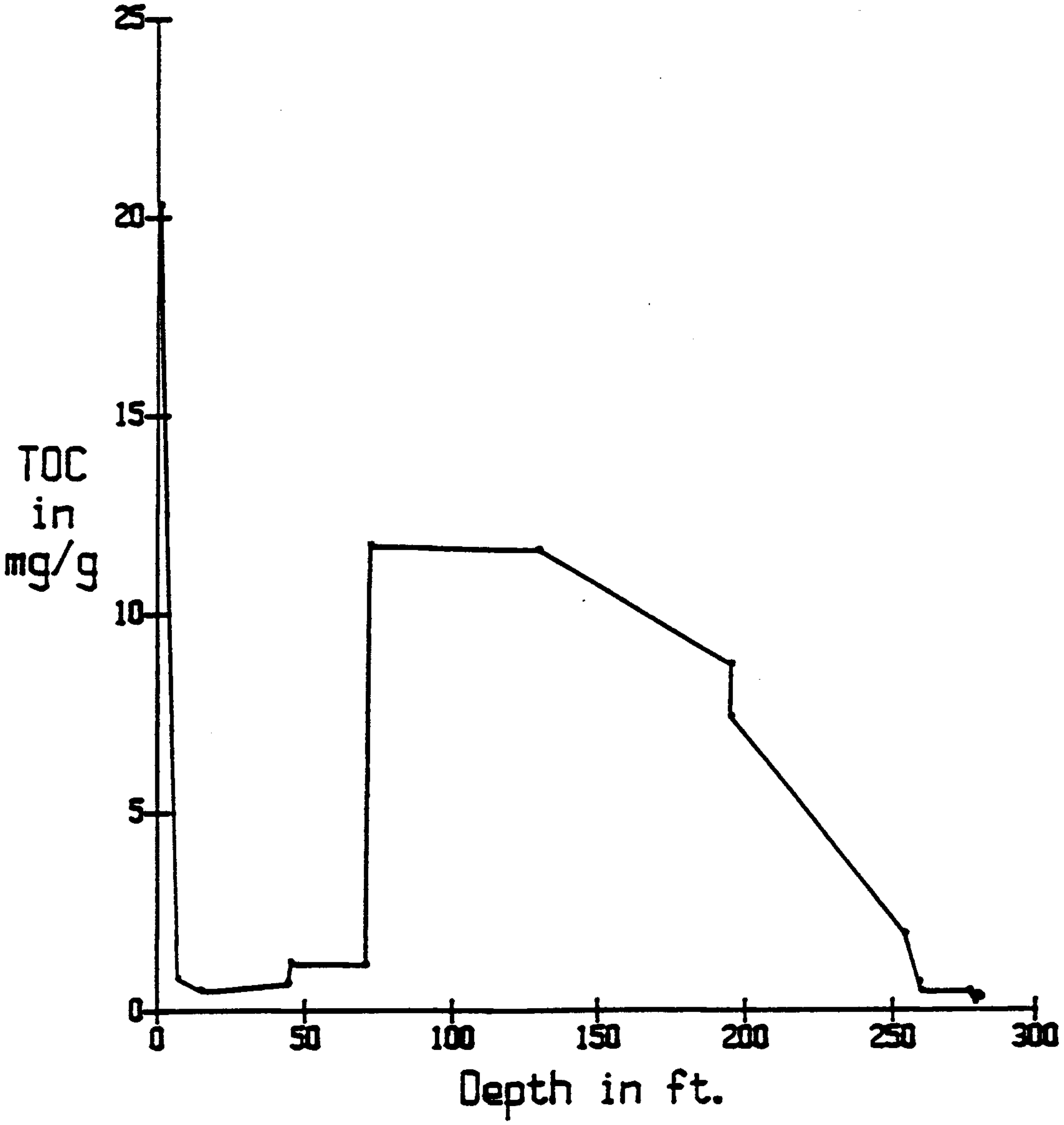

Figure 6: Depth vs TOC for Site SA

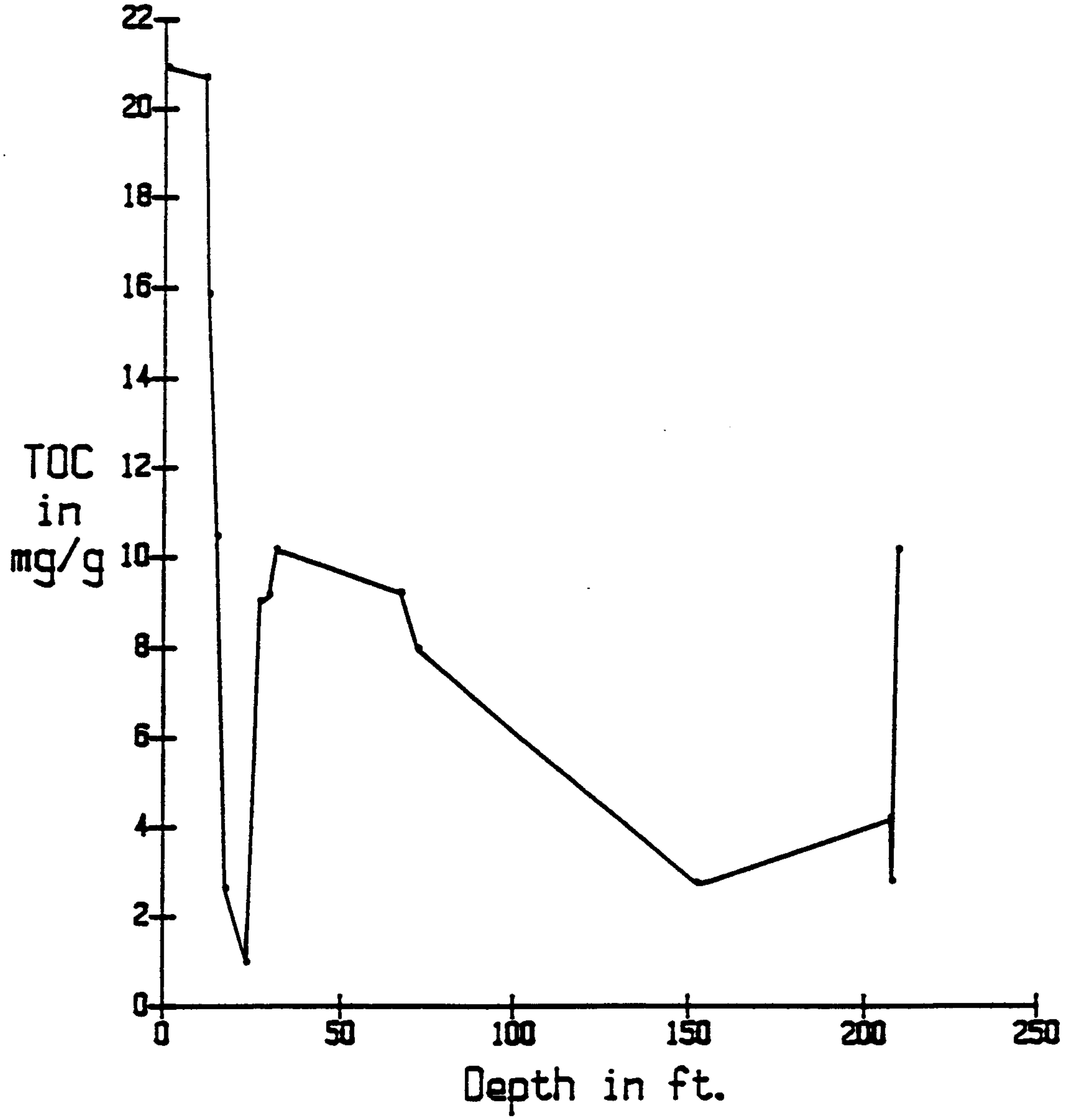

Figure 7: Depth vs TOC for Site ~~N~~ C

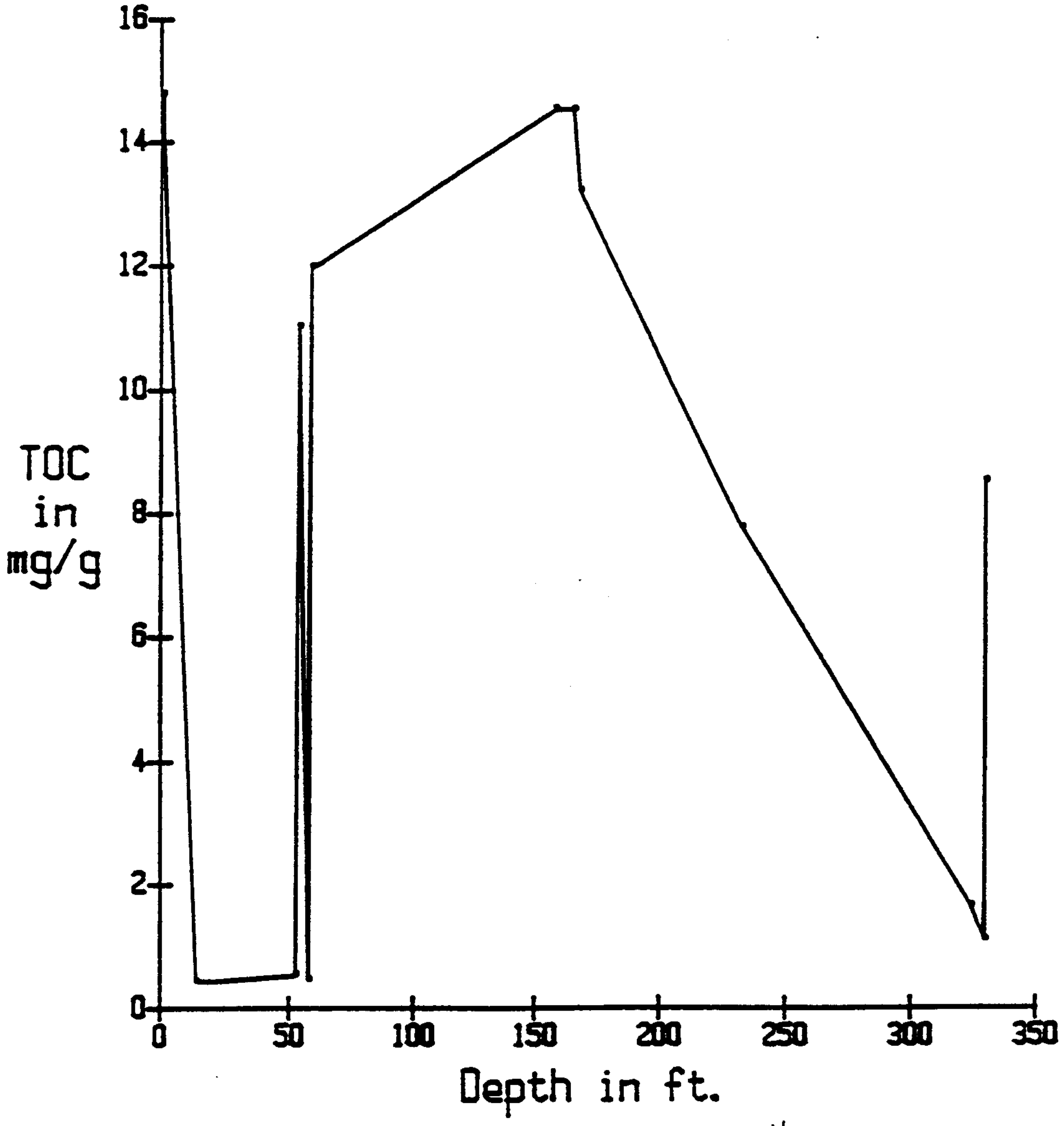

Figure 8: Depth vs TOC for Site ~~C~~ N

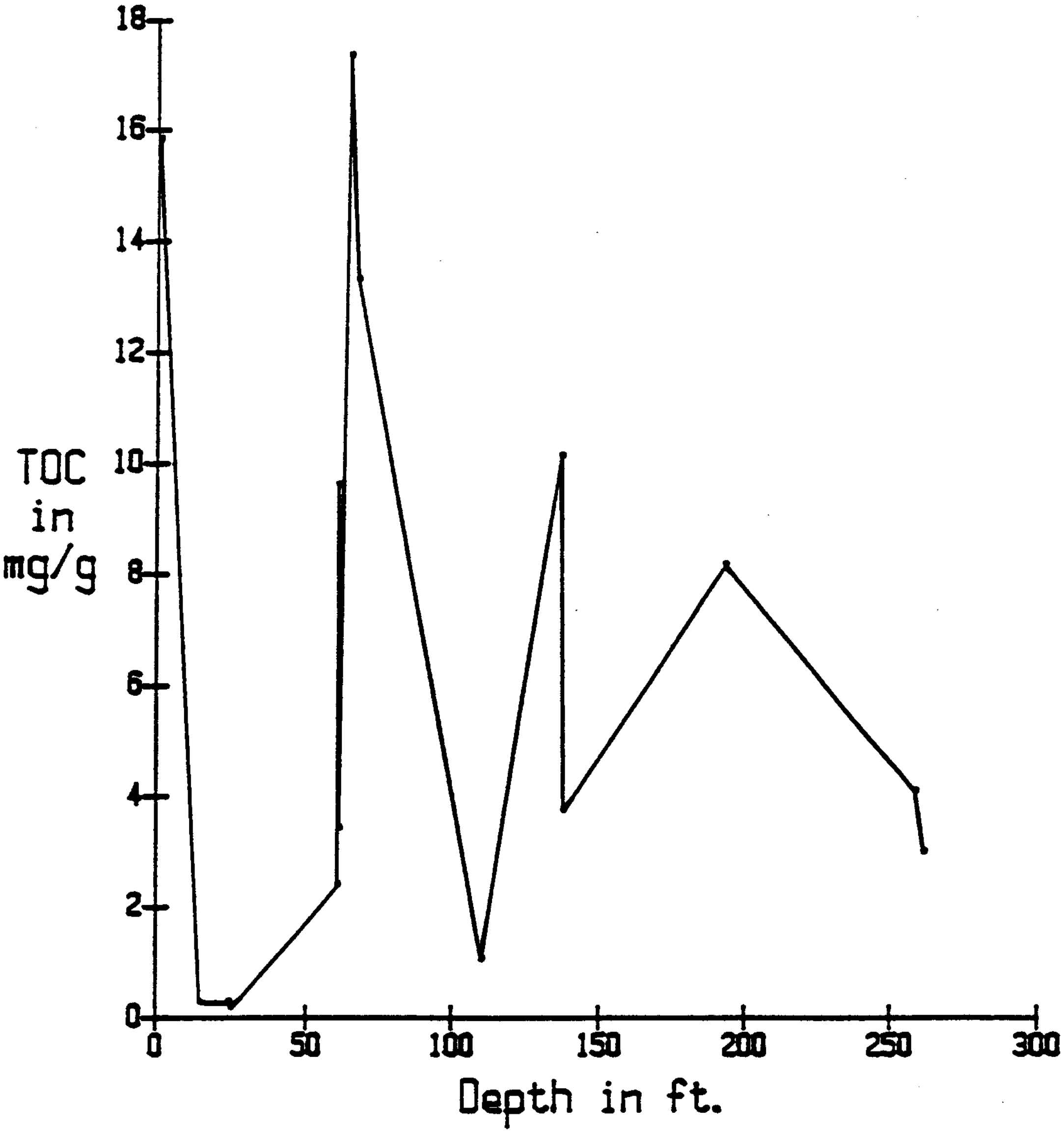

Figure 9: Depth vs TOC for Site L

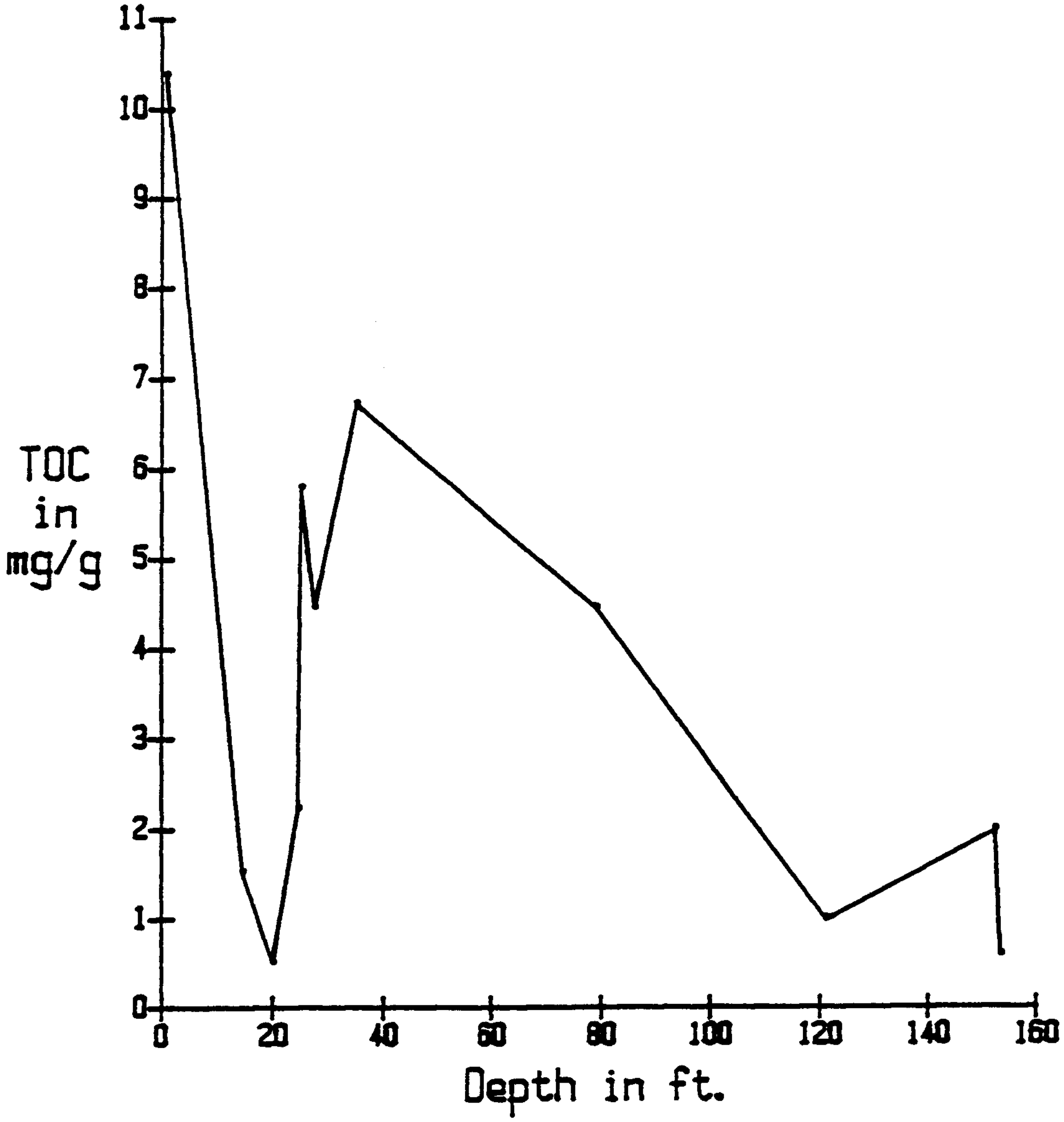

Figure 10: Depth vs TOC for Site H

value and chroma as a decimal, e.g., for N 1.0 (Munsell color 10 YR 4/2) the number used in the statistical analysis would be 4.2. Thus, the correlation coefficients are negative since the darker the sediment color the lower its designated number. As shown in Table 17, there is a significant (> 95%) correlation between sediment TOC and color at all sites.

Table 17
Correlation Coefficents for TOC vs Color

Site	(r)
ST	-0.896
SA	-0.932
N	-0.891
C	-0.847
L	-0.543
H	-0.857

Directly related to TOC and color were the %EOC values found for the sediments. These values were also widely variable. The highest %EOC values were almost always found in the topsoil samples. The only exception to this was at site C where the %EOC at C 1.0 was 28% and the highest value was 46% found at C 17.5. Figures 11-16 show the relationship between TOC and %EOC. It can be seen that for the majority of the sites the %EOC decreased with increasing TOC. The topsoil samples were an exception to this; at all sites except L the topsoil samples contained the highest TOC, and at all sites except SA and C the topsoil had the highest %EOC. The correlation coefficients for the relationship between sediment TOC and %EOC are given in Table 18. The values were computed without using the topsoil data.

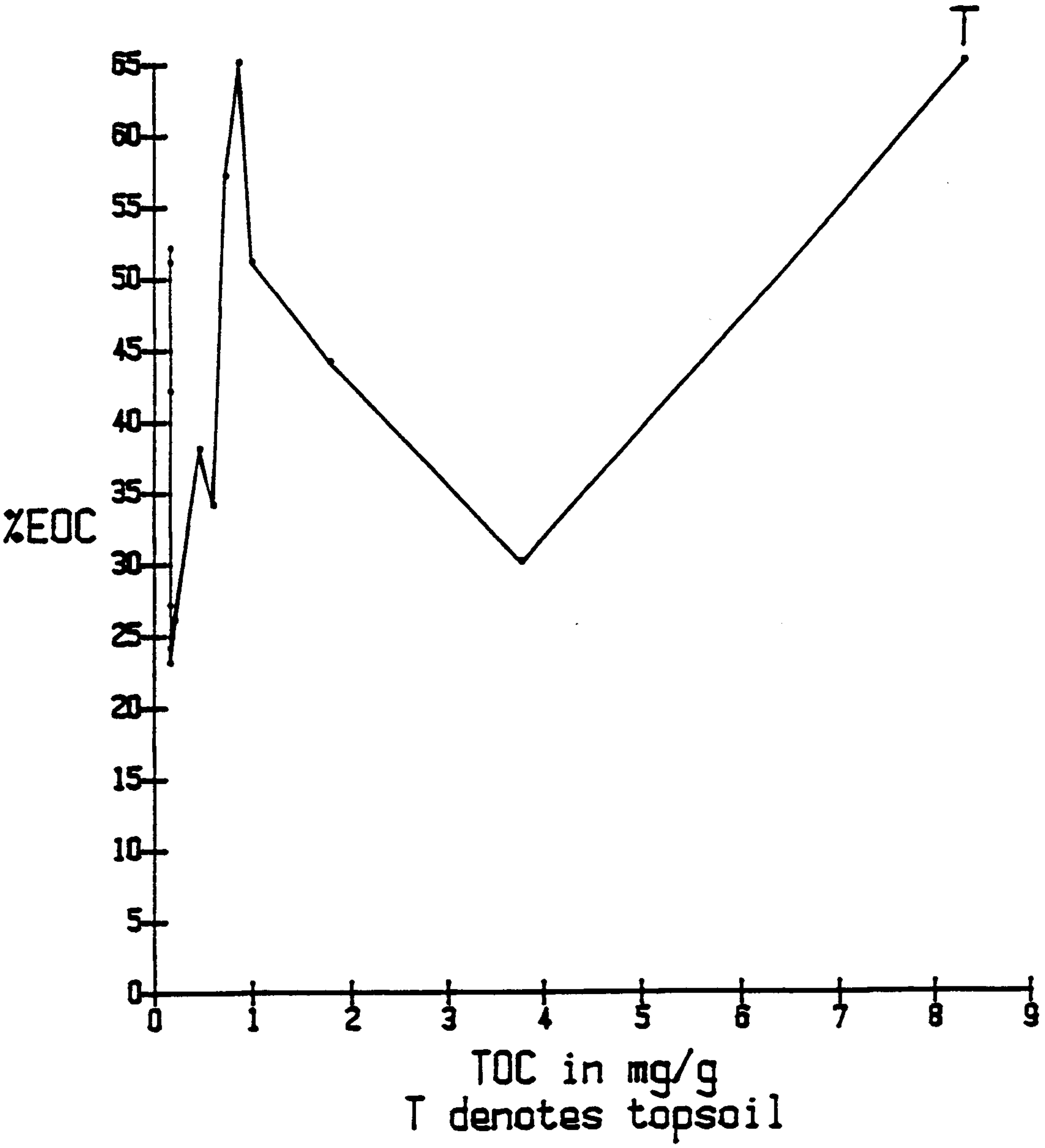

Figure 11: TOC vs %EOC for Site ST

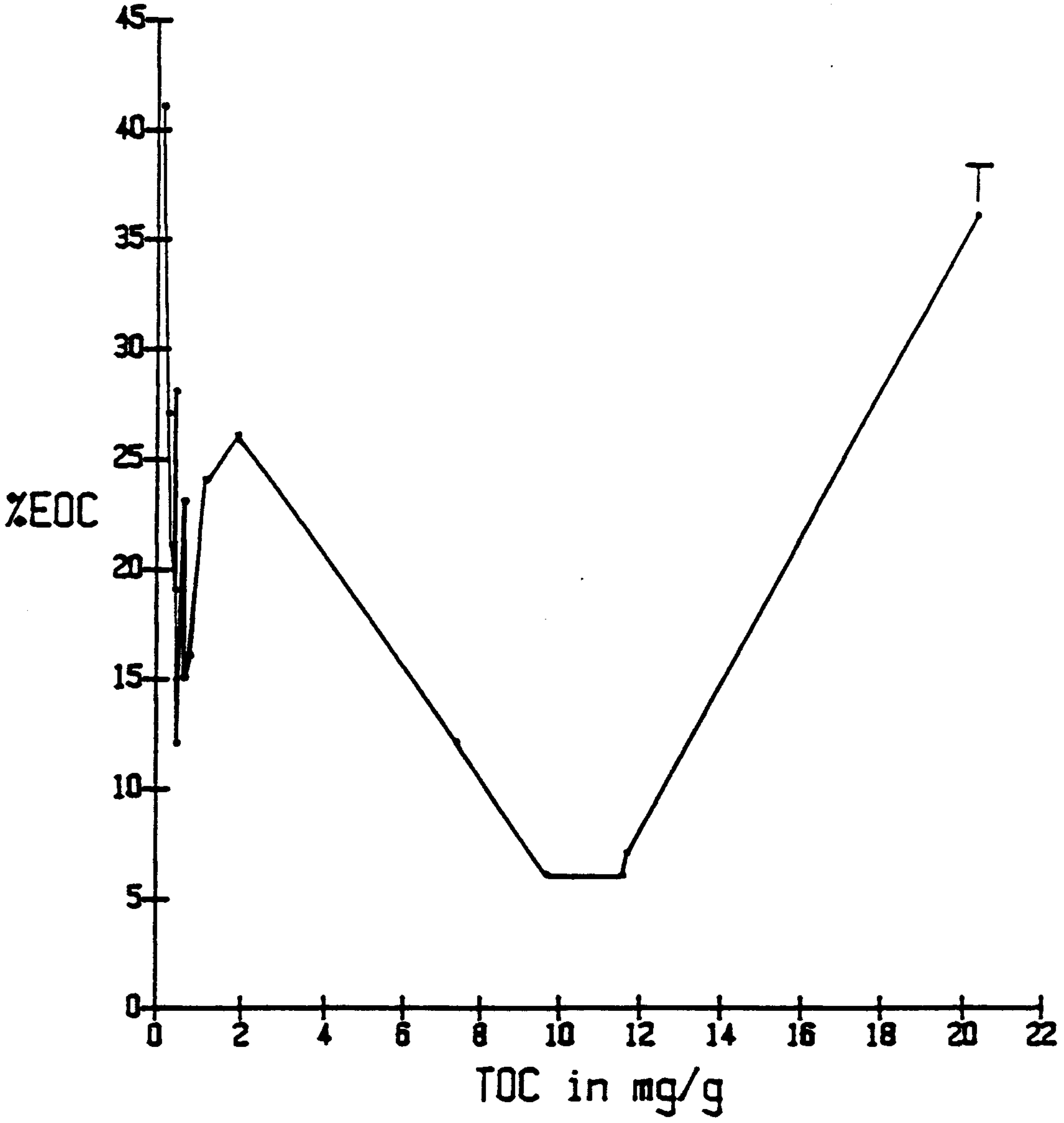

Figure 12: TOC vs %EOC for Site SA

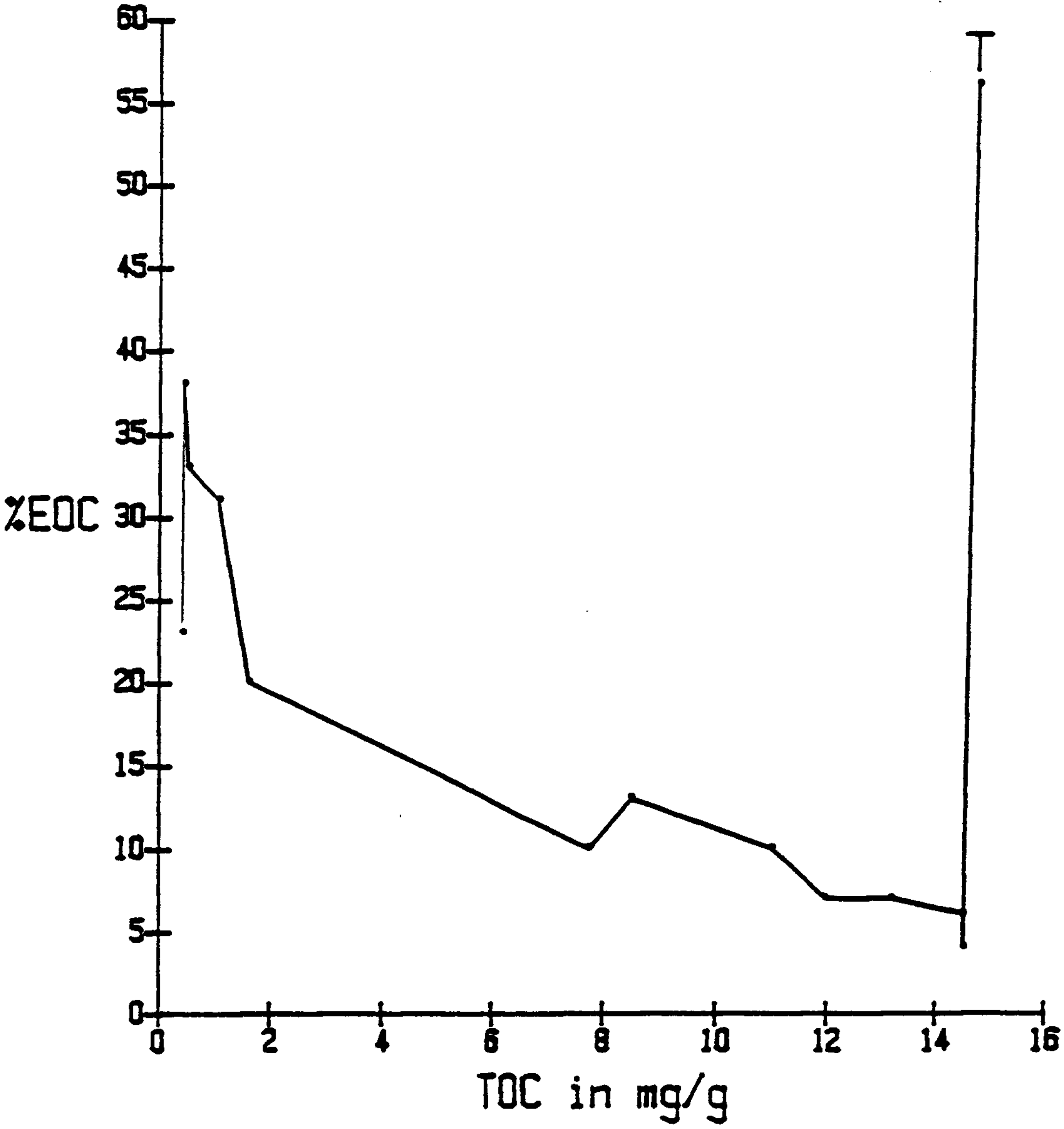

Figure 13: TOC vs %EOC for Site N

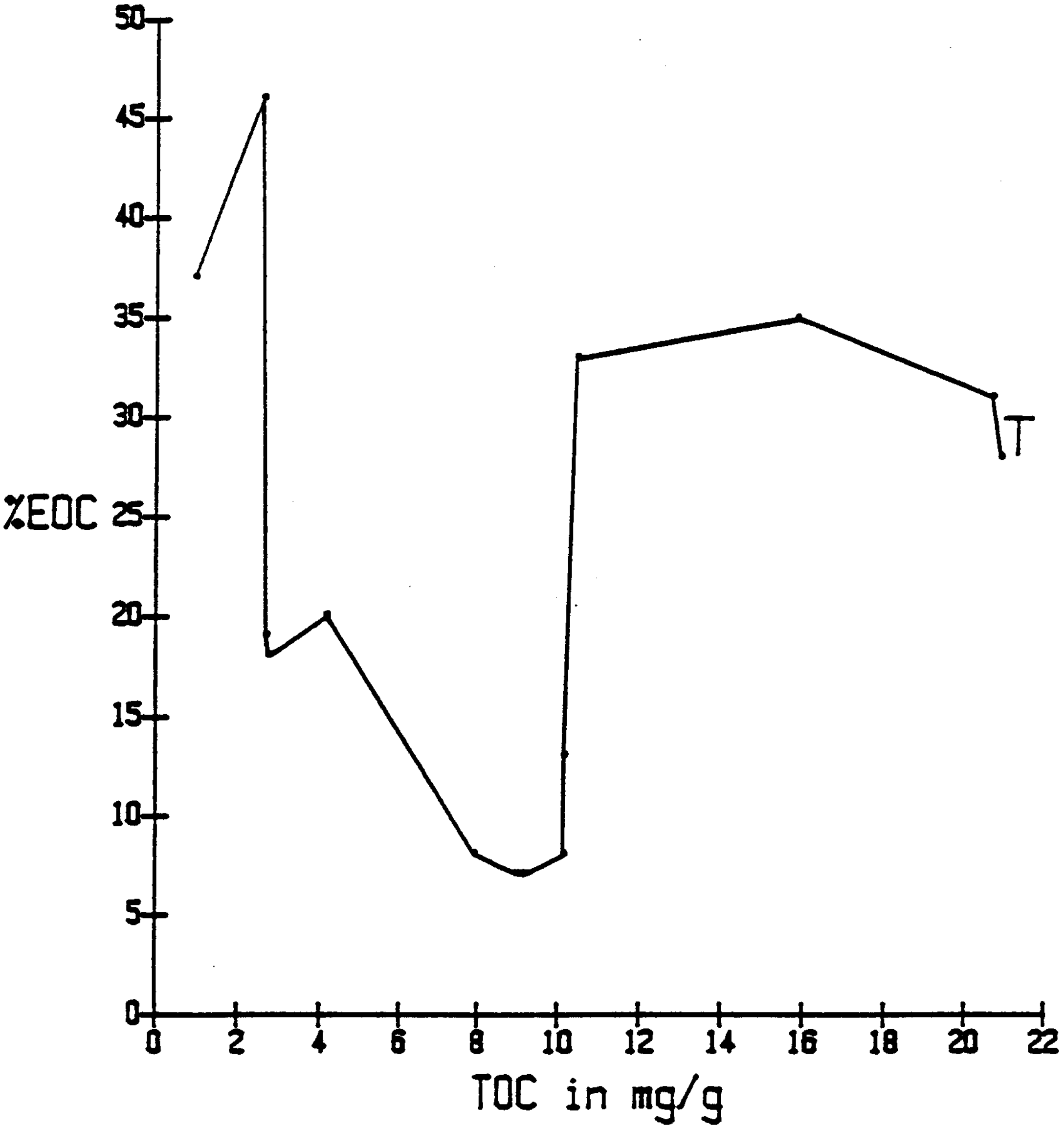

Figure 14: TOC vs %EOC for Site C

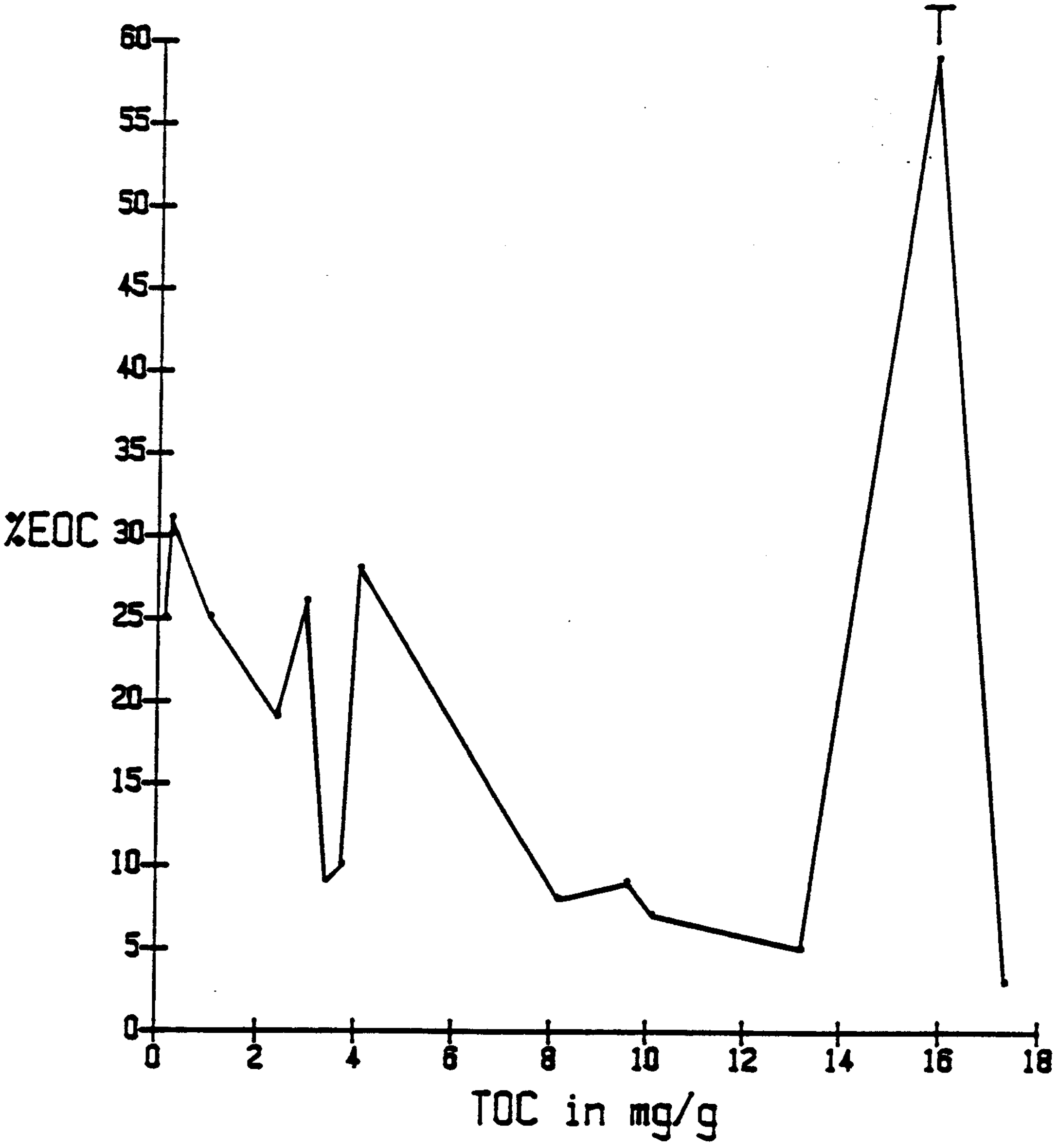

Figure 15 TOC vs %EOC for Site L

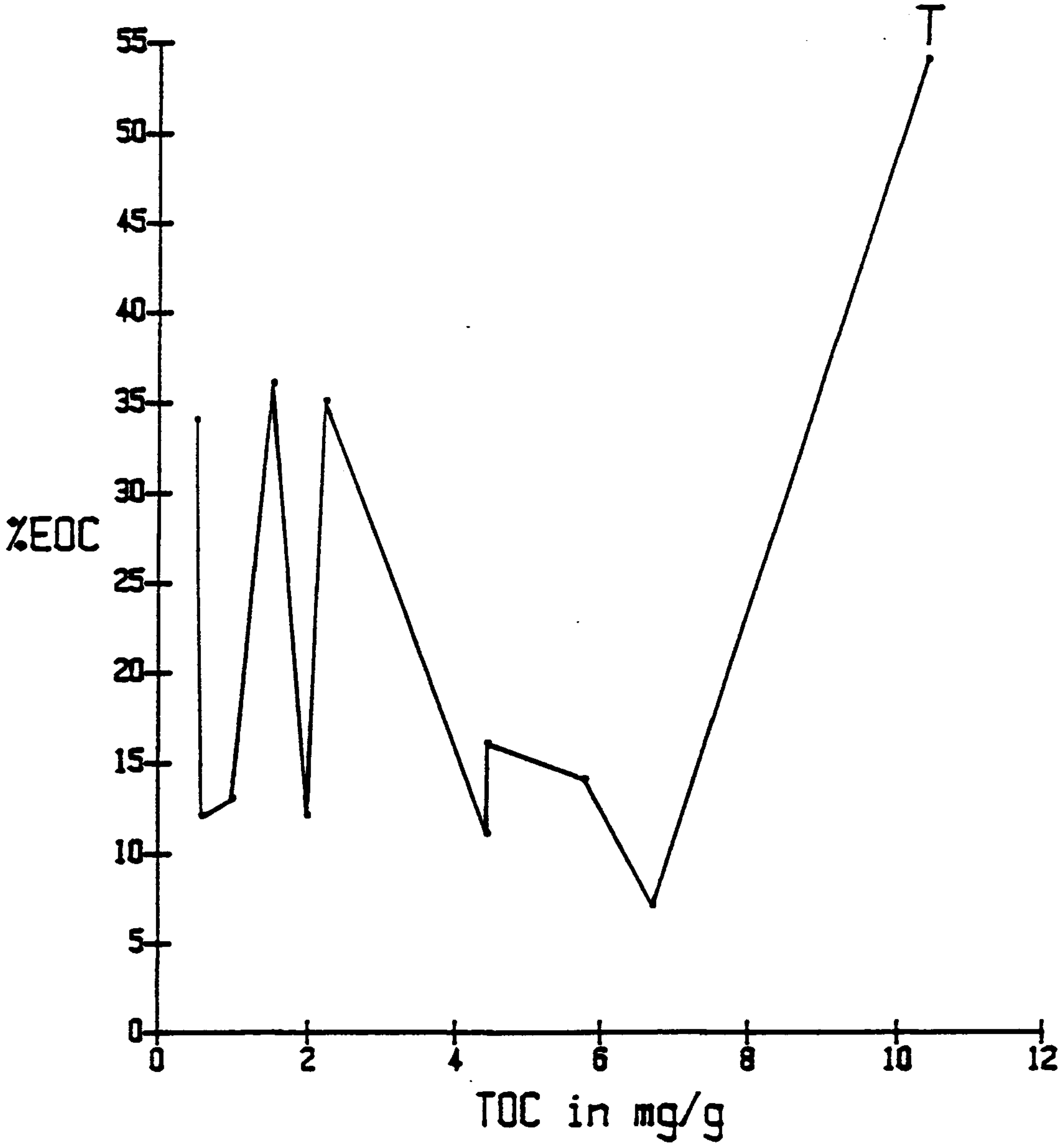

Figure 16: TOC vs %EOC for Site H

Table 18
Correlation Coefficients for TOC vs %EOC

Site	(r)
ST	-0.100
SA	-0.725
N	-0.920
C	-0.440
L	-0.824
H	-0.496

The data for sites SA, N, and L show a strong correlation of increasing %EOC with decreasing TOC. At sites C and H, the correlation coefficients (-0.440 and -0.496) are slightly below the 95% confidence level, and therefore the correlation is weak. At site ST, no significant correlation exists. This is probably due to the fact that TOC was below the accurate quantification limit in a majority of the sediments at site ST. Using a TOC of 0.16 mg/g for all those sediments having a TOC below the limit of accurate quantification does not reflect the actual relationship between TOC and %EOC because the %EOC values for the sediments having $\leq$ 0.16 mg/g TOC were computed using the actual (inaccurate) TOC values.

Since sediment TOC content correlated with sediment color and %EOC correlated with TOC, there should therefore be a correlation between %EOC and color. With the exception of the topsoil sediments, the higher TOC darker gray and brownish gray sediments tended to have lower %EOC values, generally of 3-15%. These were also the sediments having the highest TOC values. The lighter grayish and yellow sediments with low TOC contents were more extractable, often having %EOC values of 30-50%. Table 19 gives the correlation coefficients for the relationship between %EOC vs color. The same color number designation used in the TOC vs color analysis was used for this analysis. In this case, only sites SA and N had coefficients indicative of a strong correlation between increasing %EOC and increasing lightness in sediment color. Sites L and H had coefficients slightly below the 95% confidence level, thus they show a weak correlation. Site ST had a negative correlation coefficient (r=-0.545) probably resulting from the large number of samples below the accurate quantification level for TOC. Site C (r=-0.203) had some very extractable higher TOC sediments in the upper depths that behaved more like the topsoil. Exclusion of these samples (11.5, 12.5, and 15.0) produced r=0.588 which is similiar to the values found at sites L and H.

Table 19
Correlation Coefficients for %EOC vs Color

Site	(r)
ST	-0.545
SA	0.698
N	0.841
C	-0.203
L	0.419
H	0.545

The color of the sediment, its TOC content, and its %EOC could perhaps give an indication as to the composition of the sediment. As was stated earlier (Related Research), organic material tends to be associated with a darker color of soil and sediment. Also, humic substances are brown to black colored materials. A higher content of humic substances could explain why the darker colored sediments had higher TOC values, but not the differences in extractability between the darker and lighter sediments.

Samples N 330.0S and N 330.0C provide a good starting point for examining the differences in TOC and extractability. Although these samples had the same color, the TOC and %EOC values were quite different. N 330.0S had a TOC of 1.08 mg/g and was 31% extractable. N 330.0C, on the other hand, had a TOC of 8.51 mg/g and was only 13% extractable. The designation of S and C stood for sand and clay. From these samples, it appears that the presence of clay influences the TOC concentration as well as the percentage of the TOC that can be extracted. This makes sense because clay is known to attract and strongly bind organics and is therefore expected to cause higher TOC and lower %EOC values.

An attempt to explore this hypothesis proved inconclusive. Table 20 shows hydrometer data for some selected samples. The depths for which hydrometer data were available did not always correspond to the exact depth of the TOC and %EOC data. In such instances the TOC and %EOC values at the depth closest to the depth or the hydrometer data are given.

Table 20
Hydrometer Data For Selected Core Samples

Sample	Color	%Clay	%Silt	%Sand	TOC mg/g	%EOC
ST 33	10 YR 7/2	3	71	26	<0.16	51
ST 85	10 YR 7/2	7	29	64	<0.16	23
ST 185	10 YR 6/2	16	34	50	0.86	65
ST 188	10 YR 6/2	7.4	57	35.6	0.99	51
SA 73	5 Y 5/1	27	55	18	11.68	6
SA 277.5	2.5 Y 8/2	31.4	65	3.6	0.46	28
N 329*	10 YR 7/1	7.4	91	1.6	1.08/8.51	31/13
C 72	5 Y 6/1	15	57	28	7.94	8
L 25	10 YR 6/6	7	41	52	<0.16	25
H 34.5	10 YR 6/1	9	53	38	6.71	7
H 121	10 YR 7/1	2	33	65	0.98	13

* Values of TOC and %EOC are for N 330.0S and N 330.0C.

The data for H 34.5 and H 121 support the hypothesis that the samples having a higher TOC and lower %EOC have a higher clay content, but SA 73 and SA 277.5 show that the opposite is true. The fact that the hydrometer data did not necessarily correspond to the exact depths of the TOC and %EOC data probably was quite significant considering the sharp variations in TOC and %EOC values that were observed over short distances. Thus, from the sparse hydrometer data that was available, no real conclusions could be drawn as to the correlation of clay content with TOC and %EOC.

A plausible explanation for the increased TOC values found at depth cannot be readily given in the context of Figure 2, the soil profile. Although the trend of color changes in the core sections at all the sites generally fit the characteristics of the soil profile, the actual evolution of the sediment columns at these sites was very different from that of the generalized soil horizon profile, due to the glaciation of the area. The lower TOC, yellowish and brown sediments were probably deposited by streams and rivers. The higher TOC, darker brownish and gray sediments were probably buried soil horizons or deposits of glacial till.

Ammonium

As was found in a previous study (Denne et al., 1984), the amount of extractable NH_4^+ generally increased with depth. Only at sites SA and H did the highest extractable NH_4^+ value not correspond to the deepest sediment sample. However, at these sites the highest value was found at considerable depth (99 mg/kg at SA 254 and 16 mg/kg at H 79 and 121). It was interesting to note that site ST contained very little extractable NH_4^+ as compared to the other five sites. Although large concentrations of extractable NH_4^+ appeared tobe found in the gray sediments, there was no direct correlation with sediment TOC. Generally high extractable NH_4^+ concentrations were found at the sites having high TOC values. Table 21 gives a statistical analysis for NH_4^+, TOC and EOC. The Spearman rank-order correlation coefficients indicate that the average extractable NH_4^+ was strongly correlated to the average TOC concentration (r_s=0.829) and to the average EOC concentration (r_s=0.829). However, the extractable NH_4^+ was present in both the lighter and darker gray sediments having variable TOC measurements. Hence, it can be concluded that a reducing environment is associated with higher concentrations of extractable NH_4^+ and TOC, but TOC accumulates differently in the sediments than does NH_4^+.

Table 21
Statistical Analysis of TOC, EOC, and Extractable NH_4^+

Site	Avg. TOC (mg/g)	Avg. EOC (mg/g)	Avg. NH_4^+ (mg/kg)
ST	1.24	0.62	2.9
SA	4.01	0.70	37.2
N	7.72	1.19	23.4
C	9.11	1.95	38.8
L	6.71	1.07	10.8
H	4.00	0.91	8.4

Correlation	(r_s)
Ext. NH_4^+ vs TOC	0.829
Ext. NH_4^+ vs EOC	0.829

ETFP

Site SA was the only site for which Cl_2 residuals were not measured for all the samples (only for those suspected of being less than 0.2 mg/L) and for which only one chlorinated sample was extracted (the one with the lowest free chlorine residual greater than 0.2 mg/L). Because of this the ETFP values for site SA may be slightly low in comparison to those at the other sites. For the other five sites the ETFP procedure was followed as described earlier (see Analytical Methods). The ETFP data from the five sites having three measured chlorine residuals was treated in the same manner as the groundwater TFP data, resulting in ETFP concentrations and ETFP yields determined at a 3.0 mg/L Cl_2 residual.

Chlorination of the sediment extracts produced mainly $CHCl_3$, since there were only traces of bromide in the STP extract. As was seen for the groundwater samples, ETFP concentration generally increased with increasing Cl_2 dose and residual. At each site there was a very strong correlation between EOC and ETFP. Table 22 gives the correlation coefficients for this relationship.

Table 22
EOC vs ETFP

Site	(r)
ST	0.999
SA	0.999
N	0.995
C	0.982
L	0.984
H	0.992

The ETFP yields were similar to or somewhat higher than the yields found for the groundwater samples. The average ETFP yield for all the sediment samples was 0.33 umoles/mg EOC, slightly above the average TFP yield of 0.30 umoles/mg DOC for the groundwater samples. There was an interesting correlation between the TOC of the sediments and their corresponding ETFP yield. At most sites the ETFP yields generally increased with increasing sediment TOC. Figures 17-22 illustrate this relationship. The topsoil samples again did not follow the general trend. Although the topsoils at each site contained significant quantities of TOC, their corresponding ETFP yields were lower than those found in the deeper sediments having similar TOC contents. This again indicated that the organic material in the topsoil was different and not as potent a THM precursor as the material found in deeper sediments. Table 23 gives the correlation coefficients for TOC and EOC vs ETFP yield for each site, excluding the topsoil samples. The correlation coefficients for sites SA, N, and C show strong correlations for TOC and EOC vs ETFP yield, but the correlations were very poor at sites ST and L. The lack of accurate TOC data is probably the reason for the poor correlation between TOC and EOC vs ETFP yield at site ST. Site L shows no correlation for TOC vs ETFP yield but shows a strong correlation between EOC and ETFP yield. At site L, some of the lower TOC sediments had higher yields than were found in some of the higher TOC sediments. These lower TOC sediments were relatively extractable and therefore produced EOC concentrations greater than some of the higher TOC sediments. Thus, EOC correlated to ETFP yield adn TOC did not. Site H, on the other hand, shows a strong correlation for TOC vs ETFP yield but only a weak correlation for EOC vs ETFP yield. Table 23 also gives the correlation coefficients for ETFP yield vs color (again excluding the topsoil data). Sites SA, N, and C show strong

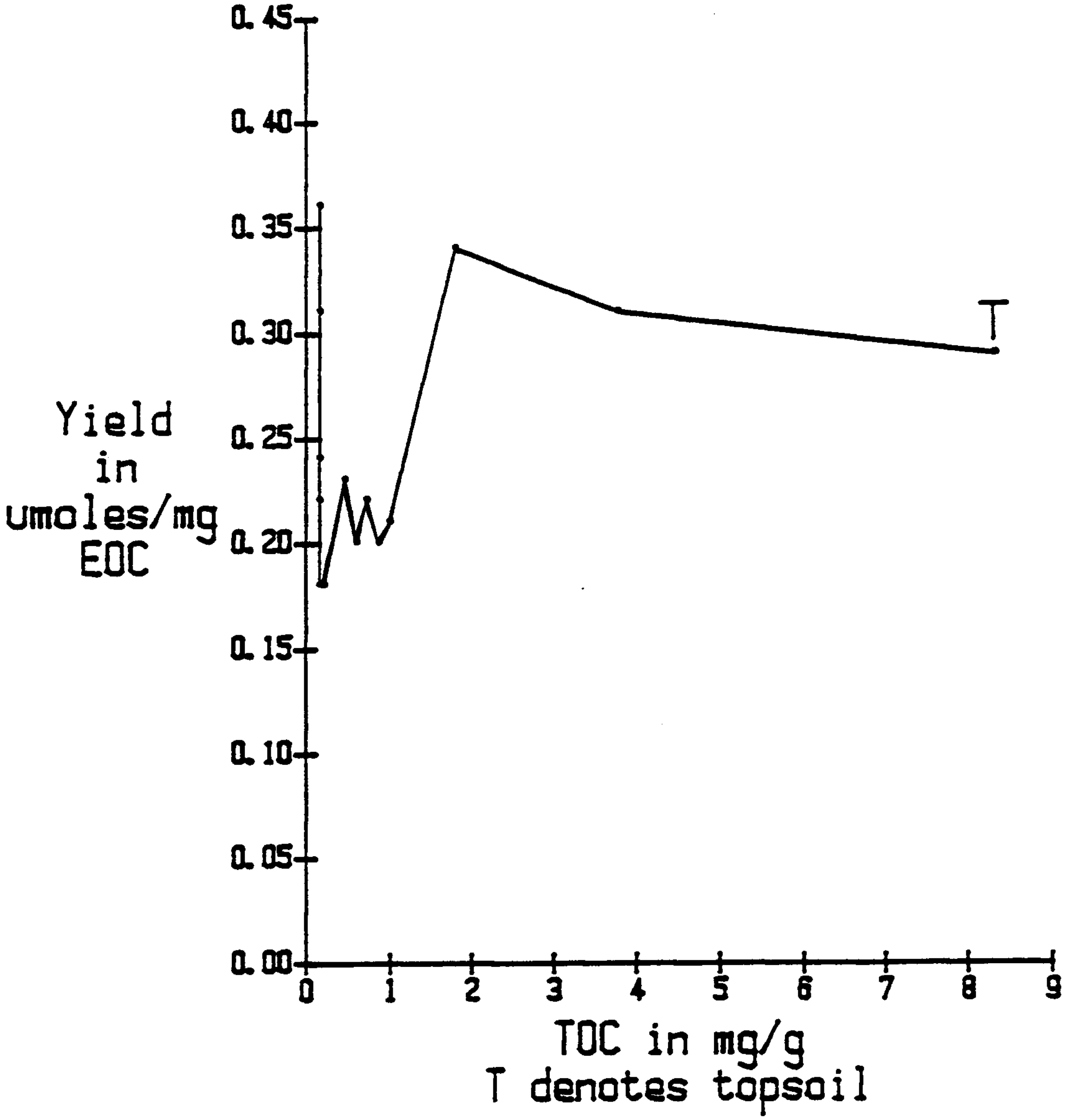

Figure 17: TOC vs ETFP Yield for Site ST

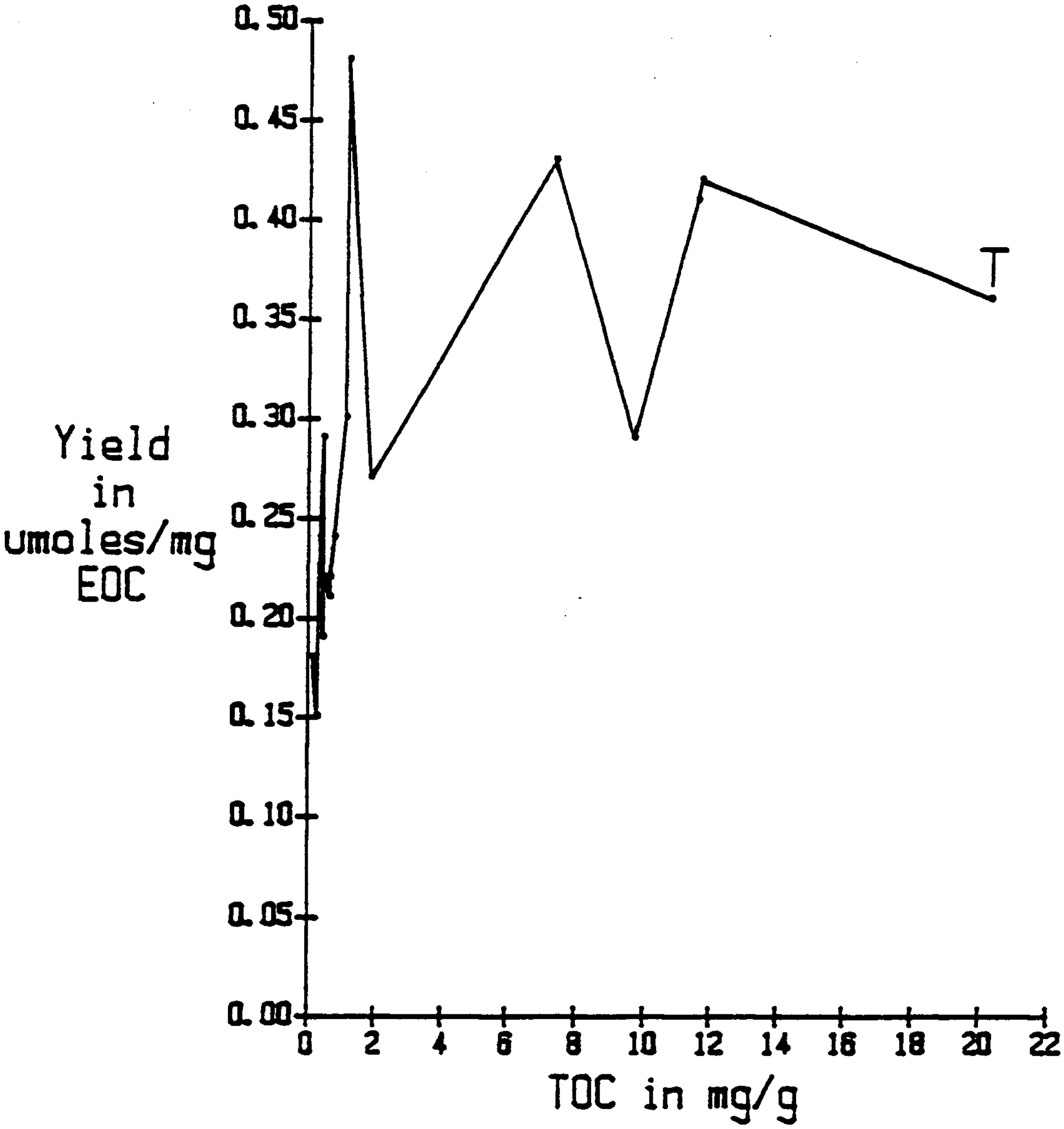

Figure 18: TOC vs ETFP Yield for Site SA

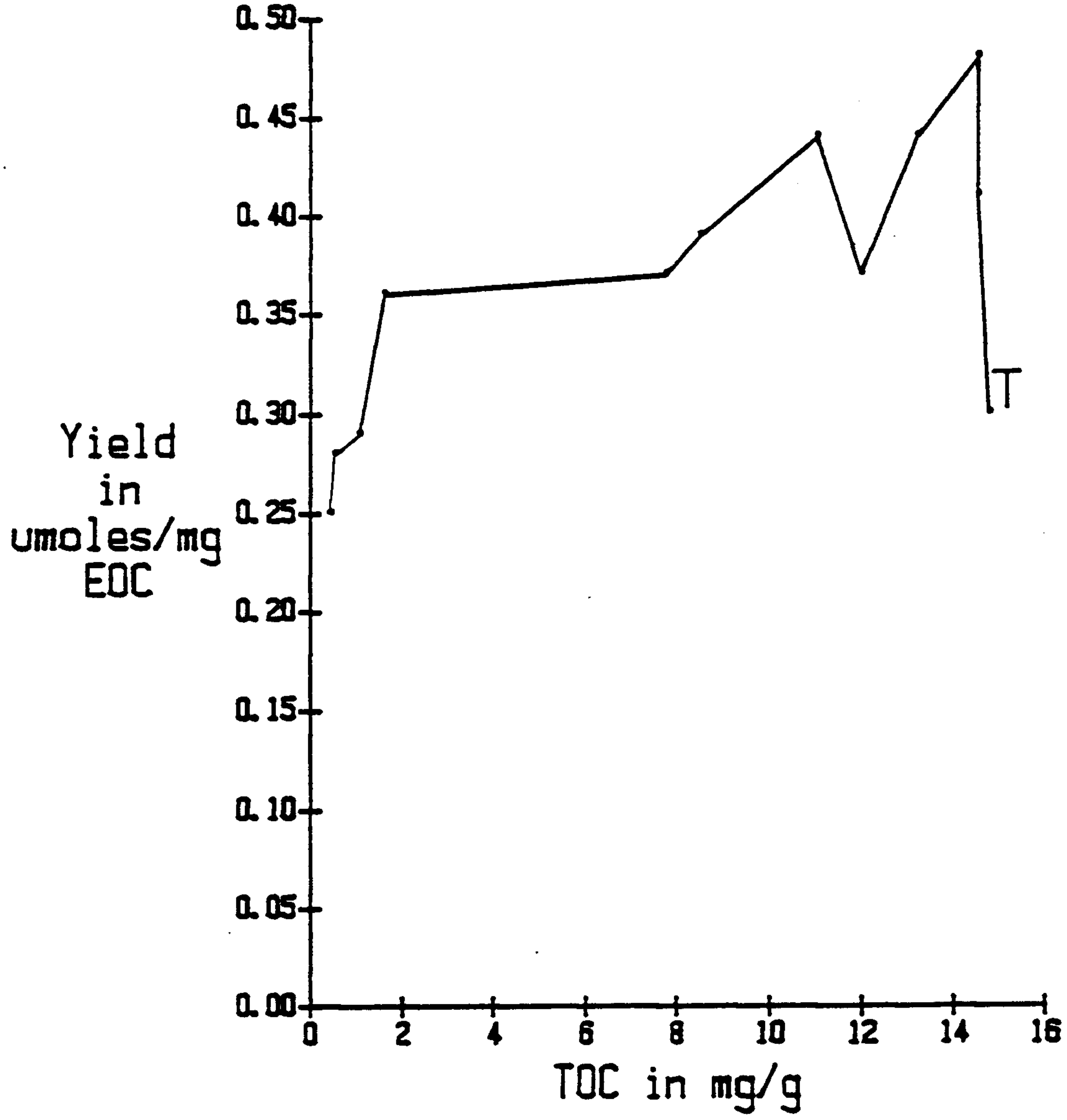

Figure 19: TOC vs ETFP Yield for Site N

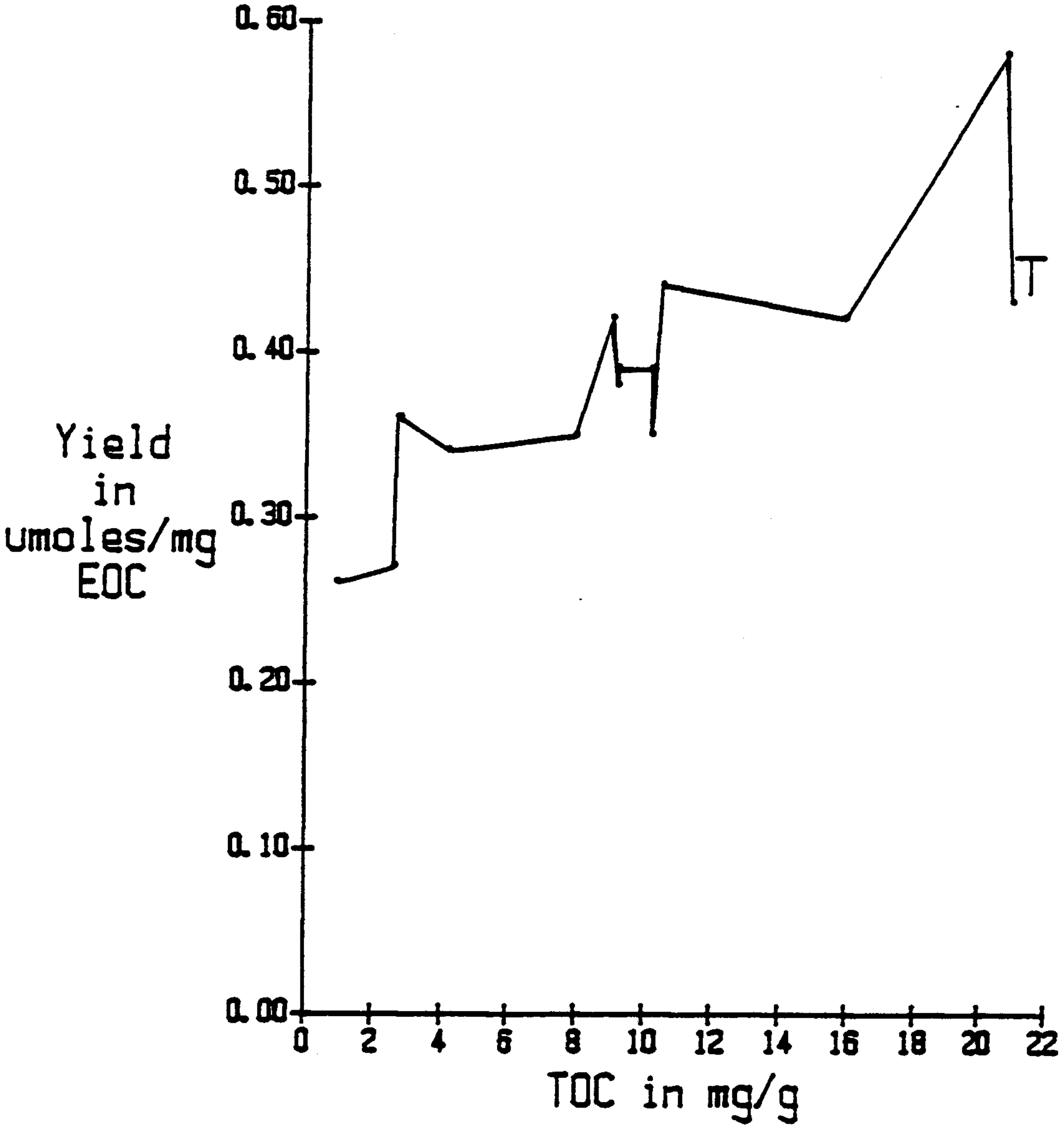

Figure 20: TOC vs ETFP Yield for Site C

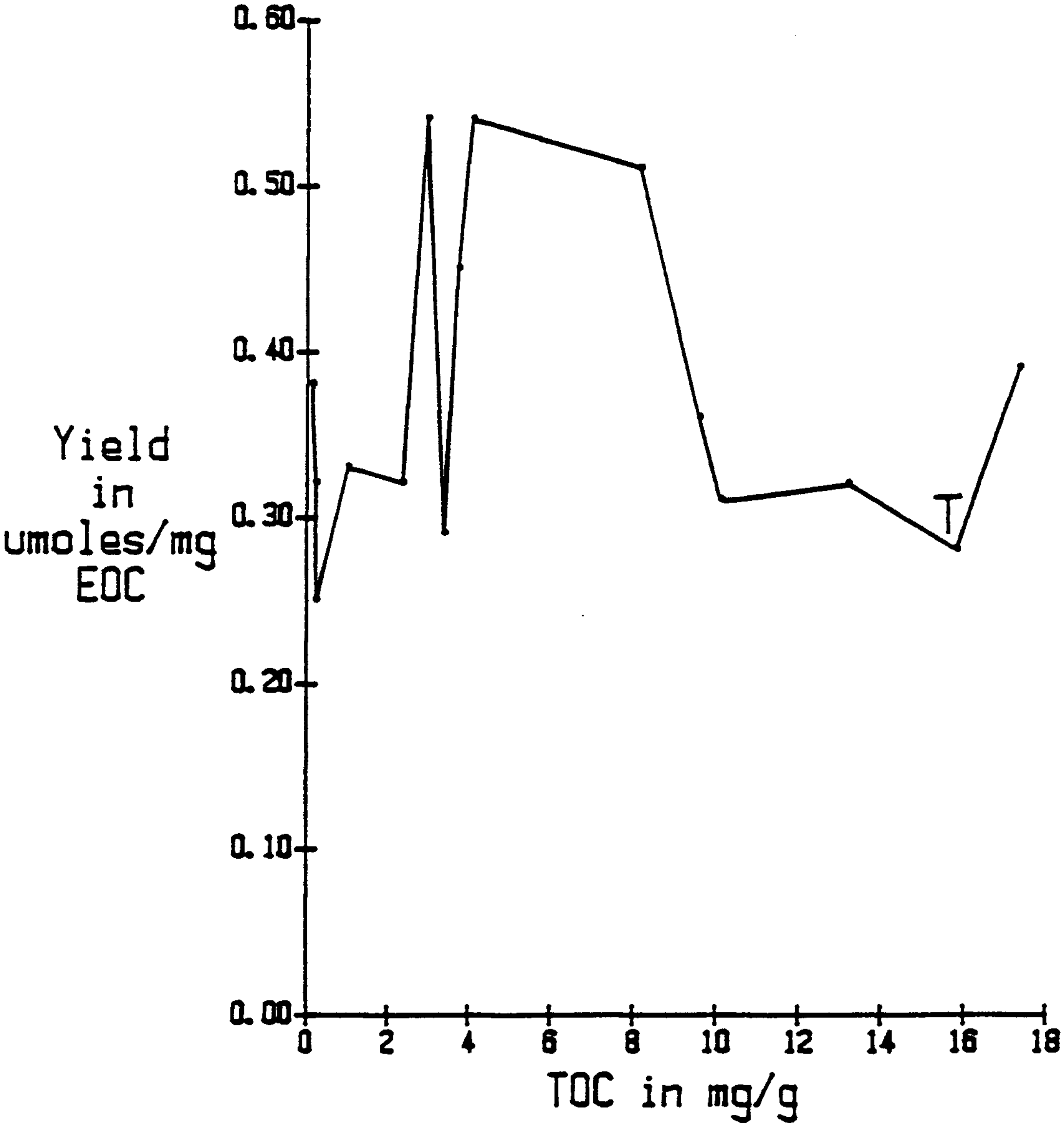

Figure 21: TOC vs ETFP Yield for Site L

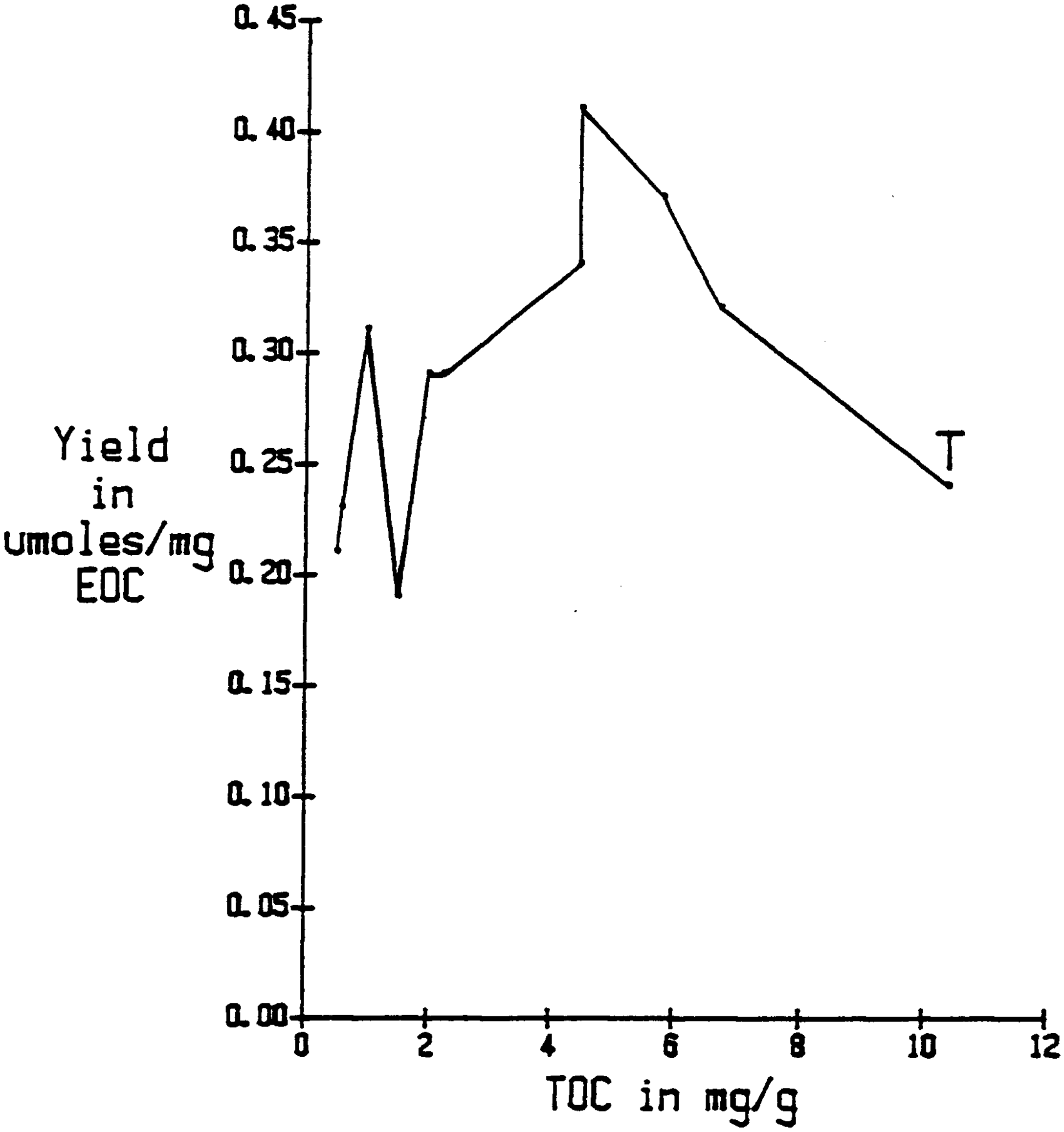

Figure 22: TOC vs ETFP Yield for Site H

correlations. The correlation at site H is below the 95% confidence level, but is close to that value. The data are uncorrelated for sites ST and L. Hence at site L, neither TOC nor color were indicative of the ETFP yield.

Table 23
Correlation Coefficients for TOC and EOC vs ETFP Yield and ETFP Yield vs Sediment Color

Site	TOC vs ETFP yield	EOC vs ETFP yield	ETFP yield vs color
ST	0.395	0.332	-0.176
SA	0.656	0.759	-0.592
N	0.903	0.850	-0.834
C	0.875	0.740	-0.789
L	0.065	0.603	-0.145
H	0.731	0.534	-0.582

The ETFP yields for all samples at site C were on the average higher than those found at any of the other sites. All but two of the yields were above 0.34 umoles/mg EOC, with the average being 0.38 umoles/mg EOC. This agrees well with the higher TOC values found at site C. The C sediments were mainly grayish brown to gray, and the %EOC values were relatively low. A statistical analysis using the data generated for all sites (including topsoil samples) gave correlation coefficients of 0.589 for ETFP yield vs TOC and -0.410 for ETFP yield vs %EOC. The greater than 95% confidence of these coefficients indicates an overall relationship between high ETFP yield, TOC, and low %EOC.

All the sites that had fairly high average ETFP yield values also had high concentrations of extractable NH_4^+ in the deeper sediments. However there was a poor correlation ($r=0.159$) between sediment ETFP yield and extractable NH_4^+.

C. Groundwater and Sediment Relationships

Groundwater Sediment Colors

After separately analyzing the groundwater and sediment data, it was apparent that some distinct similarities were present. The first indication that perhaps there were some correlations between the groundwater and sediment data became evident in the determination of groundwater sediment color, i.e., the color of the suspended solids deposited on the filter paper used to filter a groundwater sample. Table 24 gives the sediment color data (no sediment color data was available for the summer samples).

Many of the shallow- and mid-depth groundwater sediment colors differed only by Munsell soil color value from the core sample colors found at the well-screen depths. The hues and chromas were identical. This was true of wells SA-M, N-S, N-M1, L-S, H-S1, and H-S2. Well C-M had a filter paper color that exactly matched the color of the sediment in the depths from which it was taken. SA-S did not match the sediment colors at 41-45 ft, but it did match exactly with sediment SA 7.0 during the fall and winter sampling. In the spring the filter color was more similar to that of SA 15.0 ft. This indicated that the nearby sediments through which the well penetrates may exert some influence on a groundwater sample.

None of the deep groundwater sediment colors came anywhere close to matching the colors of the nearby core samples. The colors of the deep groundwater sediments were all very similar though, regardless of the site. Generally the colors were yellowish to yellowish orange, such as 2.5 Y 7,8/4 or 2.5 Y 7/6. ST-D was 5 Y 8/2

Table 24
Groundwater Sediment Colors

Well	Screen Depth (ft.)	Fall	Winter	Spring
ST-M	70-80	10 YR 8/3	2.5 Y 8/2	10 YR 8/3
ST-D	171-175	5 Y 8/2	5 Y 8/2	2.5 Y 7/4
SA-S	41-45	10 YR 7/3	10 YR 7/3	2.5 Y 8/2
SA-M	185-198	*5 Y 6/1	*5 Y 6/1	*5 Y 6/1
SA-D	277-285	2.5 Y 8/4	2.5 Y 7/4	2.5 Y 7/6
N-S	45-52	*2.5 Y 6/4	*2.5 Y 7/4	*2.5 Y 6/4
N-M1	154-164	10 YR 8/1	*2.5 Y 7/2	*2.5 Y 7/2
N-M2	213-223	5 Y 5/1	5 Y 6/1	5 Y 6/1
N-D	327-334	2.5 Y 7/4	2.5 Y 7/6	2.5 Y 7/4
C-S	23-30	7.5 YR 6/6	7.5 YR 6/8	10 YR 6/6
C-M	66-73	#5 Y 6/1	2.5 Y 7/2	#5 Y 6/1
C-D	202-207	2.5 Y 7/6	2.5 Y 7/6	2.5 Y 7/4
L-S	23-29	*10 YR 8/4	*10 YR 7/4	10 YR 7/6
L-M	139-145		2.5 Y 8/2	2.5 Y 8/2
H-S1	14-20	*10 YR 7/4	*10 YR 7/4	*10 YR 7/4
H-S2	28-35	10 YR 5/3	*2.5 Y 6/2	*2.5 Y 6/2
H-D	135-154		2.5 Y 8/4	2.5 Y 8/4

* Denotes groundwater sediments colors that correlated with core sample colors found at well-screen depths. Correlation means the colors were on the same Munsell soil color chart and had the same chroma but a different value. For example, the sediment color of SA-M was 5 Y 6/1 and SA 195 was 5 y 5/1, one value darker than the sediment color of SA-M.

\# Denotes a groundwater sediment color and core sample color matching exactly.

white in the fall and winter sampling, but did show the familiar yellow color, 2.5 Y 7/4, in the spring. The orangey tints to the colors may have been caused by the oxidation of Fe^{2+} to Fe^{3+} and the resulting precipitation of Fe(III) hydrous oxides. In general, most of the deeper samples contained high concentrations of Fe. C-S was the only shallow well to contain higher concentrations of Fe than the deeper wells. Its filter papers were very reddish orange and did not match the surrounding sediments (the filter colors had not been seen previously in any of the sediments). Also, in the spring when the Fe concentration in well C-S decreased considerably, the reddish color did also. This indicated that perhaps it was the oxidation of Fe that produced the reddish tints. The oxidation of Fe would have been expedited by the air lift pumping method used to retrieve the samples.

DOC, TOC, and Comparisons

As was stated in the discussion of the groundwater data, sites SA, N, C, and H tended to have the highest groundwater DOC values. The sites having the highest sediment TOC and EOC values were N, C, and L. Site C had the highest average groundwater DOC and sediment TOC and EOC values, while in all cases site ST had the lowest values. Hence, a correlation between DOC vs TOC and EOC seemed evident. Table 25 gives the average groundwater DOC and sediment TOC and EOC values for each site. Generally the greater the average sediment TOC and EOC, the greater is the average groundwater DOC. The Spearman rank-order correlation coefficient for DOC vs TOC is 0.829. Considering the differences in the number and distribution of the sediment samples at each site, the differences in well depths at each site, and the lack of a deep well at site L, the strength of the correlation is somewhat remarkable and indicates a very close relationship between sediment TOC and groundwater DOC. The Spearman rank-order correlation coefficient for the relationship between DOC and EOC is 0.771. This value is slightly below the 95% confidence value of 0.811, and therefore indicates that the groundwater DOC was more closely related to sediment TOC than to the EOC.

Table 25
DOC, TOC, and EOC Comparisons

Site	Avg. DOC (mg/L)	Avg. TOC (mg/g)	Avg. EOC (mg/g)
ST	1.14	1.24	0.62
SA	2.79	4.01	0.70
N	3.06	7.72	1.19
C	4.26	9.11	1.95
L	1.27	6.17	1.08
H	2.63	4.00	0.90

Although site L had a low average groundwater DOC value of 1.27 mg/L, the average sediment TOC of 6.17 was relatively high. In this situation, it appeared that perhaps the TOC values of the sediments at the well-screen depth strongly influenced the DOC concentration. L-S was screened from 20-30 ft. and had an average DOC of 1.44 mg/L, while the TOC values in the screened depths ranged from < 0.16-0.27 mg/g. Also, as was illustrated in the discussion of the sediment data, site L did not reflect many of the evident relationships present at the other sites. This may indicate that the interaction between the groundwater and sediments at site L is somewhat different from that at the other 5 sites. However, it should be noted that there was no deep well at site L, and there was no well in the vicinity of several sediment samples with a high TOC content.

TFP and ETFP Relationships

The TFP and ETFP data also bear out a correlation between the groundwater samples and the core sediments. The most notable indication of this can be seen in the comparison of TFP and ETFP yields for each site (see Table 26). As was true for the DOC, TOC, and values, the TFP and ETFP yields were generally higher or lower at the same sites. Again site C had the highest values, and site ST had the lowest values both for TFP and ETFP yield. Site L again was an exception perhaps for the reasons discussed above.

Table 26
Average TFP and ETFP Yields
(at 3.0 mg/L Cl_2 Residual)

Site	Avg. TFP Yield	Avg. ETFP
ST	0.18	0.24
SA	0.34	*0.29
N	0.34	0.36
C	0.34	0.38
L	0.18	0.37
H	0.30	0.29

* Value probably low due to chlorine residuals less than 3.0 mg/L.

Ammonium

The organic matter present in the sediments was not the only influence upon the groundwater quality. There was a definite correlation between the NH_4^+ concentrations found in the groundwater and the extractable NH_4^+ measured in the sediments. As was mentioned previously, the NH_4^+ concentrations in both the sediment and the groundwater increased with increasing depth at all sites. Table 27 shows the data for sites N and H. At site N, as the extractable NH_4^+ increases from 2 mg/kg to 74 mg/kg, the average NH_4^+ concentrations found in the groundwater rise from 0.5 to 9.2 mg/L. The groundwater and extractable NH_4^+ values at site H were much lower than those found at site N. For site H, as the extractable NH_4^+ increases from 1 mg/kg to 13 mg/kg, the average NH_4^+ concentration in the groundwater increases only from 0.1 to 1.0 mg/L. The more NH_4^+ present in the surrounding sediments, the greater the concentrations found in the groundwater. Obviously then, the NH_4^+ in the sediments is associated with the NH_4^+ in the groundwater or vice-versa.

Table 27
NH_4^+ in Groundwater and Core Sediments

Well	Screen Depth (ft.)	Sed. depth (ft.)	Ext NH_4^+ (mg/kg)	Ave. GW NH_4^+ (mg/L)
N-S	45-52	52.5	2.0	0.5
N-M1	154-164	158.0	23	1.9
N-M2	213-223	233.0	35	2.9
N-D	327-334	330.0	74	9.2
H-S1	14-20	14.5	1.0	0.1
H-S2	28-35	35.0	6.2	0.2
H-D	134-154	152.5	13	1.0

Summary

The final tying together of the most important groundwater and core sediment parameters (Table 28) demonstrates that, in general, the sites with high DOC/TOC (r_s=0.829) and high TFP/ETFP yields

(r_s=0.657) were also those with high NH_4^+ (r_s=0.943) concentrations (indicating a reducing environment). Thus reducing conditions, high DOC/TOC, and TFP/ETFP yields go hand in hand. Under reducing conditions, the precursor material appears to be more potent as well as more available in quantity.

Table 28
Statistical Analysis of Important Groundwater and Sediment Data

Site	Avg. DOC/TOC (mg/L)/(mg/g)	Avg. TFP/ETFP yield (umoles/mg DOC or EOC)	Avg. NH_4^+/Ext NH_4^+ (mg/L)/(mg/kg)
ST	1.14/1.24	0.18/0.24	0.1/2.9
SA	2.79/4.01	0.34/0.29	2.7/37.2
N	3.06/7.72	0.34/0.36	4.0/23.4
C	4.26/9.11	0.34/0.38	4.1/38.8
L	1.27/6.71	0.18/0.37	0.5/10.8
H	2.63/4.00	0.31/0.29	0.4/8.4

Correlation	(r_s)
DOC vs TOC	0.829
TFP vs ETFP	0.657
NH_4^+ vs Ext. NH_4^+	0.943

Several hypotheses may explain the close relationship between sediment TOC and groundwater DOC. Two deal directly with the mechanisms given in Thurman (1985a). First, it is thought that much of the organic matter in groundwater with DOC concentrations above 2.0 mg/L comes from direct contact between groundwater and the kerogen present in the sediment. It is also theorized that kerogen is related to the initial organic input deposited before sedimentation took place (Huc and Durand, 1977). Therefore, it is likely that at the sites with high sediment TOC contents had a greater initial organic input than the sites with lower TOC contents (i.e. site C vs Site ST). The greater the content of organic carbon in the sediment the more available it is to leach into the groundwater. Second, bacteria living in the sediment may use the organic carbon in the sediment as a food source and thus contribute to the groundwater DOC. The sites with high sediment TOC contents provide more food for bacteria. This could allow the bacteria to be more active in breaking down the organic carbon and thus to release more organic carbon into the groundwater. Third, less energy is available to microbes living in reduced environments, so a higher concentration of organic carbon may remain in both the sediments and the groundwater because its utilization by the microbes is not thermodynamically favorable.

CONCLUSIONS

A. Groundwater

Despite problems encountered because of poor well development, reasonable conclusions can still be made. The groundwater quality found in the glacial buried-valley aquifers in northeast Kansas was quite variable. Many of the aquifers had elevated levels of DOC, NH_4^+, Fe, and Mn and produced concentrations of THMs above the EPA primary drinking water standard of 100 ug/L. For the most part, both the concentration and yield of TFP were found to increase with increasing DOC concentration. It was also evident that the incidence of poor groundwater quality was related more to the site than to the depth from which the water was taken, although the highest concentrations of NH_4^+, Fe and Mn were generally found in the deepest well at each site. Referring to Figure 1, the poorest groundwater quality was found in the cross-section of the buried valley channel in Nemaha County in the wells drilled at sites SA, N, and C. These three sites had the highest average DOC, TFP yield, NH_4^+, Fe and Mn, while the sites to the west and east, ST, L, and H, had much lower average values of DOC, TFP yield, NH_4^+, Fe, and Mn.

B. Sediments

All the sites showed a trend of increasing pH with depth, and the deepest sediments often had pH values > 9.0. The color, TOC, and %EOC found in the sediments were inter-related in that the darkest sediments had the highest and least extractable TOC, while the opposite was true for the lighter sediments. The TOC decreased and the color lightened with increasing depth to a depth at which the TOC increased and the color darkened. From these depths, the sediment TOC generally tended to drop off and the color lighten as the depth increased to the bedrock. The lighter colored sediments were believed to have been deposited by streams and rivers, while the darker colored sediments are probably glacial till or buried soil horizons. Not enough hydrometer data was available to conclude that the higher TOC values found at the middle depths and the lower %EOC values found in these sediments were in fact due to an association with clay, although that is a logical hypothesis. The extractable NH_4^+ values also were found to increase with depth and to be associated with the grayish colored sediments having variable TOC contents. The concentration and yield of ETFP were found to correlate to the sediment TOC and EOC.

Although TOC, EOC, extractable NH_4^+, and ETFP yield varied greatly with sediment depth, averaging the values by site showed that the TOC, EOC, extractable NH_4^+, and ETFP yield were all higher or lower on a site specific basis. Again it was the Nemaha County cross-section of the buried valley channel, sites of SA, N, and C, that generally had the highest average sediment TOC and EOC contents, extractable NH_4^+ concentrations, and ETFP yields. Site L had some isolated instances of high values also. Reducing conditions, indicated by the presence of high concentrations of extractable NH_4^+, were associated high TOC contents. These conditions, in turn, were associated with high ETFP concentrations and yields.

C. Comparison of Groundwater and Sediments

A Comparison of the groundwater findings with the sediment data clearly shows that the sites having high average groundwater DOC, NH_4^+, and TFP yields are the same sites having high TOC, extractable NH_4^+, and ETFP yields. The Nemaha County cross-section sites of SA, N, and C fit this category. Site ST, to the west in Marshall County, had the lowest values found in both the groundwater and sediments. Site L had low values in the groundwater but somewhat higher values in the sediments, but the sediments that correlated to the well screen depths at site L all had fairly low TOC, extractable NH_4^+, and ETFP yields. Thus, it is concluded that indeed the groundwater quality is greatly influenced by the surrounding sediments.

D. Applications

The results of this study bear important implications for the future location and drilling of wells in northeast Kansas and perhaps elsewhere. Regarding northeast Kansas, the middle sections of Nemaha county, including sites SA, N, and C yielded groundwater of the poorest quality. It would appear to be advantageous to locate water supply wells to the east or west of these sites in order to obtain higher quality water. Since data from this study show that sediment characteristics are closely related to groundwater quality, examining the sediments at a site before drilling wells for a water supply may be helpful. Because the TOC and ETFP yield were so closely tied to the sediment color (which has been shown to relate to aqueous DOC and TFP), even a rough determination the sediment color would be a useful indicator of water quality. This may also apply to other geographical areas.

The highest concentrations of NH_4^+, Fe, and Mn were associated with the deepest groundwater samples which were in contact with the grayish sediments. Therefore locating the wells in the more yellowish and pale brown sediments above the deeper gray sediments should minimize the concentrations of NH_4^+, Fe, and Mn in the groundwater. The differences in the lighter brownish sediments and darker gray sediments may be indicative of differences in oxidation-reduction potential i.e., the lighter brownish sediments are oxidized and have low concentrations of NH_4^+, Fe, Mn, and TOC, while the darker gray sediments are reduced, having high concentrations of NH_4^+, Fe, Mn, and TOC. Knowing the depth where this sediment color change occurs would also be helpful in the location of water supply wells. However, the fact that the TOC and color were shown to vary substantially over short distances should be kept in mind when attempting to locate the depth of the major change in sediment color. In the situation of a well which is to be used as a city water supply, the hydraulic conductivity may not be high enough in the lighter upper sediments to support such a well. Therefore a large water utility should be prepared to treat the water produced by a deep well for possible high concentrations of Fe, Mn, THM precursors.

RECOMMENDATIONS FOR FUTURE RESEARCH

Due to the well development problems and collection of less than one year's worth of data, seasonal trends could not be adequately examined. Groundwater samples should be collected from the existing wells over a longer period of time, such as 2-3 years. This would allow for better well development and more in-depth examination of seasonal and temporal trends in water quality. It would also be interesting to see if the site specific trends in water quality found in this study would continue throughout a longer sampling period.

A detailed analysis of the characteristics of the organic matter in the groundwater and sediment could provide some interesting information. Such an analysis could include determination of: 1) the degree of humification (relative amounts of humic and fulvic acid; 2) solubility as a function of pH; 3) stability constants for various metal complexes, especially Ca, Al, and Fe; 4) adsorption isotherms on clay and sand; 5) molecular weight distribution; 6) biodegradability, including ability to serve as a food source for manganese oxidizing or denitrifying bacteria; 7) age (perhaps by carbon- 14 dating); 8) and the TFP yield of various fractions (high and low molecular weight, adsorbable and non-adsorbable, biodegradable and non-biodegradable, etc.). This information might be helpful in explaining differences in the concentrations of organic matter among the various sites, as well as changes with depth and relationships to other water quality parameters. It would also be interesting to examine the differences in the organics in the darker and lighter sediments.

A greater quantity of hydrometer data would be helpful in establishing whether or not the high sediment TOC values were associated with clay. An analysis done on a complete sediment core would be the most useful. This would also indicate whether or not the lower %EOC values found in the high TOC sediments were due to the strong interactions of the clays with the organic matter.

This research has demonstrated that sediments at depth can have significant TOC concentrations. Since TOC content is related to the ability of sediments to adsorb a variety toxic chemicals, barriers to the migration of toxic chemicals may exist at considerable depth. Research to explore this possiblity (e.g. isotherm and column adsorption tests) would be most helpful in accessing the vulnerablity of deep aquifers to contamination by toxic chemicals originating from landfills, spills, and deep-well injection of wastes.

REFERENCES

American Public Health Association (APHA), American Water Works Association, and Water Pollution Control Federation, Standard Methods for the Examination of Water and Waste Water, American Public Health Association, Washington D.C. (1985).

Amy, G.L., Chadik, P.A., and King, P.H., "Chlorine Utilization During Trihalomethane Formation in the Presence of Ammonia and Bromide," Environmental Science and Technology, 18(10), 781-786 (1984).

Barcelona, M.J., "TOC Determinations in Groundwater," Ground Water, 22(1), 18-24 (1984).

Barcelona, M.J., and Helfrich, J.A., "Well Construction and Purging Effects on Ground Water Samples," Environmental Science and Technology, 20(11), 1179-1184 (1986).

Bellar, T.A., Lichtenberg, J.J., Brass, H.J., Stevens, A.A., and Moore, L.A., "The Determination of Maximum Total Trihalomethane Potential: Method 510.1." Report No. EPA-600/4-81-044, U.S. Environmental Protection Agency, 1982.

Christman, R.F., Norwood, D.L., Millingtron, D.S., and Johnson, J.D., "Identity and Yields of Major Halogenated Products of Aquatic Fulvic Acid Chlorination," Environmental Science and Technology, 17(10), 625-628 (1983).

Denne, J.E., "Hydrogeology of Glacial Buried-Valley Aquifers in Northeastern Kansas," 28th Annual Midwest Groundwater Conference Abstracts, p.11 (1983).

Denne, J.E., Hathaway, L.R., and McCool, S.P., "Ammonium Ion, Humic Materials, and Trihalomethane Potential in Northeastern Kansas Ground Waters," Ground Water, 22(6), 755-763 (1984).

Denne, J.E., Miller, R.E., and Hathaway, L.R., (in preparation), "The Hydrogeology and Geochemistry of Glacial Deposits in Northeastern Kansas:" Kansas Geological Survey, (1986)b.

Denne, J.E., Randtke, S.J., and Hathaway, L.R., "Geological and Geochemical Factors Influencing Water Quality in a Buried Valley in Northeastern Kansas: Report of Year 1 Results," Project Completion Report, Kansas Water Resources Institute, University of Kansas, Contribution No. 253, June, 1986a, 53pp.

Denne, J.E., Randtke, S.J., and Hathaway, L.R., "Geological and Geochemical Factors Influencing Water Quality in a Buried Valley in Northeastern Kansas: Final Project Completion Report," Kansas Water Resources Institute, University of Kansas, in preparation (1987).

Dunbar, D., Tuchfeld, H., Siegel, R., and Sterbentz, R., "Ground Water Quality Anomalies Encountered During Well Construction, Sampling and Analysis in the Environs of A Hazardous Waste Management Facility," *Groundwater Monitoring Review*, *5*(2), 70-74 (1985).

Fleischacker, S.J., and Randtke, S.J., "Formation of Organic Chlorine in Public Water Supplies," *Journal of American Water Works Association*, *75*(3), 132-138 (March, 1983).

Froelich, P.N., "Analysis of Organic Carbon in Marine Sediments," *Limnology Oceanography*, *25*(3), 564-572 (1980).

Graham, L. Lawrence, Heath, R.C., Hinkle, L., Love, O.T., McNabb, J.F., Miltner, R.J., Pettyjohn, W.A., "Protection of Public Water Supplies from Ground-Water Contamination," Rept. No. EPA-625?4-85/016, U.S. Environmental Protection Agency, 1985.

Hathaway, L.R., Denne, J.E. , and McCool, S.P., "Where's the Residual Chlorine in Public Water Supplies of Northeastern Kansas," Proceedings of Conference on Trace Substances in Environment Health - XVIII, University of Missouri, Columbia, 163-169 (1984).

Huc, A.Y., and Durand, B.M., "Occurrence and Significance of Humic Acids in Ancient Sediments," *Fuel*, *56*(1), 73-80 (1977).

Junk, G.A., Spaulding, R.F., and Richard, J.J., "Areal, Vertical, and Temporal Differences in Ground Water Chemistry: II. Organic Constiuents", *J. Environmental Quality*, *9*(3), 479-483 (1980).

Kingstad, K.P., Ljungquist, P.O., deSousa, F., and Stromberg, L.M., "On the Formation of Mutagens in the Chlorination of Humic Acid," *Environmental Science and Technology*, *17*(9), 553-555 (1983).

Leenheer, J.A., Malcolm, R.L., McKinley, P.W., and Eccles, L.A., "Occurence of Dissolved Organic Carbon in Selected Ground-Water Samples in the United States," *Journal Res. U.S. Geol.Surv.*, 2(3), 361-369 (1974).

Maier, W.J., Gast, R.C., Anderson, C.T., and Nelson, W.W, "Carbon Contents of Surface and Underground Waters in South-Central Minnesota," *Journal of Environmental Quality*, *5*, 124-128 (1976).

Miller, R.E., Randtke, S.J., Hathaway, L.R., and Denne, J.E., "Evaluation of the Trihalomehtane Formation Potential of Kansas Groundwaters," Unpublished data, 1986.

National Academy of Sciences, *Drinking Water and Health*, National Academy Press, Washington, D.C., 939pp. (1977).

National Academy of Sciences, *Drinking Water and Health*, *Volume 2*, National Academy Press, Washington, D.C., 415pp. (1980).

National Academy of Sciences, Drinking Water and Health, Volume 3, National Academy Press, Washington D.C., 299pp. (1982).

Nielsen, D.M., and Yeats, G.L., "A Comparison of Sampling Mechanisms Available for Small Diameter Ground Water Monitoring Well," Groundwater Monitoring Review, 5(1), 83-91 (1985).

Oliver, B.G., "Dihaloacetonitriles in Drinking Water: Algae and Fulvic Acid as Precursors," Environmental Science and Technology, 17(2), 80-83 (1983).

Spaulding, R.F., Gormly, J.R., and Nash K.G., "Carbon Contents and Sources in Groundwaters of the Central Platte Region in Nebraska," Journal of Environmental Quality, 7, 428-434 (1978).

Stevens, A.A. and Symons, J.M., "Measurement of Trihalomethane and Concentration Changes," Journal American Water Works Association, 69(10), 546 (1977).

Stevenson, F.J., Humus Chemistry: Genesis, Composition, Reactions, John Wiley & Sons, N.Y., 1982, 443pp.

Stevenson, F.J., "Geochemistry of Soil Humic Substances," in Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization, Aiken, G.R., McKnight, D.M., Wershaw, R.L., and MacCarthy, P. (eds.), John Wiley and Sons, N.Y., p.13-52 (1985)

Symons, J.M., Bellar, T.A., Carswell, J.K., DeMarco, J.,Kropp, K.L., Robeck, G.G., Seeger, D.R., Slocum, C.J., Smith, B.L., and Stevens, A.A., "National Organics Reconnaissance Survey for Halogenated Organics," Journal American Water Works Association, 67(11), 634-637 (Nov., 1975).

Symons, J.M., Stevens, A.A., Clark, R.M., Geldreich, E.E., Love, O.T., Jr., and DeMarco, J., "Treatment Techniques for Controlling Trihalomethanes in Drinking Water," Report No. EPA-600/2-81-156, U.S. Environmental Protection Agency, September 1981.

Thurman, E.M., Organic Geochemistry of Natural Waters, Martinus Nijhoff/Dr. W. Junk Publishers, Dordrecht, The Netherlands, 1985a.

Thurman, E.M., "Humic Substances in Groundwater," in Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization, Aiken, G.R., McKnight, D.M., Wershaw, R.L., and MacCarthy, P. (eds.), John Wiley and Sons, N.Y., p.87-103 (1985b).

U.S. Environmental Protection Agency, "National Interim Primary Drinking Water Regulations; Control of Trihalomethanes in Drinking Water; Final Rule," Federal Register, 44(231), 68624-68707 (1979).