A SURVEY OF ORGANIC CARBON AND TRIHALOMETHANE FORMATION POTENTIAL IN KANSAS GROUNDWATERS

by

Rachel E. Miller
B.S., University of Kansas, 1980.

Submitted to the Department of
Civil Engineering and the Faculty of the
Graduate School of the
University of Kansas in partial
fulfillment of the requirements
for the degree of Master of Science.

Stephen J Randtke
Professor in Charge

Lawrence R. Hathaway

Ernest C. Pogge
Committee Members

John T. Easley
For the Department

July 23, 1987
Date Thesis Accepted

ACKNOWLEDGEMENTS

I would like to express my appreciation to Jane Denne and Larry Hathaway, who offered their suggestions during the site selection process; and to Larry Hathaway (KGS), Anne Melia, and Stephen Randtke (Dept. of Civil Engineering, University of Kansas), who conducted the laboratory analyses for this study. The use of KGS vehicles for sample collection, KGS monies for travel, and a General Research Fund Allocation from the Universtiy of Kansas (1986) made this study possible. Information helpful in contacting public water utiltiies was obtained from the Kansas Department of Health and Environment. Alan Macfarlane generously helped to supply well logs and to collect samples from the Cambro-Ordovician aquifers. Margaret Townsend offered suggestions concerning methods of statistical anslysis. Stephen Randtke critically and technically reviewed this manuscript.

A SURVEY OF ORGANIC CARBON AND TRIHALOMETHANE FORMATION POTENTIAL IN KANSAS GROUNDWATERS

Rachel E. Miller
M.S. in Water Resources Science

ABSTRACT

A survey of Kansas groundwaters to determine their total organic carbon (TOC) concentrations and trihalomethane formation potentials (TFPs) was conducted in the Spring of 1986. Wells (of known construction) were carefully selected from well logs to represent a particular geologic interval. Thirty-four samples were collected from public water supply wells and 16 samples were collected from private water wells. Samples from 11 alluvial aquifers, 4 unconsolidated aquifers in Quaternary and Tertiary formations, and 4 consolidated aquifers in Cretaceous, Permian, Pennsylvanian, and Cambro-Ordovician rocks were taken.

The mean TOC concentration was 1.05 ± 0.77 mg/L and the median concentration was 0.85 mg/L. TOC ranged from 0.21 to 3.31 mg/L and TFP ranged from 5.3 to 178 ug/L. TFP was strongly correlated with TOC (r=0.95); and the average yield of TFP was 0.242 ± 0.07 micromoles/mg TOC. The alluvial aquifers were found to exhibit much higher levels of TOC and TFP than other aquifers. Glacial and Ogallala aquifers had the highest TOC and TFP concentrations among the non-alluvial aquifers.

Statistical analyses were conducted to determine if there were significant relationships between the various inorganic constituents (e.g., major cations and anions) and the TOC concentrations in the samples. Hardness, bicarbonate, ammonium, iron, manganese, potassium, and barium were found to be relatively highly correlated ($r \geq 0.410$) with TOC. Eleven percent of the study samples had TFPs greater than the national primary drinking water standard for trihalomethanes (THMs) of 100 ug/L, 89 percent had TFPs greater than 10 ug/L, and 53 percent had TFPs greater than 25 mg/L, indicating that many chlorinated ground water supplies in Kansas might have difficulty in meeting a substantially lower THM standard.

Department of Civil Engineering
May, 1987

Thesis Supervisor
Dr. Stephen J. Randtke
Associate Professor

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Background

Since the discovery of trihalomethanes (THMs) in drinking water by Rook in 1974, there has been growing concern over the possible carcinogenicity of these compounds, the most abundant of the synthetic organic chemicals found in public water supplies. THMs are a group of predominantly volatile organic compounds with a basic chemical structure of methane in which three hydrogen atoms have been replaced with halogen atoms, usually chlorine (Cl) or bromine (Br). They are formed as the result of the reaction of chlorine, used for disinfection, with the naturally occurring organic material present to some extent in virtually every water supply.

On November 29, 1979 the U. S. Environmental Protection Agency (EPA) promulgated an amendment to the National Interim Primary Drinking Water Regulations, limiting the concentration of THMs in drinking water to 100 micrograms per liter (ug/L) for public water supplies serving over 10,000 persons (Federal Register, 1979). Consideration is presently being given to lowering of the standard, perhaps to 10 ug/L, in the future.

Although much attention has been given to the control of THMs in surface water supplies, groundwaters in most areas of the United States have not been extensively studied in this respect. Surface waters, including rivers and lakes, generally contain more organic matter than groundwater supplies, and are therefore more likely to have high THM concentrations. However, certain groundwater sources have been found to produce THM concentrations above the maximum contaminant level (MCL) of 100 ug/L (Symons et al., 1975).

Research Objectives

Since the total organic carbon (TOC) concentrations in naturally occurring, uncontaminated Kansas groundwaters were not known and since the potential for Kansas groundwaters to form THMs had not been systematically investigated, the major goal of this study was to provide and evaluate this information. Other objectives of the study were: 1) to statistically examine the geological and geochemical characteristics of the different Kansas aquifers in relation to TOC concentrations and THM formation in order to establish important associations; 2) to identify problem aquifers or problem areas in the State; and 3) to provide information that would be helpful in assessing the impact on Kansas of a lowering of the THM standard.

PREVIOUS INVESTIGATIONS AND RELATED RESEARCH

Chlorine Chemistry

Basic Chlorination Reactions

In aqueous solution, chlorine hydrolyzes to form chloride ion and hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), the latter two collectively are referred to as "free" chlorine. If bromide or iodide is present in the water, the added chlorine will oxidize them rapidly, producing hypobromous acid (HOBr) or hypoiodous acid (HOI), respectively. Hypobromous acid and hypoiodous acid are usually detected by the same analytical methods as free chlorine (Jolley and Carpenter, 1983). Equilibrium concentrations of HOCl and OCl depend on the pH of the water. Increasing the pH causes a shift to a higher concentration of OCl^- (Jolley and Carpenter, 1983).

Free chlorine is a very active oxidizing agent and readily reacts with ammonia in water to form chloramines or "combined" chlorine. The chloramines include monochloramine, dichloramine, and trichloramine. Monochloramine is the principal chloramine that is encountered under the usual conditions of water chlorination. Dichloramine is unstable and is produced primarily at high chlorine to ammonia ratios or low pH (4-5). At higher chlorine to nitrogen ratios, ammonia is converted to diatomic nitrogen. At the pH range of most natural waters, the reaction of chlorine and ammonia is usually 90% complete in about one minute (Jolley and Carpenter, 1983). Hypobromous acid will also react with ammonia to produce bromamines that can be detected as free chlorine. Ferrous iron (Fe II), manganese (Mn II), nitrite (NO_2^-), hydrogen sulfide (H_2S), and organic substances can also react with free chlorine.

Chlorine initially oxidizes any Fe(II) and H_2S in the water and then begins to oxidize any Mn(II) and nitrite (NO_2^-) which might be present. Chlorine reacts with raw groundwater in a manner illustrated by the breakpoint chlorination curve (see Figure 1). Unless the chlorine dosage is sufficient to oxidize any Fe, H_2S, Mn, or NO_2^- in the water, no chlorine residual (free or combined) is present and little or no disinfection occurs. Additional chlorine will react with ammonia and organic compounds to form chloramine and chloroorganic compounds and the chlorine residual will increase (Figure 1). Monochloramine is formed at low chlorine to ammonia ratios, and the combined residual gradually increases to a maximum. After this peak amount is reached, continued chlorination will destroy some of the ammonia (by converting it to diatomic nitrogen), and the chlorine residual will be reduced. The combined chlorine residual will be reduced. The combined chlorine residual reaches its lowest point (called the

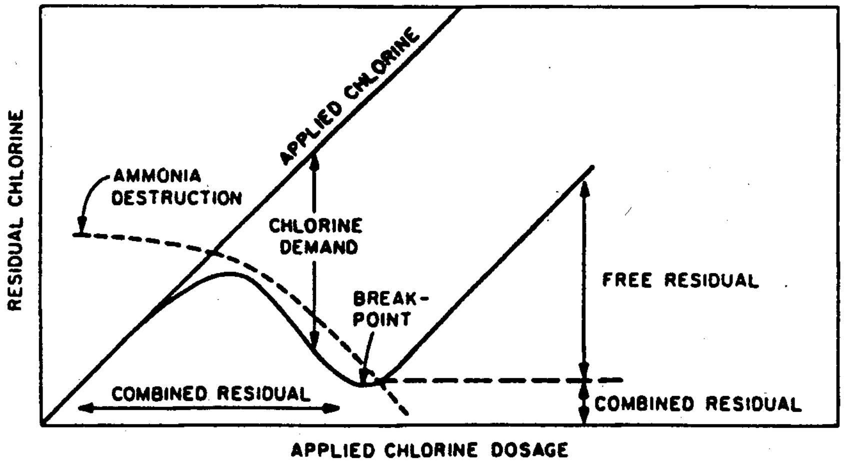

Figure 1: The Breakpoint Chlorination Curve (from Jolley and Carpenter, 1983)

breakpoint) when the chlorine to ammonia molar ratio is approximately 1.5. The rise in the curve beyond the breakpoint reflects the presence of combined chlorine (often attributed to organic chloramines not destroyed by the free chlorine) plus increasing amounts of free chlorine residual. The chlorine demand is the quantity of chlorine that is reduced or converted to inert or less active forms of chlorine by chlorine consuming substances (ammonia, organic matter, cyanide, Fe, Mn, NO_2^-, and sulfide).

Trihalomethane Formation

In his 1974 study, Rook conducted experiments with acetone, a known THM precursor for the haloform reaction, but concluded that the concentrations of acetone which were needed to produce haloforms were not present in the raw waters. However, a good correlation was found between $CHCL_3$ formation and color intensities of the river waters, and the coloration in these waters was due to humic substances which are the by-products of plant decay. Rook proceeded to prove that humic substances could be precursors by injecting peat into water samples and then chlorinating them and obtaining positive results upon analysis for haloforms.

Numerous studies on the effects of chloramine disinfection versus free-chlorine disinfection have shown that combined chlorine in the form of monochloramine greatly reduces THM levels, generally without significant deterioration of the bacteriological quality of the water. Fleischacker and Randtke (1983) showed that combined chlorine does not form THMs at low dosages under laboratory conditions; however, small amounts of THMs are likely to be formed upon chloramination of treated water supplies because of the manner in which the chlorine is added. It has also been shown that THM concentrations can be reduced by avoiding prechlorination, avoiding higher concentrations of chlorine than are necessary for good disinfection, and where possible, by selecting waters of lower temperature.

Amy et al. (1984) studied THM formation in laboratory experiments using natural and synthetic waters containing ammonia. Above the breakpoint concentration, THM formation was markedly increased in response to the presence of free chlorine residual. Amy et al. (1984) were able to account for most of the chlorine utilization (chlorine demand) during the chlorination of waters containing humic substances, ammonia, and bromide; but all of the chlorine utilized could not be attributed to these substances. They attributed the difference to other chlorine-demanding reactions, such as: 1) the oxidation of reduced inorganic substances (e.g., Fe_2 + and Mn_2 +); 2) the occurrence of breakpoint reactions involving end products other than N_2; 3) the oxidative destruction of humic substances to produce both chlorinated and non-chlorinated organic by-products; and 4) lack of precision in estimating the quantity of THMs formed per unit mass of chlorine utilized.

Bromide has a great influence on chlorination reactions, even at low concentrations. Bromide is rapidly oxidized to hypobromous acid (HOBr) by aqueous chlorine. Rook (1974) found that the resulting HOBr reacts more extensively and more rapidly with ammonia and organic matter than does HOCl, and that bromo forms were formed in proportions much greater than the ratio of added chlorine to the bromide concentrations of the river water.

Later investigations which focused on the effects of bromide in the formation of THMs (Amy et al., 1984; Cooper et al., 1983; and Minear and Bird, 1983) confirmed and expanded on Rook's initial study. Generally, investigators have found that THM yields and total THM concentrations increase in the presence of Br^- and that bromide ion concentrations affect both the species distribution and the rate of formation of THMs. Cooper et al. (1983) found that the total concentration of THMs was not influenced to a great extent by the addition of Br^- (except at very high concentrations--$1X10^{-4}$ moles/L), but higher Br^- concentrations did effect the distribution of THMs and created more brominated THMs. In these experiments, 40 to 60 percent of the bromide was recovered as THM-bromide in contrast to the normally much lower percent recovery of chloride as THM-chloride. Amy et al. (1984) reported elevated levels of brominated species at high chlorine doses in the free-chlorine portion of the breakpoint curve. It was also shown that the presence or absence of ammonia was not a factor in the formation of brominated species.

Experimental studies of the rate-determining conditions for the haloform reactions have been performed using the variable factors of time, temperature, pH, and concentration. Rook (1976) demonstrated increased chloroform formation with higher pH, especially >pH9, in accordance with the increased formation of the most reactive organic ions. Concentrations of chloroform were shown to increase over a 4-hour period with a TOC level of 240 mg/L (using a fulvic acid solution), but after 4 hours there was no appreciable additional reaction. A linear relationship was shown between increasing TOC concentrations (From 0 to 250 mg/L) and haloform formation; and haloforms were also shown to generally increase with higher levels of chlorine.

Oliver (1980) studied the effects of temperature on chloroform formation at different pH using humic-chlorine solutions. In experiments where these solutions were quenched after 24 hours, the effects of heating and/or adjusting the pH to 11 were examined. It was found that heating the samples chlorinated at pH 7 or adjusting their pH upward produced increased amounts of chloroform.

Total Organic Halogen Formation

In the search for simplified methods of detecting groundwater contamination, total organic halogen (TOX) has been given attention as a monitoring parameter. In studies of finished drinking waters, the non-purgeable fraction of halogenated organics (NPOX) has been found to be two to three times larger than the purgeable fraction (POX), which is chiefly THMs (Harper, 1984). These studies have called attention to chlorination by-products other than THMs. Consideration of these substances was given in setting the THM MCL, and the intent was to control not only THMs but other chlorination by-products as well (Christman, 1983).

Total organic chlorine (TOCl) further specializes the TOX parameter into only chlorinated organics. Fleischacker and Randtke (1983) found that, under most conditions, chloroform represented only a small fraction of the total amount of organic chlorine formed, and that the ratio of chloroform to organic chlorine increased at higher pH values. They also reported that the amount of non-volatile organic chlorine (NVOCl) increased with increasing chlorine dosage, increasing TOC concentration, increasing temperature, and decreasing pH. NVOCl formation was more rapid than haloform formation or chlorine consumption. Christman et al. (1983) suggested that the presence of chlorinated reaction products other than THMs was indicated by discrepancy between THM concentrations and chlorine demand. They analyzed the chlorination reaction products from humic and fulvic acids and found more than 100 different chlorinated reaction products.

Oliver (1980) studied the effects of pH and has shown that a greater percentage of chlorinated compounds produced at low pH were nonvolatile although the same degree of organic chlorine incorporation into humic materials occurred at low pH as at high pH.

Natural Organic Matter

Measurement

TOC is used as a general indicator of the amount of carbonaceous organic matter present in a water sample, although it is actually a measure of only the organic carbon rather than the total amount of organic matter present. TOC is more directly related to the concentration of organic matter than either biological oxygen demand (BOD) or chemical oxygen demand (COD), and it can be determined in a few minutes. TOC is the sum of dissolved organic carbon (DOC) and particulate organic carbon (POC). DOC is operationally defined as the concentration of organic matter in a water sample passed through a 0.45 micrometer membrane filter, and includes both microcolloids and truly dissolved materials in homogeneous solution. TOC is also divided into volatile (VOC) and nonvolatile (NVOC) fractions. The nonvolatile organic carbon levels of uncontaminated groundwater are generally observed to be quite low, 0.1 to 15 mg/L (Leenheer et al., 1974; and Symons et al., 1975).

The routine TOC procedure consists of three steps (Standard Methods, 1986). Firstly, acidification and purging of the water sample are performed to remove inorganic carbon species as CO_2. Secondly, an oxidation procedure converts organic carbon to CO_2. The principal procedures in use are wet-chemical oxidation, ultraviolet photooxidation, and high temperature oxidation. The oxidation efficiencies of these procedures may vary relative to the mixture of organic compounds making up the TOC. Thirdly, the CO_2 produced in the oxidation step is then quantified, usually performed by infrared absorption spectrometry.

TOC in groundwater indicates the presence of compounds that are either naturally occurring or resulting from human activities. VOC levels may be useful in determining contamination from leaking gasoline storage tanks, industrial lagoons, spillage during transportation, or the use of agricultural chemicals (Barcelona, 1984). The major fraction of naturally occurring organic compounds is nonvolatile and consists of fulvic acid (Pettyjohn, 1983).

Occurrence of THM Precursors

The organic substances identified by Rook (1974) as THM precursors were humic materials and there is considerable variability in their chemical nature. There have been many investigations of THM formation potentials in relation to different types of humic materials.

The organic fraction of soils can be partly brought into solution by treating the soil with a sodium hydroxide solution and then acid treated. This causes part of the organic material to precipitate. This acid-insoluble fraction is termed "humic acid" and the acid-soluble fraction is termed "fulvic acid" (Hem, 1985).

Schnoor et al. (1979) conducted a study to determine the apparent molecular weight range of THM precursor compounds in the Iowa River. Soluble organics (fulvic acids) were size-fractionated by gel permeation chromatography, and then chlorinated and analyzed for THM yield by electron-capture gas chromatography. The results showed that 90 percent of the organics were of molecular weights of <3000 while 75 percent of the THMs were derived from this fraction. Only 7 percent of the organics had molecular weights <1000, 20 percent of the THMs were derived from this weight fraction.

Oliver and Thurman (1984) also studied the influence of aquatic humic substances on THM formation potential. In focusing on the fulvic fractions of aquatic humic materials, they state that, in general, groundwater fulvics had the lowest THM formation potentials, with surface water having greater potentials, and marsh/bog fulvics having the largest THM potentials. Since groundwater contains the oldest organic material and marsh/bog water the youngest, they reasoned that structural changes that occur during the maturation process must lead to a lowering of THM potential.

On analysis of the humic acid fraction, Oliver and Thurman found that 18 to 52 percent more THMs were produced than from fulvic acids from the same source (sources included groundwater, surface water, and marsh/bog water). They concluded that the molecular size of humic organics is related to THM yield; and, as the size of the organic material increases, so does the THM yield. The formation potential was also found to be 25 percent higher at pH 11 (probably from the much faster hydrolysis rate of the intermediates).

A very good correlation between color and THM formation potential was found, with correlation coefficients of 0.85 (pH 11) and 0.82 (pH 7) at a 1 percent confidence level. Oliver and Thurman concluded that color could be used to estimate THM formation potential for water in which most of the organic carbon present is humic material and could also be used to monitor seasonal fluctuations in the THM formation potential of water from a specific source.

Veenstra and Schnoor (1983) studied seasonal patterns in Iowa River water and noted peak THM formation for the molecular weight fractions of 700 to 3000 (mostly in the fulvic acid molecular weight range) throughout the seasons. Starting in late summer and continuing into the fall, a second but somewhat smaller peak developed for the molecular weight fraction $\geq$ 40,000 (humic acids). Chloroform was produced over the entire molecular weight spectrum of humic material while the brominated compounds were confined to the lower molecular weight ranges.

Increasing attention has been given to algal precursors and some work has shown that algae and extracellular products derived from algal growth produce THM concentrations that are comparable to yields observed from humic and fulvic acids (Briley et al., 1983).

In 1976, Rook reported on his findings concerning the structure of humic substances, and fulvic acids in particular, and the actual reaction mechanism involved in the formation of haloforms from these substances. In Rook's view, hydroxylated aromatic rings (the humic precursor) with two free meta-positioned OH- groups are available sites for haloform formation. Rook determined that the most readily available reaction site is the carbon atom situated between two meta-OH groups. Under the given experimental conditions, only 1 out of 500 C atoms had been transformed into chloroform. Rook concluded that this reaction mechanism was a valid explanation for the formation of haloforms from fulvic acids.

Drinking Water Investigations

In 1974, Rook presented a paper which discussed the identification of THMs in chlorinated samples of river water used for a public water supply. This study also focused on the possible causes of their presence in the chlorinated water. Analyses of commercial chlorine were performed to show that the haloforms found in the water after chlorination were not introduced by the chlorine itself, but must have originated in the water upon chlorination. Since that time, there have been many investigations related to THMs in drinking water.

In 1975, water samples were taken from 80 public water supplies by an EPA research team. This study, the National Organics Reconnaissance Survey for Halogenated Organics (NORS), conducted quantitative analyses for 6 organic chemicals which included four THMs, carbon tetrachloride, and 1,2 - dichloroethane (Symons et al., 1975). The water samples included groundwaters, waters from lakes or reservoirs, and river waters. Various types of treatment were examined (99 percent of the supplies used chlorination for disinfection and 1 supply used ozonation). Sixty locations practiced raw water chlorination with 86 percent of these using chlorine dosages from 0 to 6 mg/L. Raw and finished water were analyzed for the four THMs, although <1 ug/L showed up in 49 locations. Most of the finished waters contained THMs, the concentrations of which generally (but not always) occurred in the following descending order: chloroform, bromodichloromethane, dibromochloromethane, and bromoform. The levels of organic matter in these waters was investigated by measuring their nonvolatile total organic carbon concentrations. The range of these data was from <0.05 to 12.2 mg/L and the median was 1.5 mg/L. Examination of the NORS data revealed that "the dominant factor influencing the chlorination by-products was the general organic level of the water, provided sufficient chlorine was added to produce a chlorine residual at the time of sampling." A plot of finished water total THM (TTHM) concentrations versus raw-water NVTOC concentrations showed good correlation, leading the authors to conclude that the NVTOC concentration is a reasonable indication of the THM precursor concentration. Chlorine demand (total chlorine minus total chlorine residual) also correlated to some extent with TTHM concentration, but it was concluded that the correlation was probably influenced by the other forms of chlorine demand.

Raw water samples were classified into six divisions according to NVTOC concentration. The 16 groundwater sources sampled were found to have a lower average TTHM concentration than surface water sources, except in the upper division (NVTOC >5 mg/L). This reflected the average NVTOC concentrations from the different sources including: 1.85 ± 2.79 for 16 groundwater samples, 3.33 ± 2.02 for 26 lake/reservoir samples, and 3.98 ± 3.23 for 39 river samples. River water sources had a higher average TTHM concentration in four of the six divisions. Twenty-four of 39 river water samples were in the upper 3 divisions (NVTOC >3 mg/L), compared to only 3 of 16 groundwaters and 10 of 25 impounded waters.

Higher TTHM concentrations were observed at locations where raw-water chlorination and/or precipitative softening were practiced. Symons _et al_. (1975) reasoned that this followed "the expected trend for pH dependency of the classical haloform reaction and indicates that chlorination at higher pH will produce higher concentrations of THMs." Treatment influences were also examined in the light of the NVTOC divisions. If more than 0.4 mg/L of free chlorine residual were present, higher TTHM concentrations were found. NVTOC concentrations were not correlated with UV absorption, fluorescence, and carbon chloroform extract concentrations, indicating that these parameters are not valid indicators for THM precursors.

The measurement of organic carbon levels in groundwater has recently been given greater attention as an indication of organic contaminants. In 1974, Leenheer _et al_. conducted a study which included 100 sites in 27 states where groundwaters were sampled. These sites included many different aquifer sources including: pleistocene deposits (sand and gravel), Cretaceous rocks, Mississippian rocks (sandstone), river alluviums, limestones, crystalline rocks, dolomite and basalt. The study focused on the occurrence of nonvolatile, natural organic materials (DOC--filtered with a 0.45 um silver membrane filter at the time of collection) in groundwater. Uncontaminated sample locations were selected so that the DOC analyses would indicate the amount of natural organic materials dissolved in the water in the various aquifers. Statistical analyses were performed to determine if DOC concentrations were affected by the pH, conductivity, or alkalinity of the water. They reported that increasing DOC levels were directly correlated with increasing specific conductance and alkalinity; but no correlation was found with pH and well depth. DOC values ranged from < 0.1 to 15.0 mg/L; the median value was 0.7mg/L and the mean was 1.2 mg/L. The same median value was found for sandstone, limestone and sand and gravel aquifers. Crystalline rock aquifers had lower DOC concentrations, ranging from 0.4 to 0.5 mg/L. The availability of organic source materials was related to high DOC levels in certain samples. A site in Miami, Florida, apparently received its high DOC concentrations from infiltration of surface waters which had high DOC levels.

Junk et al. (1980) investigated vertical, areal and temporal differences in DOC, nitrate and pesticide concentrations of surface waters of the Platte River and adjacent groundwater regimes in Iowa. Groundwater sites were chosen in irrigated bottomlands, near-pristine areas affected by river seepage, and inland terrace deposits. Shallow and deep wells were constructed to determine vertical stratification. DOC concentrations in shallow groundwater from near-pristine areas ranged from 1.4 to 3.3 mg/L with an average of 2.3 mg/L; and DOC concentrations in shallow bottomland wells downgradient from irrigated cropland ranged from 3.1 to 4.8 mg/L. Seasonal data indicated that in 34 of 35 cases, DOC concentrations decreased with depth. River DOC concentrations were found to be higher than the adjacent groundwater regardless of season, although DOC levels in groundwaters were highest in September and levels in river waters were highest in April.

Junk et al. concluded that the most probable mechanism of DOC removal with increasing depth appeared to be adsorption on saturated aquifer sediments and that the source of DOC was primarily from overlying soils. Processes such as the dissolution of the summer's accumulation of decaying organic matter on the river banks and bottom sediments in September, combined with the fluvial seepage contribution of DOC (not removed at the water-sediment interface) were proposed as mechanisms for the observed seasonal differences in the maximum DOC concentrations of river water and adjacent groundwater.

In 1981 and 1982, the EPA conducted a survey of public groundwater supplies which included 466 randomly selected communities and 479 communities selected by state agencies (Westrick *et al*., 1984). In this survey concentrations of 29 volatile compounds were determined for the finished water of these supplies. THM concentrations were analyzed after 1 to 4 weeks of low temperature storage in which any reaction was allowed to continue until the depletion of either residual chlorine or the precursor material. Median values and maximum values were given for 5 THMs including: chloroform, bromodichloromethane, dibromochloromethane, dichloroiodomethane, and bromoform.

The sampling sites were divided into sites serving fewer than 10,000 persons and those serving more than 10,000 persons. It was found that THMs occurred more frequently in the larger systems; but this was probably due to a higher percentage of the larger systems which chlorinate their water. Median values of the different THMs were generally low and ranged from 1.2 to 5.1 ug/L, although maximum values determined were 430 ug/L for chloroform, 110 ug/L for bromodichloromethane, 63 ug/L for dibromochloromethane, 4.2 ug/L for dichloroiodomethane, and 110 ug/L for bromoform. Chloroform and bromodichloromethane had their highest median and maximum concentrations in the state-selected sites which served more than 10,000 persons.

O'Conner and Chaffee (1985) have investigated areas where poor well construction, poor plugging procedures, and high well densities have had a major effect on water quality and TOC levels. Time-series sampling of 10 wells in the Lincolnville area of Marion County, Kansas was conducted over a one-year period. The wells were screened in Permian age aquifers and TOC levels were observed to range from 0.74 to 6.12 mg/L in May and 1.25 to 5.80 mg/L in August. The average TOC concentrations for this study are 3.04 and 3.26 mg/L for the two sampling periods.

In January of 1984, seven wells were sampled in a glacial buried valley aquifer system in northeastern Kansas for TOC levels (Denne et al., 1984); and TOC levels ranged from 0.9 to 2.4 mg/L with a mean concentration of 1.4 mg/L. Some areas of this aquifer are known to contain high levels of ammonium ion, iron, manganese and hydrogen sulfide, indicative of reducing conditions. Since these constituents consume chlorine, Denne et al. suggest that water supplies in the area which use free chlorine exercise caution, since the potential for producing THMs increases beyond the breakpoint. Two chlorinated samples analyzed for THMs in these waters were found to have TTHM levels of 81 and 61 ug/L when quenched seven days after collection.

Study of this area of Kansas concerning the geochemistry of the glacial aquifers is continuing. The TOC and ammonium ion contents of the aquifer material itself are being investigated as well as the chemistry of the groundwaters from different aquifer zones, representing reduced and oxidized geochemical environments (Denne <u>et al.</u>, 1986).

METHODS OF INVESTIGATION

Site Selection Procedure

Sampling sites were selected to include each of the major aquifer systems in Kansas. Multiple sampling sites were selected for aquifers extending over a large geographic area so that the spatial variability of the water quality in such aquifers might be included.

Water wells were chosen after consulting water well records, filed by county, at the Kansas Geological Survey (KGS). Since 1974, drillers have been required by law to send records of wells they drill to the Kansas Department of Health and Environment (KDHE). Sites were selected from these records so that water well construction materials, screened intervals, geologic logs and construction methods could be examined and documented. Geologic logs and construction information for wells tapping the Arbuckle aquifer were obtained from a KGS file because there were no recent water well records (1974-present) for this aquifer. Due to the great depths (and accompanying high construction costs) of these wells, there are few wells drilled over a long time period. The oldest well deriving water from the Arbuckle aquifer system sampled in this study was drilled in 1964 and the others were drilled between 1972 and 1979.

Table 1 gives a listing of the sampling sites along with aquifer types and construction methods and materials. Each well was chosen to reflect a particular geologic interval or aquifer. The screened interval was examined to determine the aquifer's representation. Wells which had screens at multiple depths or included contributions by an aquifer other than the aquifer of interest were eliminated as possible sampling sites.

Public water supply wells were chosen, wherever possible, because of their generally high quality of construction and the relevance of this study to chlorinated water supplies. In the selection of private wells, irrigation wells were rejected and domestic wells were preferred, although stock wells were used in a few cases. Well yields were stipulated to be 20 gallons per minute or greater.

Any known or possible areas of contamination were avoided, since the objective of this study was to examine the characteristics of naturally occurring groundwater. Contamination sources would include oil field brines, farm chemicals, animal wastes, mineral wastes from mining operations, and nearness to poorly constructed wells. Wells were rejected if they were found to be near industries, grain elevators, oil wells, feed lots or areas with a high density of water wells, especially those of older construction.

TABLE 1: Sampling Sites, Aquifers, and Well Construction

SN#	LEGAL LOCATION	WELL TYPE	SCREENED INTERVAL	SCREENED MATERIAL	GEOLOGIC SOURCE	TOTAL DEPTH	WATER LEVEL	EST. YIELD	CASING MATER	CASING JOINTS	GROUTED INTERVAL
1	1220E17ABA	PWS	58–77	MCS,GR B	KANSAS R. ALLUV	78	22	350	STL	WELD	18–20
2	5537W19CCA (IN MISSOURI)	IND	60–807	MCS,GR	MISSOURI R. ALLUV	80			STL		
3	923E08DAA	PWS	49–69	CMS,GR	MISSOURI R. ALLUV	69	12	2000	STL	WELD	0–20
4	1818E06ACC	PWS	141–200	SS	PENNSYLV. TONGANOXIE	210	99	19	STL		3–51
5	1417E36DDD	PWS	420–500 OH	SS	PENNSYL. TONGANOXIE	500	348	30	STL	THR	0–420
6	1012E15ABB	PWS	47–26	GR	KANSAS R. ALLUV	47	21	1200	PVC	CL	0–20
7	1105E35B	PWS	42–62	MCS,GR	SMOKY HILL R. ALLUV	63	17	1500	STL	WELD	0–20
8	803E07BAA	PWS	38–53	CS,GR FS	REPUBLICAN R. ALLUV	55	22	700	STL	WELD	0–20
9	304W17DAD	PWS	29–42	GR	REPUBLICAN R. ALLUV	42	18	400	AS–CE	CL	0–20
10	1104W01CBB	PR	56–59	FCS,GR	SOLOMON R. ALLUV	60	25	50	PVC		3–13
11	1603W25DAB	PWS	43–53	MCS	SMOKY HILL R. ALLUV	54	25	90	STL	WELD	5–25
12	1801E33DDD	PWS	58–68	FMSS	CRETACEOUS DAKOTA	68	25	125	STL	WELD	5–20
13	2004W01DDD	PWS	138–178	MCS,GR	EQUUS BEDS	215	71	2500	STL	WELD	0–20
14	2401W06CBC	PWS	123–148	FCS FMGR	EQUUS BEDS	151	23	600	STL	WELD	1–20
15	2803W01DDD	PR	14–45	FMCS	EQUUS BEDS	45	25		RMP	GLU	14–40
16	3504E01AA	PWS	18–30	MCS	ARKANSAS R. ALLUV	30	10	300	STL	WELD	0–12
17	2207W10CAA	PWS	38–53	MCS,GR	ARKANSAS R. ALLUV	55	13	800	STL	WELD	0–20
18	101E07AAA	PWS	265–205	SS	CRETACEOUS DAKOTA	285	195	100	PVC	WELD	0–20
19	410E17AB	PR	175–185	GR	GLACIAL	185	53	90	PVC		0–20
20	119E09DBD	PWS	68–72	SYGR,B	MISSOURI R. ALLUV	73	13		PVC		4–22
21	316E01DAC	PR	38–58	SND,GR SH	GLACIAL	58	20	15	PVC	GLU	0–10
22	616E21BCB	PR	132–142	CS,MGR	GLACIAL	145	90	50	PVC	GLU	0–10
23	618E27DAD	PR	190–200	CRS SND PEA GR	GLACIAL	200	80	100	PVC	GLU	0–15
24	834W12DBA	PWS	200–220 241–261	FMS,GR FS,GR	OGALLALA OGALLALA	261	134		STL	WELD	0–20
25	1837W14DD	PWS	154–172	MCS,GR	OGALLALA	175	118	260	STL	WELD	0–20

TABLE 1: Sampling Sites, Aquifers, and Well Construction (cont'd)

SN#	LEGAL LOCATION	WELL TYPE	SCREENED INTERVAL	SCREENED MATERIAL	GEOLOGIC SOURCE	TOTAL DEPTH	WATER LEVEL	EST. YIELD	CASING MATER	CASING JOINTS	GROUTED INTERVAL
26	3233W27ABC	PR	60-100	MCS	CIMARRON R.ALLUV	100	25	50	PVC	GLU	0-10
27	3034W13DAB	PWS	401-426 329-379	FMCS FMCS,GR	OGALLALA	430	261	2000	SSTL		0-20
28	2416E20DD	PWS	70-100	S,GR SNDY CL	GIG BEND	100	21	500	PVC	GLU	0-20
29	1817W03BCC	PWS	60-100	SS,LS	CRETACEOUS DAKOTA	102	46	50	PVC	GLU	5-25
30	1817W22DA	PWS	48-58	S,GR	WALNUT CK.ALLUV	58	33	200	STL	WELD	0-20
31	2023W24ADD	PR	55-65	S	PAWNEE R. ALLUV	60	40	80	PVC	WELD	4-15
32	1518W30D	PWS	37-47	FMS,GR CGR	SMOKY HILL R. ALLUV	47	9	300	SSTL		0-20
33	3529W13BBC	PR	36-42	MS	CIMARRON R.ALLUV	42	7	25	PVC	GLU	0-10
34	3529W10CCB	PR	(no log)		PLEIST.?						
35	3008W05ABD	PR	62-74	SH	PERMIAN HARPER SLTS	74	55	15	PVC	WELD	5-15
36	3325E18DDA	PWS	OH 575-900		CAM-ORD	900	145		STL	WELD	
37	3425E13CCC	PWS	OH 514-1272		CAM-ORD	1272			STL	WELD	
38	3025E28DAA	PWS	OH 550-1050		CAM-ORD	1050	217		STL	WELD	0-550
39	3024E02DDD	PWS	OH 723-1113		CAM-ORD	1113	270		STL	WELD	
40	611W28ACD	PWS	42-68	S	SOLOMON R.ALLUV	68	34	800	C,ASD	THR	0-34
41	1206W15ABD	PWS	(no log)		SALINE R.ALLUV						
42	1206W15BCD	PWS	47-55	CS,GR	SALINE R. ALLUV	55	18	200	SSTL	GLU	0-22
43	1303E17AB	PWS	43-58	MCS,GR	SOLOMON R. ALLUV	59	11	2000	STL		7-20
44	1704E12CCC	PR	65-93	LS,SH	PERMIAN WINFIELD	93	65	55	PLTS	GLU	0-10
45	2203E04AAB	PWS	23-53	LS,SH	PERMIAN WELLINGTON	60	14	100	PVC	GLU	0-20
46	2409W16ACB	PR	52-72	CL,S,GR	BIG BEND	72	33		RMP	GLU	0-10
47	1913E29CCC	PR	11-28	CL,SLT GR,SH	NEOSHO R. ALLUV	28	10	25	PVC	GLU	3-10
48	1220E15ADA	PR	120-160	SS	PENNSYLV. TONGANOXIE	160	80	50	PVC	GLU	0-10
49	3121E16	PWS	26-31	MCS,GR	NEOSHO R. ALLUV	33	24	20	STL	WELD	18-20
50	3025E28DDA	PWS	OH 550-1050		CAM-ORD	1050	217	2250	STL	WELD	0-550

OH=open hole
S=sand
SS=sandstone
GR=gravel
LS=limestone
SH=shale
CL=clay
SLT=silt
B=boulders
M=mediam
C=coarse
F=fine

The possible leaching of chlorinated organic substances from well casing material and construction materials has recently been pointed out by Gibb and Barcelona (1984). PVC pipes and casing, as well as sealing cements used in well construction, can leach significant amounts of chlorinated organics. Iron oxides from aged steel casing may be a source of adsorption losses of trace metals or organic compounds. Sampling procedures were designed to minimize these effects, and Table 1 documents the construction materials of the individual wells.

Fifty wells were sampled in this study, including 23 wells in 11 different alluvial aquifers, 4 wells in glacial buried valley aquifers, 3 wells in the Ogallala aquifer, 3 wells in the Equus Beds aquifer, 2 wells in the Big Bend aquifer, 3 wells in the aquifer of Dakota age, 3 wells in Permian age aquifers, 3 wells in Pennsylvanian aquifers and 5 wells in the Arbuckle (Cambro-Ordovician) age aquifer. Thirty-four of these were public supply wells and 16 were privately-owned wells. A few of the original sites selected were later rejected due to problems in the actual sampling of the water well. Discontinued use of some of the wells meant that they had either been plugged or that the electrical power supply for their pumps had been disconnected. If it was not possible to sample the first choice site, an alternate site was chosen. In some cases, there was no acceptable alternate site.

Figure 2 is a map of Kansas showing the locations of the 50 sampling sites. Three of the sites sampled are not included in the statistical analyses included in this report. Site #34 was rejected because there is no water well record to confirm the well construction. Site #41 was not included due to its proximity to site #42 which represents the same aquifer. Site #38 was discarded because of analytical problems and the subsequent sampling of a nearby well (site #50).

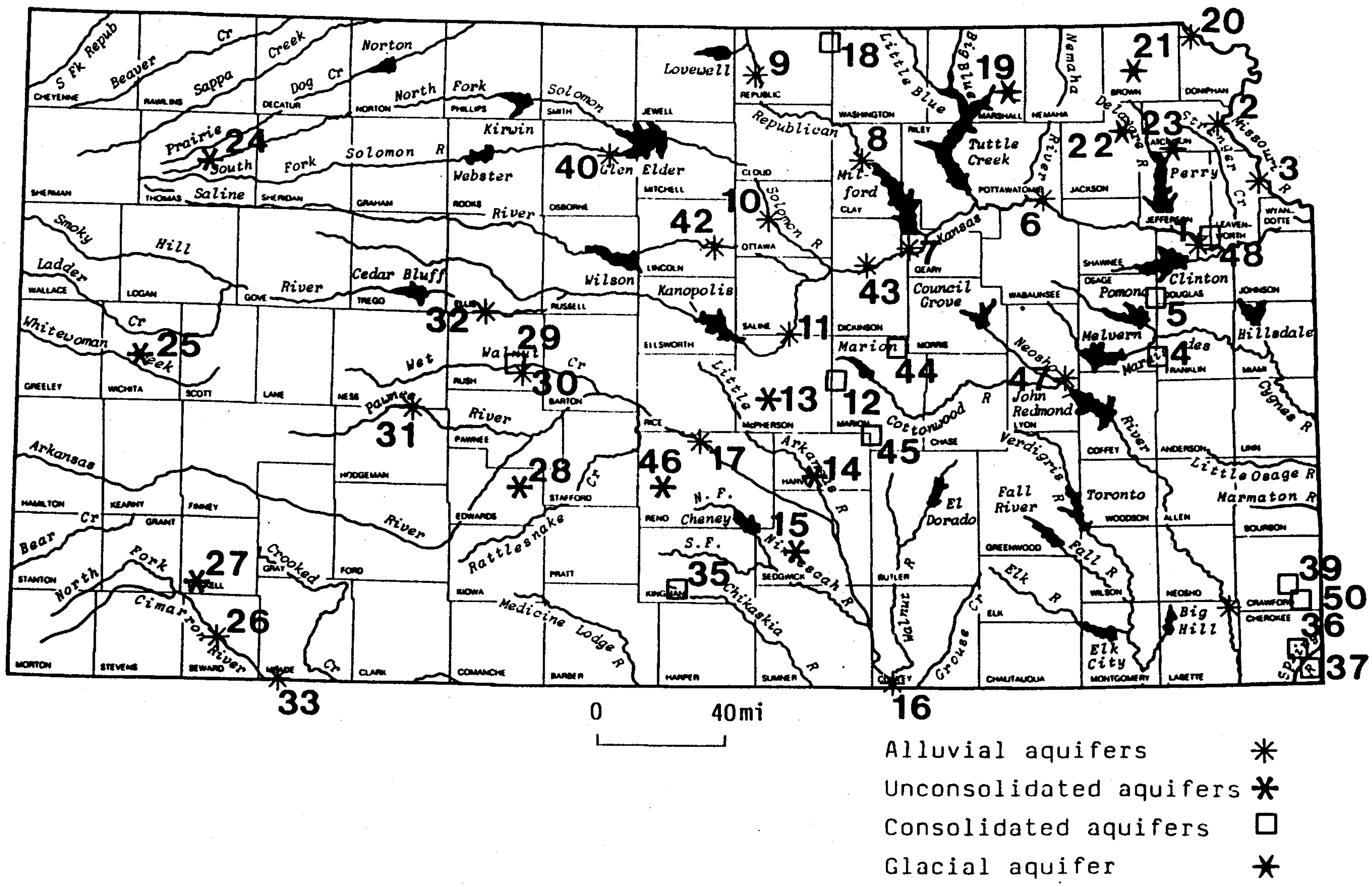

Figure 2: Sampling Sites with Kansas Rivers and Reservoirs (Steeples and Buchanan, 1983)

Sampling Procedure

After permission to sample a well was granted, raw water samples were taken from the outlet closest to the well. The well was allowed to pump for a period considered sufficient to obtain formation water. Since the water in the casing itself may be chemically altered, at least one casing volume of water was pumped before sampling. The water temperature was observed until it stabilized, serving as an indication of the 'freshness' of the water. Generally, public supply wells did not need a long pumping period because their pumping rates were much higher and they had often been operating for long periods of time before the sample was taken. Most public supply systems had a raw water outlet where a sample could be taken before treatment. Other systems had to turn off their chlorination or softening processes before untreated raw water could be obtained. In a few cases, chlorine was still detected in the raw water sample, which was probably the result of backflow in the system or valve leakage from the chlorinator.

At each site three sample bottles were filled with the raw water: one 500-mL polyethelene bottle for determination of pH, specific conductance and major anions and cations; one 250-mL polyethelene bottle acidified with 2 mL of redistilled 6N hydrochloric acid filled to 200 mL, for analysis of trace metals, nitrate, and ammonium; and one

250-mL glass bottle (with a Teflon-lined cap) for the determination of TOC and THM formation potential (TFP).

Finished water samples were also collected from public supply wells so that instantaneous and terminal THM concentrations at the normal chlorination levels could be determined. Samples were usually taken at the well-house in small systems, where the only treatment was chlorination. In larger systems, finished water was taken from inside the water plant and was usually a combination of water from several different wells taking water from a single aquifer. The finished water was collected in two 50-mL glass serum bottles (one containing about 0.5 gm of powdered sodium sulfite). Each bottle was filled to overflowing so that a convex meniscus was formed at the top. A PTFE-lined septum was then inserted in an aluminum seal and carefully placed over the bottle and crimped into place. The sample treated with sodium sulfite and the unaltered sample were used to determine instantaneous and terminal THM concentrations, respectively.

Water temperature was determined at the time of water sampling. Field measurements were made immediately after the water was sampled. Portable pH (Model 607, Fisher Scientific Co., St. Louis, Mo.) and conductivity (Lectro-MHO Meter Model MC-1, Mark 4, Lab-Line Instr. Co., Melrose Park, IL.) meters were used to determine pH and specific conductivity. Hydrogen sulfide (H_2S) concentration (detection limit = 0.1 mg/L) was determined using a hydrogen sulfide kit (CHEMet, CHEMetrics Inc., Calverton, VA.) employing a colorimetric method. Free and total residual chlorine concentrations in the finished water samples were measured with a colorimetric comparator kit (Hellige Inc., No. 605-A, Garden City, NY) employing DPD tablets.

Most of the samples were collected between March 7 and April 11 of 1986, but samples 48 through 50 were collected from June 5 to July 17 of 1986. All samples, raw and finished, were numbered by site, stored on ice and transported to Lawrence for analysis. The glass bottles were taken to the C.L. Burt Laboratory housed at Learned Hall for analysis of TOC, THM, and TFP. The polyethelene bottles were taken to the Analytical Services laboratory of the Kansas Geological Survey housed in Moore Hall. All samples were refrigerated while awaiting analysis.

Analytical Methods

TOC Analysis

TOC was determined using a Dohrman DC-80 TOC Analyzer (Xertex Corp., Santa Clara, CA) according to the persulfate-ultraviolet oxidation method described in Standard Methods (1987). Samples were acidified to pH<2, purged with nitrogen to remove CO_2 and shaken well prior to injection. TOC concentrations were determined for all raw-water samples and 45 of the finished-water samples. The following paragraphs outline various problems associated with the analysis of TOC in these samples as noted by Randtke (1986).

When TOC levels are very low, there are several problems that can affect the results: 1) traces of CO_2 left after purging can be significant; 2) traces of CO_2 can enter the sample after purging; 3) the system blank is significant; and 4) precision is poorer at lower concentrations. Checks were run to insure that items 1 and 2 were not a problem. The system blank of 0.055 mg/L, determined on 11 replicates of fluid drawn from the reactor inside the TOC analyzer, was subtracted from all of the measured values of TOC. Analytical precision was ± 2% for concentrations greater than 1.0 mg/L.

Although most of the samples were fairly clear, three (#5, #20, and #49) contained a large amount of suspended solids and were filtered through a glass fiber filter (934 AH) to remove suspended solids. Table 2 shows TOC concentrations determined for 6 samples under various suspended solids conditions. These samples were somewhat turbid and most of them had a yellowish color. Samples #5 and #20 were filtered prior to TFP analysis because they were found to contain high concentrations of particulate organic carbon. Sample #5 had fine dark solids high in TOC. The TOC concentrations of the samples containing yellowish orange suspended solids (samples #2, #3, #10 and #13) were similar for filtered and unfiltered portions. Since it was thought that the TOC associated with the solids in these samples had been absorbed from solution after oxidation and precipitation of iron, these samples were not filtered prior to TFP analysis.

TFP Analysis

After the TOC concentration of a raw-water sample was determined, TFP analysis was performed. Samples were adjusted to pH 8.2, divided into a series of small bottles dosed with free chlorine in 5 mg/L increments, and incubated for 96 hours. The sample in the bottle having the lowest free chlorine residual in excess of 0.2 mg/L (determined using the DPD titrimetric procedure described in Standard Methods) was then quenched with sodium sulfite and extracted with pentane. The THM concentrations in the extracts were determined using liquid-liquid extraction and gas chromatography (Varian Model 2400, Varian Corp., Palo Alto, CA). Chlorinated blank samples produced less than 5

TABLE 2: TOC Concentrations of Filtered and Unfiltered Turbid Samples

Sample No.	TOC, mg/L		
	Whole Mixed	Settled Decanted	Filtered
2	3.31*	2.59	ND**
3	2.56*	2.09	ND
5	11.45	1.45	0.48*
10	1.03*	0.92	ND
11	1.90*	1.66	ND
20	7.43	2.40	2.84*

* This sample was chlorinated to determine TFP.
** Not determined.

mg/L of THMs, and analysis of independent quality control samples always produced results within ± 3% of the stated value. A more detailed description of the analytical procedure for TFP is given by Randtke et al., (1987).

After the odor of chlorine was noticed in one of the raw water samples (#8), subsequent raw-water samples were tested for free chlorine, with 3 out of the 13 samples tested showing detectable amounts. In these samples, it is probable that a portion of the THMs escaped during sample collection and analysis.

Instantaneous and Terminal THM Analysis

Instantaneous THM samples were analyzed to determine the THM levels at the time of sampling and were refrigerated at 4 degrees Centigrade in the laboratory for up to 2 days until they could be extracted. They were then extracted at room temperature. For all but three samples, the remainder of the sample was then acidified, purged, and analyzed for TOC.

Terminal THM samples were analyzed to determine THMs in the finished-water after a 4-day (96-hour) incubation period, allowing time for the chlorine added at the treatment plant to react with any precursors present in the sample. After incubation, the samples were extracted at room temperature and analyzed for THMs. TOC was not determined for these samples.

Statistical Methods

Statistical analyses of water quality data should consider the behavior of the water quality variables, as pointed out by Montgomery et al., (1987). Many groundwater variables are not normally, or even symmetrically, distributed and many of the frequency distributions tend to be skewed right (log normal distributions) with the degree of skewness varying considerably from parameter to parameter.

Right-skewed frequencies often result from the presence of a "few" very large values or from groundwater parameters where there are numerous values near zero or the detection limit. The presence of large values may be due to: 1) measurement errors; 2) groundwater contamination, or 3) the presence of more than one sampling population (Montgomery et al., 1987). Some variables might have their median equal to zero or the detection limit.

In this study, samples were taken from a variety of aquifers so that population differences might be studied. Many of the groundwater quality variables exhibited right-skewed frequencies. Hydrogen sulfide was detected in only 4 samples; ammonium ion concentrations were predominantly less than 0.1 mg/L; 16 nitrate concentrations were less than, or equal to, 0.1 mg/L; and many iron and manganese concentrations were below the quantifiable limits. Variables having a "few" very high values included: chloride, iron, manganese, nitrate, sodium, barium and sulfate. Sample #20, previously noted for its turbidity, had anomalously high values for barium, iron and manganese. This was probably due to the detection of these metals in the sediment as well as in a dissolved form. The TOC data for this study is also skewed-right (see figure 3), with many data points at low concentrations.

Many statistical computer programs are available for use on the KGS MV20000 computer system. These programs, written in Fortran 77, are described in detail in Statistics and Data Analysis in Geology (Davis, 1973). Three of these programs (VAR, POLYD, and RMULT) were used to assist in evaluation of the data.

The VAR program was used to calculate the standard deviation (SD) and mean of "n" samples. The standard deviation describes the dispersion or spread of data around the mean, and is in the units of the measurements of the data. POLYD was used to correlate one variable with another using least squares linear regression. The program generates a unique line about which the variance of the dependent variable is a minimum. A correlation coefficient (r) is calculated using this program.

The RMULT program was used to consider relationships among several parameters simultaneously. Variables are standardized and considered as spacial coordinates. A dependent variable is considered and the relative effective-

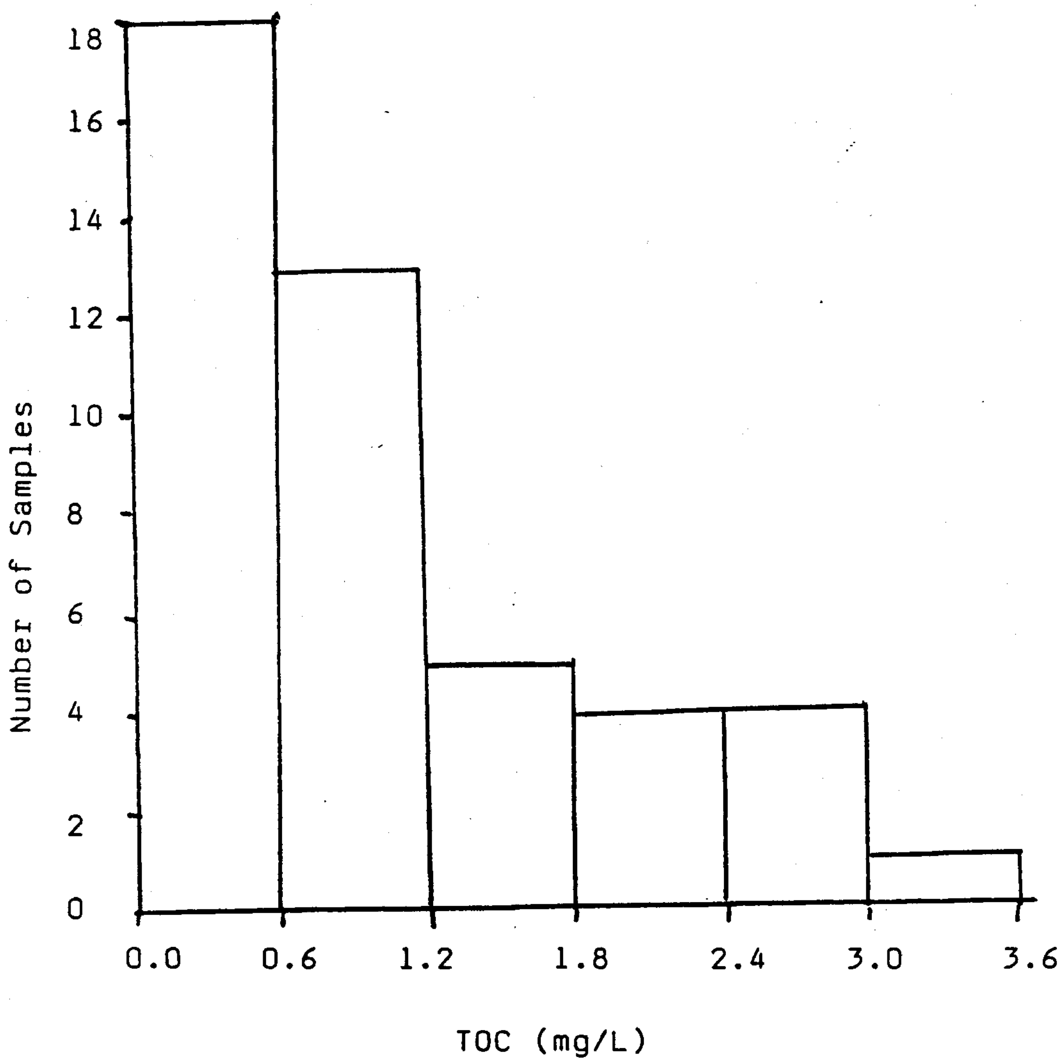

FIGURE 3

Frequency Histogram for TOC

ness of the independent variables as predictors of the dependent variable is evaluated. A test of correlation was done for the multiple regression analyses to test the statistical significance of a given correlation coefficient for a specific level of significance. The 5 percent level of significance was chosen for this study.

GEOLOGICAL DESCRIPTION OF AQUIFERS AND SAMPLING SITES

The geochemical character of fresh water aquifers in Kansas varies widely across the state. Alluvial and unconsolidated aquifers are mainly composed of silt, sand and gravel; and their wells are generally less than 200 feet in depth. The consolidated aquifers are composed of sandstone, limestone, or sandy dolomite; and the wells tapping them can be 1000 feet in depth in areas of southeastern Kansas. Climatic and geographic changes within the state also effect the recharge and discharge relationships of the aquifers.

The major alluvial aquifers are located in the northeaster, eastern, and north-central regions of the state. Major unconsolidated aquifers include the Ogallala in western Kansas, the Big Bend and Equus Beds aquifers in central and south-central Kansas and the glacial buried valley deposits in northeastern Kansas. The Dakota Sandstone aquifer is present in the Cretaceous geologic sequence (Figure 4) and is used extensively in some areas. Permian aquifers are used by small communities and farms in central and south-central Kansas where suitable supplies can be found. In northeastern Kansas, where alluvial and glacial deposits are not present, Pennsylvanian sandstone aquifers are used to supply small communities and farms. The large fresh-water supplies in the Arbuckle (Cambro-Ordovician) aquifer are

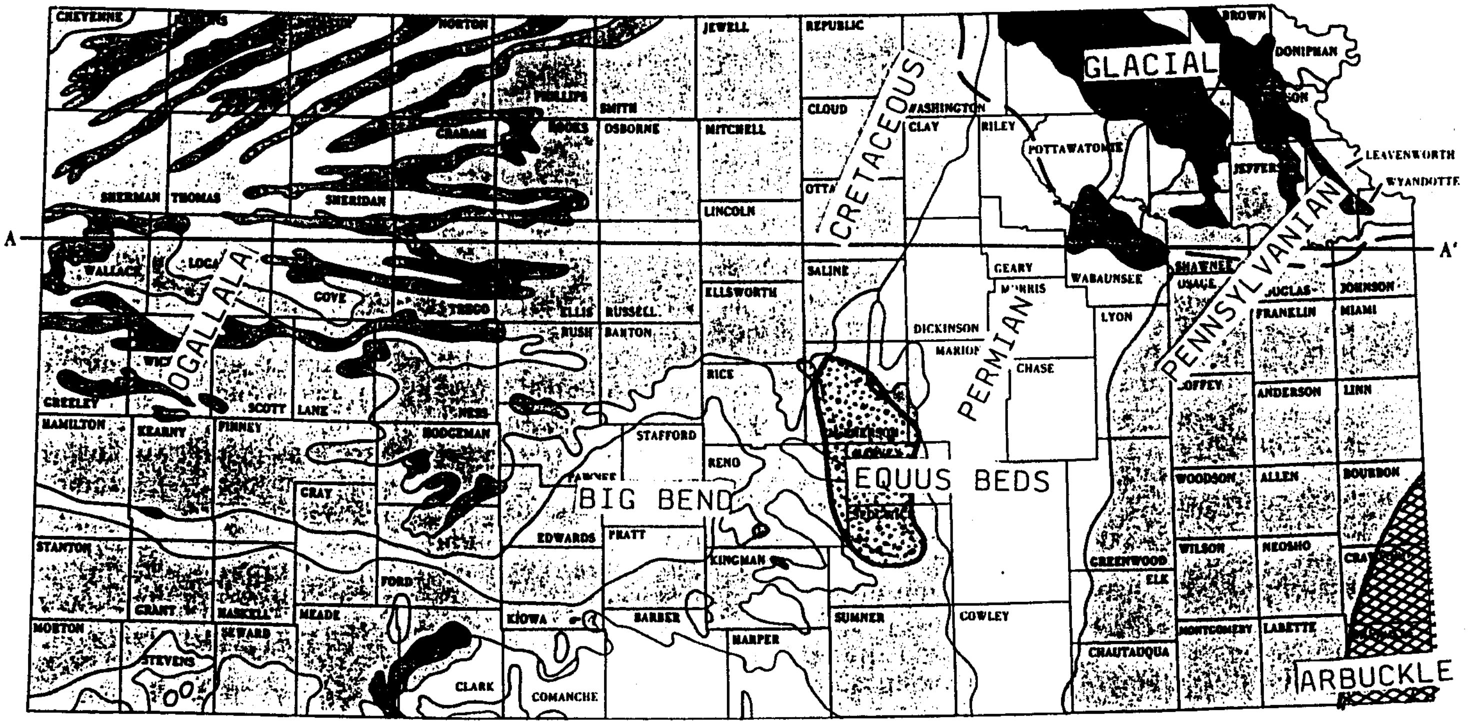

Figure 4: Generalized Geologic Map of Kansas with General Locations of Non-Alluvial Aquifers

used as the sole source of water by large communities in southeastern Kansas. A generalized map of these aquifers and the geology of Kansas is shown in Figure 4.

Alluvial Aquifers

The major alluvial aquifers of Kansas are predominantly in the central and eastern parts of the State. The Smoky Hill, Republican, and Solomon rivers join to form the Kansas River and flow in a general eastward direction (see Figure 2). The Kansas River continues eastward into the Missouri River which forms the northeastern state border. The principle alluvial system in the southern region of the state is associated with the Arkansas River, which enters Kansas from Colorado, continues through central Kansas (where it takes a southerly direction), and leaves the state in Cowley County. The Neosho River travels in a general southward direction in the eastern third of Kansas.

Alluvial aquifer materials consist of sand, gravel, silt and clay. Generally, the aquifer grades from coarser materials, such as sand and gravel, at the basal section, to finer materials in the upper portions. Alluvial deposit thicknesses range from a few feet to around 100 feet. The major water bearing formation and the formation which is usually screened in a well is the basal sand and gravel.

Alluvial deposits are formed as a river erodes surrounding deposits and as suspended particles settle to the river bed. Terraces are formed as the river cuts into previously deposited alluvial materials. The alluvial groundwater exists in equilibrium with the river water and the surrounding groundwater. The alluvium can receive recharge from the river or can supply water to the river, depending on the hydrogeologic conditions.

The Missouri River is the largest river in the state and cuts through an area of Pleistocene glacial deposits. Three samples (#2, #3, and #20) were taken from the Missouri alluvium, representing the City of White Cloud, the City of Leavenworth, and Midwest Solvents (an industrial supply well). The City of Leavenworth well has a maximum yield of 2000 gpm and the City of White Cloud reports a yield of 75 gpm. The White Cloud well has four feet of screened aquifer material consisting of gravel, gray sand and boulders. The Leavenworth well has 20 feet of screened aquifer material consisting of medium- and coarse-grained sand with traces of gravel. Screening information was not available for the Midwest Solvents well; but the well log shows about 40 feet of aquifer material with gravel present.

The Kansas River is fed by the Solomon, Republican, Saline, and Smoky Hill rivers which originate in western Kansas. The river flows eastward from Junction City to Kansas City where it joins the Missouri River. The Kansas

River alluvial deposits grade upward from locally derived flat limestone pebbles and boulders on the bedrock surface to fine sand, silt and silty clay in the upper part (Fader, 1974). The river cuts through Permian and Pennsylvanian age formations, and Pleistocene glacial deposits. Two public supply wells were sampled in the Kansas River alluvium (#1 and #6). The Jefferson RWD #13 well is in the Newman Terrace deposits and is screened in 19 feet of medium to coarse grained sand and gravel and rough boulders. The City of St. Marys well is screened in 20 feet of medium to coarse brown gravel. The shale bedrock in the Jefferson RWD #13 well is of Pennsylvanian age and the shale bedrock in the St. Marys well is of Permian age.

The Republican River extends from north-central Kansas across the Nebraska border and back into Kansas to Junction City where it joins the Kansas River. It crosses the Smoky Hills area of Kansas which is characterized by outcropping rock of the Cretaceous System. In the Junction City area, Permian age rocks form the Flint Hills physiographic region. South of Clay Center and north of Junction City, the Republican River flows into Milford Reservoir.

Three samples (#7, #8, and #9) were taken from wells in the Republican River alluvium. The City of Scandia well log reported 16 feet of screened alluvial gravel overlying bedrock of the Cretaceous System (Greenhorn and Carlile Formations). The Clay Center well is screened in 15 feet of medium to coarse sand and gravel with rocks and is underlain by Permian (Sumner) rocks. The Junction City well has 20 feet of coarse sand and gravel with rocks and is underlain by Permian (Gearyan) bedrock.

The Solomon River originates in northwestern Kansas and flows in a general eastern and slightly southern direction until it reaches Junction City where it joins the Kansas River. Kirwin and Webster reservoirs are located along the North and South forks, respectively, of the Solomon River. The Solomon River alluvium is 44 to 65 feet in thickness and is made up of peat, clay, sandy silt, and sand in the upper portion and coarse sand and gravel in the basal section (Latta, 1949).

Three sampling sites (#10, #40, and #43) are located in the Solomon River alluvium. The City of Downs well is located on the North fork about 6 miles from where it joins the South fork. This well is screened in 26 feet of sand and is underlain by Cretaceous age gray shale at a depth of 84 feet. A private well near the City of Minneapolis is screened in 3 feet of fine to coarse sand and gravel overlying Cretaceous age bedrock. The City of Enterprise well, located downstream from the junction of the Smoky Hill River, is screened in 15 feet of medium to coarse sand and gravel with some rock and is underlain by Permian (Gearyan) red shale.

The Saline River originates in western Kansas and forms Wilson Lake Reservoir located in Russell County. It then flows eastward where it joins the Smoky Hill River west of Salina. The Saline River alluvium is 20 to 92 feet in thickness and is composed of sand and gravel overlain by clay and silt with lenses of peat. Limestone, sandstone, and shale fragments are abundant in the coarse gravel deposits (Latta, 1949). Two samples (#41 and #42) were taken from the Saline River alluvium at public supply wells in the City of Beverly. A well record could not be found for site #41 which was an old well. The well which produced sample #42 is screened in 6 feet of sand and gravel underlain by Cretaceous (Dakota) blue shale.

The Smoky Hill River extends from western Kansas eastward to Bridgeport where it goes northward to Salina and joins the Saline and Solomon Rivers. Two reservoirs, the Cedar Bluff and Kanopolis Lake are contained along its length. The Smoky Hill River alluvium has a thickness of 30 to 90 feet. The upper 8 to 45 feet is composed of silt, sandy silt and fine sand and is underlain by poorly sorted sand and gravel (Latta, 1949).

Two wells (#11 and #44) are situated in the Smoky Hill River alluvium. The Saline County RWD #5 well is screened in 10 feet of medium to coarse sand underlain by Permian (Sumner) gray shale. The Ellis County RWD #1 well is screened in 10 feet of fine to medium sand and gravel with coarse gravel underlain by Cretaceous (Greenhorn) black shale.

The Arkansas River cuts across almost the entire length of Kansas. It enters southwest Kansas from Colorado. East of Dodge City it continues in a northeastern direction, and at Great Bend it veers southeastward and leaves the state near Arkansas City. The Arkansas River alluvial deposits are composed of limestone, chert, and arkosic gravel and sands intermixed with differing amounts of silt and clay (Bayne, 1962). Only two water samples were taken from the Arkansas River alluvium. Logs were not available for most of the wells in the western part of the river's length. In these areas, other aquifers are generally used for drinking water because better qualities and quantities of water may be obtained from the Ogallala, Big Bend, and Dakota aquifers. The City of Nickerson well, located northwest of Hutchinson, is screened in 15 feet of medium to coarse sand and gravel. The Arkansas River cuts through Quarternary (Big Bend), Cretaceous, and Permian sediments in this area. The Cowley County RWD #3 well is screened in 12 feet of very coarse sand underlain by Permian (Gearyan) shale.

The Pawnee River is a tributary to the Arkansas River in western Kansas. One water sample (#31) was taken from its alluvium. This well is privately owned and is screened in 10 feet of sand underlain by Cretaceous (Carlile or Greenhorn) black shale.

The Cimarron River originates in extreme southwestern Kansas and flows southeastward into Oklahoma. Two samples (#26 and #33) were taken from the Cimarron River alluvial aquifer. A privately owned well in Seward County is screened in 40 feet of medium to large sand. The Cimarron River cuts through Ogallala, Pleistocene, Cretaceous, and Permian sediments in this region of Kansas. Another privately owned well in Meade County was screened in 20 feet of fine to coarse sand and gravel.

The Neosho River extends from Morris County southwestward to Cherokee County where it continues into Oklahoma. Council Grove Lake and John Redmond Reservoir are located along its length. Two samples (#47 and #49) were taken from the Neosho River alluvial aquifer. The Crawford County RWD #6 well was screened in 5 feet of medium to coarse sand and gravel underlain by Pennsylvanian (Marmaton or Cherokee) bedrock. A private well in Lyon County was screened in 6 feet of gravel and underlain by Pennsylvania (Wabaunsee Group) bedrock.

Unconsolidated Aquifers

The Ogallala aquifer is the principle water supply in the high plains region. High yielding irrigation wells tap this aquifer throughout western Kansas. The Ogallala formation originated predominantly by sands which were deposited during Tertiary time by streams flowing eastward from the Rocky Mountains area (Moore, 1940). The thickness of the Ogallala deposits can vary over a wide range and thicknesses of less than 200 feet are present at most places north of the Arkansas River (Moore, 1940).

Sand is the most common material in the Ogallala and is mainly composed of quartz with some feldspar and other minerals. Beds of gravel usually contain sand and silt; and beds of sand and gravel may be cemented by calcium carbonate. These cemented beds of coarse material are referred to as "mortar beds" (Prescott et al., 1954). The texture of the Ogallala Formation is not uniform and there are gradations within short distances. The coarser materials are generally in the lower part of the formation where there are lenses and sinuous beds of gravel (Moore, 1940). Calcium carbonate occurs as stringers, nodules, and caliche; and there are many colors of silt including gray, red-brown, tan, buff and white (Prescott et al., 1954). Recharge into the Ogallala is mainly from precipitation.

Three public supply wells (samples #24, #25, and #27) derive water from the Ogallala aquifer. The City of Colby well is screened in 40 feet of fine sand and medium gravel and has a total depth of 261 feet. The City of Leoti well is screened in 18 feet of medium to coarse sand and gravel and is 175 feet in depth. The City of Satanta well is screened in 75 feet of sand and traces of gravel to a total depth of 430 feet.

The Equus Beds (sometimes referred to as the McPherson Formation), originated in Pleistocene time and cover a broad area between the Smoky Hill and Arkansas River valleys. This aquifer is a principal source of groundwater in the south-central area of Kansas, although some areas have had oil field brine contamination (Williams et al., 1949).

The Equus Beds are composed of stream borne material deposited by a Pleistocene river that flowed southward from the present Smoky Hill River valley joining the Arkansas River above Wichita (Moore, 1940). The early Pleistocene stream deposits are composed of coarse-grained sand and gravel. As the McPherson valley became filled after the diversion of the major stream, silt, clay and fine sand were more prevalent in the Equus Beds deposits (Williams and Lohman, 1949). The sand and gravel were derived from weathered shale of Cretaceous and Permian age and from reworking of eolian silt probably transported from the southwest. The Equus Beds are from 0 to 290 feet in thickness (Williams and Lohman, 1949).

Three wells were sampled (#13, #14, and #15) from the area of the Equus Beds aquifer. The City of McPherson public supply well is screened in 50 feet of sand and gravel and its total depth is 215 feet. The City of Halstead well was screened in 25 feet of fine to coarse sand and fine to medium gravel and has a depth of 151 feet. A privately owned well in Sedgwick county is screened in 10 feet of medium to coarse sand with a depth of 45 feet.

A major groundwater source in south-central Kansas contains thick deposits of silt, sand, and gravel that overlie Cretaceous bedrock. This aquifer is commonly referred to as the Big Bend aquifer and may encompass several formations of the Pleistocene series. The sediments represent stream-laid debris from the Rocky Mountains deposited during the Pleistocene epoch (McLaughlin, 1949). Pleistocene sand dunes overlie these sediments south of the Arkansas River although water levels are usually below the sand dune thicknesses. Basal gravels from these eastward flowing streams consist of granite, caliche, and material derived from Permian and Cretaceous age rocks. Thicknesses of these deposits can reach 300 feet (Bayne, 1956). Most of the public and private water supplies in the aquifer area are obtained from the Big Bend aquifer, although saline groundwaters are present in the Big Bend aquifer at depth in the eastern half of the Big Bend area, south of the Arkansas River (Bayne, 1956).

Two wells (samples #28 and #46) in the Big Bend aquifer were sampled. A private well in Reno County has a total depth of 72 feet and is screened in 25 feet of sand and gravel. The City of Belpre well in Edwards County, has a total depth of 100 feet to shale bedrock and is screened in 30 feet of sand and gravel.

Glacial sediments of Pleistocene age overlie Paleozoic bedrock in a large area of northeastern Kansas. The basal sands and gravels in these sediments are an important groundwater source in this area. These coarse grained beds are mainly located in a buried valley aquifer system. Glacial buried valleys were formed as glacial ice deposited sediments in Pleistocene age stream valleys. The valley sediments can be up to 400 feet in thickness (Denne et al., 1984).

Glacial sediments are predominantly composed of gravelly, silty, sandy clays (glacial till) which can be brown, tan, or blue-gray in color. Generally, the brown and tan clay is present in the upper section and has a thickness of about 40 feet. The gray and blue-gray glacial clays are present in the lower section and are usually much thicker in the buried valleys. Lenses or beds containing varying amounts of sand and gravel are present throughout the glacial sediment thickness. The gravels are composed of limestone, chert, igneous, and metamorphic fragments (Ward, 1974). A major glacial buried valley system extends from southeastern Marshall County through Nemaha, Jackson, and Atchison counties in Kansas. The valley width can be up to one and one-half miles (Ward, 1974).

Three water samples (#19, #22, and #23) were collected from wells associated with the major buried valley system. A privately owned well in Marshall County has 182 feet of glacial sediments and is screened in 10 feet of gravel. Another privately owned well in Jackson County is constructed in 145 feet of glacial sediments and is screened in 10 feet of coarse sand, medium gravel and pea gravel. Further east, along the course of the buried valley, in Atchison County, a private well in 200 feet of glacial material is screened in 10 feet of pea gravel. A fourth well tapping a glacial aquifer in Brown County, was also sampled. These glacial sediments were only 45 feet in thickness and were not a part of the major buried valley to the south. The well is screened in 7 feet of sand and gravel and 13 feet of the underlying shale bedrock.

Consolidated Aquifers

The Dakota Formation of the Lower Cretaceous System is composed of sandstone (some conglomeritic) separated by layers of siltstone, mudstone, shale and clay (Leonard, 1983). The sandstone is iron rich and salt water occurs in parts of this formation (Moore, 1940). It has a wide outcrop area in the north-central region of Kansas (see Figure 4). Early workers referred to this aquifer as a classical artesian system, receiving recharge at the higher outcrops along the Rocky Mountains and Black Hills and transmitting water into areas of lower head eastward. Subsequent investigations revealed that the aquifer has more hydrologic complexity (Helgesen et al., 1982). Recharge to the Dakota aquifer in sampling areas of this study is from precipitation on outcrop areas or precipitation through overlying permeable formations such as the Ogallala and Pleistocene deposits. The thickness of the Dakota aquifer can range up to 580 feet (Kume and Spinozola, 1985).

The sandstone of the Dakota Formation is a widely used aquifer unit in the outcrop areas of Kansas as well as in some areas of western Kansas where it is buried deeply in the subsurface. Yields in irrigation wells can be up to 2200 gpm (Kume and Spinozola, 1985).

Three water samples (#12, #18 and #29) were taken from wells screened in the Dakota Sandstone aquifer of the Cretaceous System. The City of Mahaska public supply well is 285 feet in depth and is screened in 10 feet of sandstone. Mahaska is located in Washington County near the Nebraska border in a Dakota Formation outcrop area. The City of Durham public supply well is 68 feet in depth and is screened in 10 feet of tan, fine to medium sandstone. Durham is located in Marion County in an outcrop island of the Dakota Formation. The City of Bison well is 102 feet in depth and is screened in 40 feet of loose sand rock and limestone. Bison is located in a small outcrop area of the

Cretaceous System and is adjacent to the Walnut Creek alluvium.

Two wells were sampled (#44 and #45) which have screened sections in Lower Permian rocks. The Lower Permian Series comprises more than 1900 feet of evaporite-bearing siltstones, sandstones, and shales in the upper portion and a little less than 800 feet of alternating limestone, shale and minor amounts of gypsum in the lower part (Zeller, 1968). Groundwaters in Permian age deposits vary widely in quality and quantity depending on the location and aquifer material. In Marion County, the Winfield Limestone Formation, the Nolans Limestone Formation, and the Wellington Formation are known to be aquifers. The Winfield Limestone and the Nolans Limestone are part of the Chase Group which is about 335 feet in thickness. The Chase Group consists of limestones alternating with shales which are often red and green in color. The Winfield Limestone is about 25 feet thick and consists mainly of cherty limestone and contains a massive fossiliferous limestone where cavernous weathering is characteristic (Zeller, 1968). Above this formation lies the Odell Shale which is chiefly red and green shale with some gray and yellow shale. The Nolans Limestone contains two limestone members separated by a shale member and lies above the Odell. The lower limestone is yellowish-brown and is about 4 feet in thickness (Zeller, 1968). The upper limestone is yellowish-tan and is dolomitic with a thickness of 6 to 10 feet. The Nolans Limestone Formation is 22 to 40 feet in thickness.

The Wellington Formation is predominantly shale with limestone, dolomite, siltstone, gypsum and anhydrite. The shale is gray to greenish-gray with some red, maroon and purple shale. The limestone is light colored and argillaceous (Zeller, 1968). The Wellington is part of the Sumner Group and is several hundred feet thick in Marion County. The Wellington Formation outcrops in the southern region of Marion County. Thin shale beds alternating with beds of white, pink or gray gypsum can be as great as 20 feet in thickness (Bryne, 1959). The limestone of the Wellington weathers blocky and cavernous to porous (Byrne, 1959).

A privately owned well constructed to a total depth of 93 feet in northeastern Marion County, is screened in 28 feet of limestone and shale which is probably part of the Nolans Limestone Formation (O'Connor, 1987). The City of Peabody public supply well, located in the southern part of Marion County, is 60 feet in depth and is screened in 30 feet of limestone and shale of the Wellington Formation.

One sample (#35) was taken from a private well which was screened in the "Red Beds" section of the Nippevalla Group in the Permian System. These rocks are exposed in south-central Kansas and water is believed to occur only in the weathered part of the formation (Lane, 1960). A privately owned well is 74 feet deep and is screened in 12 feet of shale in the Harper Siltstone Formation. This well is located in the southwestern part of Kingman County.

Rocks of the Pennsylvanian System crop out in the eastern quarter of the state. Sandstones of the Douglas Group provide potable water to small public and private users in areas of Leavenworth, Douglas and Franklin counties.

The Tonganoxie Sandstone Member of the Stanger Formation occupies an erosional river valley cut into older rocks of the Stranger and Stanton formations. The valley is 14 to 20 miles wide and trends southwestward (O'Connor, 1960). The Tonganoxie Sandstone Member is made up of conglomerate, sandstone, shale and coal and can be as great as 120 feet in thickness. The sandstone is light to dark gray and contains fine to very fine angular to subangular clear quartz and is up to 70 feet in thickness (O'Connor, 1960).

The Ireland Sandstone Member of the Lawrence Shale is an important sandstone aquifer occupying a west-southwest trending erosional valley in southern Douglas and parts of Franklin counties (O'Connor, 1960). The valley is one-half mile wide and the Ireland Sandstone can reach a thickness of 115 feet. The sandstone is similar to the Tonganoxie except that it is coarser. It is light gray where it is clean and medium to dark gray where carbonaceous material is more abundant. The sandstone contains a small percent of mica, pyrite and clay minerals and weathers tan or yellow brown

(O'Connor, 1960).

Recharge to both sandstone aquifers is mainly through precipitation in the outcrop areas and the water quality becomes more mineralized farther from the recharge area. There is recharge to the Tonganoxie Sandstone from the Ireland Sandstone where they are both interconnected. Discharge occurs from the Tonganoxie into alluvial deposits of the Wakarusa and Kansas River valleys (O'Connor, 1960). Douglas Group sandstones yield 5 to 100 gpm to wells.

Three water samples (#4, #5 and #48) were taken from wells in the Douglas Group sandstones. The City of Williamsburg well, located in Franklin County, was screened in 59 feet of white sandstone and has a depth of 200 feet. The City of Overbrook well, located in Douglas County, was constructed to a depth of 500 feet and has 80 feet of uncased open hole at its base. The aquifer material consists of sandy shale and sandstone. A privately-owned well in northeastern Douglas County is 160 feet in depth and is screened in 40 feet of sandstone.

The Arbuckle Aquifer refers to the Lower Paleozoic units of Cambro-Ordivician age located in southeast Kansas and adjoining areas of Oklahoma, Arkansas and Missouri. The Mississippian and Cambro-Ordivician aquifers are separated by confining layers of shale and dense dolomite except in a few areas (Macfarlane et al., 1981).

Freshwater wells in the Arbuckle aquifer are on the order of 1000 feet in depth and are usually completed as open bore holes. The first fresh water wells were drilled in the 1800's and were used for milling lead-zinc ores which were being mined in the area. At the present time, the fresh water of the Arbuckle is widely used for public supplies and industry (Macfarlane et al., 1981).

Recharge into the Cambro-Ordovician aquifer is from the outcrop area in the Ozark region of Missouri and the general flow of the water is westward. The Mississippian and Cambro-Ordivician aquifers produce oil west of Crawford and Cherokee counties and water in these units also increase in salinity in a westward direction. The presence of a water quality transition zone in the aquifer is demonstrated by increasing amounts of sodium, chloride and hydrogen sulfide (Macfarlane et al., 1981).

The bedrock in southeastern Kansas consists of sedimentary rocks ranging in age from Middle Pennsylvanian to Late Cambrian and rests unconformably on the PreCambrian surface. These sedimentary rocks range in thickness from 1200 to 2800 feet and are composed of limestone, dolomite, sandstone and shale.

The Cambro-Ordovician section contains many different formations among which are the Cotter and Roubidoux and the Gasconade Dolomite. These formations are considered to encompass the major permeable zones of the aquifer system (Macfarlane et al., 1981).

The Cotter Formation is composed of cherty, silty dolomite with lenses of sandstone; and has a thickness ranging from 0 to 300 feet. A particular layer of sandstone from 5 to 10 feet in thickness has been informally named the "Swan Creek". The Roubidoux Formation is composed of white sandstone, gray, medium grained sandy dolomite and cherty dolomite and is generally around 140 feet in thickness. The Gasconade Dolomite is primarily vuggy, cherty dolomite with a basal section composed of sandstone or sandy dolomite which is named the Gunter Sandstone Member.

Five water samples (#36, #37, #38, #39 and #50) were taken from wells deriving water from the Cambro-Ordovician aquifer system. All of these were public supply wells. Two wells from the City of Pittsburg water supply were sampled. These wells had 500 feet of open-bore hole drilled in the Cotter and Jefferson City Dolomite, the Roubidoux Formation and the Gasconade Dolomite. The Crawford County RWD #7 well has a total depth of 1113 feet and has 390 feet of open-bore hole in the Lower Ordovician section including the Cotter, Jefferson City, Roubidoux and Gasconade. The Cherokee County RWD #1 well or "Crestline" well has a total depth of 900 feet and has 325 feet of open hole including the Jefferson City Dolomite and the Roubidoux Formation. The City of Galena well has a total depth of 1272 feet and has 758 feet of open hole in the Cotter, Jefferson City, Roubidoux, Gasconade and a small section of the Eminence.

ANALYTICAL RESULTS

Table 3 shows the concentrations of TFP and TOC in the untreated, raw groundwater samples. The four individual THM concentrations (chloroform, bromodichloromethane, dibromochloromethane and bromoform) are given for each sample in ug/L and then summed to give TFP in ug/L and micromoles per liter (uM). "Percent Cl" is the percentage of halogen atoms in the THMs that are chlorine, the rest being bromine. Yield is the TFP in micromoles per liter divided by the TOC in mg/L. The chlorine demand expressed in mg/L is the amount of free chlorine consumed in 96 hours by substances in the sample.

Table 4 shows the terminal THM concentrations in the finished water samples. The "free-chlorine remaining" data indicate that most of the samples still contained free chlorine at the time the water was analyzed for THMs. Table 5 shows the instantaneous THM and TOC concentrations for the finished water samples. TOC levels were analyzed in the finished water for all but the first three of these samples.

Table 6 gives the results of the geochemical analyses of the water samples. The first five columns contain the field data and laboratory data for specific conductance and pH. The laboratory pH is generally higher than the field pH, as would be expected with the escape of CO gas. The field and laboratory conductance values were generally very close. A large difference in these values might indicate that there was precipitation of minerals from the water after sampling. The ionic balances computed for these results indicate that the analyses are very good with the greatest deviation from electroneutrality (the difference between the sums of milliequivalents/L of anions and cations divided by total milliequivalents/L) equal to 1.87 percent.

TABLE 3: TFP and TOC in Untreated Groundwater Samples.

Sample	$CHCl_3$ ug/L	$CHCl_2Br$ ug/L	$CHClBr_2$ ug/L	$CHBr_3$ ug/L	TFP ug/L	TFP uM	TFP %Cl	TOC mg/L	Yield umoles/mg	Chlorine Demand mg/L
1	8.9	12.0	8.7	1.3	30.9	0.195	71	0.69	0.282	1.40
2	85.2	14.1	3.4	<0.1	102.7	0.816	95	3.31	0.247	8.70
3	91.2	22.8	7.2	<0.1	121.2	0.938	93	2.56	0.366	5.90
4	9.0	3.7	1.6	<0.1	14.3	0.106	88	0.36	0.294	1.60
5*	1.7	2.2	9.0	12.7	25.6	0.121	31	0.48	0.252	5.90
6	7.5	16.2	28.5	19.4	71.7	0.375	47	1.04	0.361	1.40
7	36.1	32.2	24.4	4.9	97.6	0.635	74	1.90	0.334	2.00
8**	27.9	21.9	30.7	15.8	96.3	0.577	64	1.37	0.421	1.45
9	26.7	28.4	23.3	5.6	83.9	0.530	71	2.19	0.242	2.30
10	8.3	13.4	13.1	3.7	38.4	0.228	63	1.03	0.221	3.05
11	37.0	28.6	18.7	3.3	87.7	0.588	78	1.90	0.309	6.10
12	3.4	4.5	4.5	2.4	14.8	0.087	62	0.41	0.212	0.30
13	3.2	2.5	3.0	2.7	11.4	0.067	62	0.31	0.217	0.20
14	4.0	3.2	2.3	0.2	9.7	0.065	77	0.30	0.217	1.00
15	4.3	7.3	7.6	3.0	22.2	0.129	60	0.85	0.152	0.50
16	27.3	20.1	14.2	2.5	64.1	0.429	78	1.52	0.282	1.75
17	4.1	13.6	24.9	19.1	61.6	0.312	42	1.06	0.294	1.35
18	9.5	8.7	5.6	1.0	24.8	0.163	76	0.87	0.188	5.60
19	6.1	3.9	3.9	<0.1	14.0	0.094	78	0.45	0.209	1.10
20*	64.2	29.2	12.7	0.8	106.9	0.780	87	2.84	0.275	8.10
21	1.2	5.3	27.0	44.9	78.4	0.349	21	1.20	0.291	2.60
22	3.4	6.7	12.4	4.4	26.9	0.146	52	0.58	0.252	0.80
23	9.1	10.2	8.7	2.0	30.0	0.188	70	0.83	0.227	3.20
24	2.8	4.4	4.8	2.3	14.3	0.083	60	0.52	0.159	0.20
25**	3.5	11.5	22.2	19.6	56.8	0.283	39	1.34	0.211	0.00
26	6.5	12.6	15.3	4.6	38.9	0.222	58	0.72	0.308	0.50
27**	<0.1	3.3	7.6	7.4	18.3	0.086	30	0.47	0.183	0.00
28	4.5	5.3	3.8	<0.1	13.5	0.087	74	0.55	0.159	0.00
29	3.1	4.1	4.3	1.4	12.9	0.078	64	0.49	0.158	0.05
30	4.3	18.4	33.1	21.6	77.5	0.393	42	1.54	0.255	1.50
31	3.6	13.4	19.7	10.4	47.1	0.248	47	1.00	0.248	0.95
32	35.7	27.5	19.4	3.4	86.0	0.573	77	2.43	0.236	1.90
33	1.1	4.3	8.5	5.9	19.8	0.100	41	0.60	0.166	0.10
34	3.4	5.2	5.4	1.9	15.8	0.093	62	0.50	0.186	0.00
35	11.0	10.7	7.9	1.0	30.6	0.199	74	0.88	0.226	1.00
36	3.6	3.1	1.6	<0.1	8.3	0.057	80	0.27	0.210	0.70
37	1.5	2.1	1.7	<0.1	5.3	0.033	71	0.21	0.158	0.00
38	<0.1	0.4	1.4	3.9	5.8	0.025	16	0.29	0.086	20.00***
39	0.3	1.3	3.6	4.0	9.2	0.044	31	0.31	0.141	5.25
40	4.2	10.7	12.7	5.7	33.4	0.184	54	0.98	0.188	0.20
41	9.6	17.9	22.3	9.4	59.2	0.334	57	1.27	0.263	0.50
42	7.4	12.4	15.6	6.4	41.8	0.238	58	1.10	0.216	2.85
43	5.9	15.0	29.3	23.2	73.5	0.374	42	1.02	0.366	1.50
44	0.4	6.5	7.2	3.1	17.3	0.090	46	0.50	0.180	0.05

TABLE 3: TFP and TOC in Untreated Groundwater Samples (continued)

Sample	$CHCl_3$ ug/L	$CHCl_2Br$ ug/L	$CHClBr_2$ ug/L	$CHBr_3$ ug/L	TFP ug/L	TFP uM	TFP %Cl	TOC mg/L	Yield umoles/mg	Chlorine Demand mg/L
45	3.4	6.8	8.1	3.4	21.8	0.123	57	0.80	0.153	0.45
46	1.3	3.7	4.6	1.9	11.4	0.063	53	0.36	0.174	0.00
47	1.3	11.6	58.2	107	178.0	0.784	19	2.14	0.367	ND****
48	7.2	4.3	2.0	<0.1	13.5	0.096	84	0.37	0.257	ND
49*	52.6	43.5	32.9	5.5	134.4	0.885	76	2.45	0.362	8.15
50	2.3	3.9	5.2	2.2	13.6	0.077	57	0.48	0.160	5.20
Average (47 samples)	13.6	11.7	13.3	8.3	47.0	0.283	61	1.05	0.242	2.07

* Sample filtered through a glass fiber filter (934 AH) to remove suspended solids

** Free chlorine detected in untreated sample (was not checked in samles 1-23 or 36-50, except for sample 8)

*** No free chlorine residual detected (perhaps due to the high concentration of H2S)

**** Not determined

TABLE 4: Terminal Trihalomethane Concentrations in Finished Water Samples

	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	Term. THM			Yield*	Free Chlorine
Sample	ug/L	ug/L	ug/L	ug/L	ug/L	uM	%Cl	umoles/mg	Remaining
1	4.7	8.5	9.8	3.7	26.7	0.153	59	0.222	yes
3	53.9	18.6	9.5	1.4	83.5	0.617	88	0.241	yes
4	0.5	0.9	0.6	<0.1	2.0	0.012	70	0.033	no
5	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA**	<0.004	yes
6	<0.1	1.0	7.5	31.1	39.5	0.165	10	0.118	no
7	12.0	17.7	24.8	16.9	71.4	0.394	54	0.296	yes
8	20.5	19.0	23.1	6.2	68.8	0.423	68	0.338	yes
9	<0.1	0.2	0.2	<0.1	0.3	0.002	52	<0.001	no
11	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	<0.002	no
12	<0.1	1.5	2.0	0.9	4.3	0.022	42	0.032	yes
13	<0.1	1.3	2.2	2.1	5.6	0.027	33	0.159	yes
14	<0.1	2.1	1.9	0.7	4.7	0.025	47	0.147	yes
16	12.9	15.1	12.1	2.1	42.2	0.266	71	0.169	yes
17	14.4	14.8	10.5	1.4	41.2	0.267	74	0.267	yes
18	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	<0.005	no
20	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	<0.001	no
24	0.8	1.6	3.3	3.4	9.1	0.046	40	0.208	yes
25	1.5	5.8	17.5	19.9	44.7	0.211	30	0.155	yes
27	<0.1	0.8	2.5	3.4	6.7	0.030	24	0.178	yes
28	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	<0.007	no
30	5.7	17.5	25.4	13.4	62.0	0.329	48	0.212	yes
32	10.3	15.0	13.9	3.3	42.5	0.257	66	0.105	yes
36	2.9	2.4	1.4	<0.1	6.7	0.045	80	0.182	yes
37	0.7	1.3	1.4	0.4	3.8	0.022	61	0.136	yes
38	0.5	1.2	4.0	5.1	10.8	0.051	30	0.106	yes
39	<0.1	0.7	4.0	10.7	15.4	0.066	14	0.095	yes
40	0.4	2.6	7.1	6.9	17.1	0.081	31	0.072	yes
42	0.3	<0.1	<0.1	<0.1	0.3	0.003	100	0.002	no
45	0.2	<0.1	<0.1	<0.1	0.2	0.002	100	<0.001	no
49	91.9	42.7	17.8	1.9	154.2	1.123	87	0.459	yes
50	1.6	4.6	10.7	10.4	27.2	0.133	37	0.278	yes
Average (31 samples)	7.6	6.4	6.9	4.7	25.6	0.154		0.136	

* Based on TOC concentration of ITHM sample (except samples 49 & 50, based on the TOC values of the raw samples).

** Not applicable

TABLE 5: Instantaneous THM and TOC Concentrations in Finished Water Samples

Sample	$CHCl_3$ ug/L	$CHCl_2Br$ ug/L	$CHClBr_2$ ug/L	$CHBr_3$ ug/L	TFP ug/L	TFP uM	TFP %Cl	TOC mg/L	Yield umoles/mg	Field Cl_2(free) mg/L
1	0.7	2.4	3.7	1.8	8.5	0.045	48	0.69*	0.065	2.5
3	19.3	10.4	5.6	0.6	35.9	0.254	84	2.56*	0.099	2.5
4	0.5	0.6	0.5	0.0	1.6	0.010	73	0.36*	0.028	0.2
5	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA**	0.83	<0.004	0.2 (1.3)***
6	<0.1	<0.1	1.2	5.7	6.9	0.028	7	1.40	0.020	0.5
7	3.1	4.3	6.9	4.5	18.8	0.103	53	1.33	0.077	2.0
8	12.4	0.9	1.4	1.0	15.7	0.120	91	1.25	0.096	4.0
9	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	2.48	<0.001	0.2
11	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	1.93	<0.002	0.2
12	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	0.69	<0.004	1.7
13	<0.1	0.5	1.0	1.3	2.8	0.013	28	0.17	0.076	1.0
14	<0.1	0.2	0.4	0.3	0.9	0.004	34	0.17	0.023	2.0
16	0.6	1.3	1.8	0.6	4.3	0.023	55	1.57	0.015	2.7
17	1.1	0.7	0.8	0.9	3.5	0.021	64	1.00	0.021	1.5
18	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	0.64	<0.005	0.2
20	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	2.08	<0.001	1.0
24	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	0.22	<0.014	1.0
25	<0.1	0.8	2.9	5.0	8.7	0.038	20	1.36	0.028	2.0
27	<0.1	<0.1	0.5	1.1	1.6	0.007	12	0.17	0.041	1.3
28	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	0.42	<0.007	0.2
30	1.3	1.9	3.7	3.3	10.2	0.053	46	1.55	0.034	4.0
32	0.4	1.1	2.1	0.5	4.1	0.022	51	2.44	0.009	1.3
36	<0.1	1.1	0.2	<0.1	1.3	0.007	63	0.25	0.030	2.7
37	0.3	<0.1	<0.1	<0.1	0.3	0.002	100	0.16	0.015	2.7
38	<0.1	0.2	0.4	<0.1	0.6	0.003	46	0.48	0.006	4.0
39	<0.1	0.1	0.4	<0.1	0.5	0.002	41	0.69	0.003	1.3
40	0.4	0.1	<0.1	<0.1	0.5	0.004	95	1.12	0.004	1.2
42	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	NA	1.34	<0.002	0.2
45	0.3	<0.1	<0.1	<0.1	0.3	0.002	100	2.61	<0.001	0.2
49	42.4	27.3	12.4	1.3	83.4	0.586	83	2.45*	0.239	2.0 (2.5)***
50	1.4	0.9	0.9	<0.1	3.1	0.021	78	0.48*	0.044	4.0
Average (31 samples)	2.8	1.8	1.5	1.0	7.0	0.045		1.12	0.033	

* Raw water TOC (other TOC values determined on the treated sample taken for ITHM)

** Not Applicable

*** Total Residual Chlorine was greater than the amount of free chlorine detected (as indicated)

TABLE 6: Geochemical Results

SAMPLE NUMBER	TEMP (CEL)	pH FLD	pH LAB	COND FLD	COND LAB	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	HCO_3 mg/L	SO_4 mg/L	Cl mg/L	NO_3 mg/L	NH_4 mg/L	Ba ug/L	Fe ug/L	Mn ug/L	H_2S mg/L
01	12.0	6.95	7.40	740	663	106	14.0	15	1.6	0.5	371	36.0	5.2	0.1	0.1	490	1530	422	ND
02	15.0	6.95	7.52	940	908	123	35.0	29	5.4	0.9	588	15.0	6.6	<0.1	1.1	868	12900	713	ND
03	15.0	7.05	7.60	830	810	90	28.0	46	5.9	0.7	398	96.0	14.0	<0.1	0.7	674	11100	706	ND
04	16.0	7.05	7.60	550	562	90	13.0	16	1.1	0.8	352	12.0	2.2	<0.1	0.2	131	664	24	ND
05	19.0	7.70	8.00	1450	1300	20	8.2	251	2.7	1.0	333	19.0	248.0	<0.1	1.0	31	4300	36	1.0
06	11.0	6.95	7.45	950	1020	142	26.0	33	5.3	2.3	407	94.0	56.0	46.0	0.1	193	152	9	ND
07	15.0	7.05	7.90	660	685	69	17.0	43	11.0	0.6	241	95.0	40.0	2.0	0.1	371	93	769	ND
08	16.0	6.95	7.59	1450	1430	207	42.0	52	11.0	2.7	420	382.0	45.0	24.0	0.1	55	BQ	411	ND
09	14.0	7.15	7.59	1030	1098	138	17.0	68	12.0	0.7	381	154.0	74.0	17.0	0.1	207	311	545	ND
10	14.0	6.85	7.45	720	750	103	16.0	34	4.1	0.4	395	64.0	16.0	0.1	0.4	168	2630	837	ND
11	14.0	7.10	7.70	960	1000	140	28.0	34	6.0	1.6	457	119.0	43.0	0.1	0.7	108	7520	937	ND
12	14.5	6.35	6.80	310	333	30	6.9	24	2.1	0.2	86	46.0	19.0	20.0	<0.1	158	BQ	16	ND
13	14.0	7.10	7.65	530	570	89	9.0	17	2.5	0.4	292	21.0	26.0	4.2	<0.1	188	BQ	BQ	ND
14	14.0	7.10	7.60	380	412	58	7.5	18	1.2	0.3	208	20.0	6.1	21.0	<0.1	122	BQ	BQ	ND
15	14.0	7.15	7.60	850	909	94	14.0	84	1.0	0.4	391	46.0	73.0	19.0	<0.1	130	BQ	BQ	ND
16	15.5	7.05	7.50	780	830	124	26.0	18	1.3	2.4	485	54.0	13.0	6.7	0.1	218	BQ	BQ	ND
17	14.5	7.05	7.85	2250	2350	167	37.0	263	7.1	1.3	322	188.0	487.0	22.0	<0.1	65	947	BQ	ND
18	13.5	7.25	7.85	1130	1180	29	7.7	229	6.1	0.4	418	116.0	102.0	0.4	0.8	24	127	25	ND
19	15.0	7.15	7.80	620	602	82	14.0	29	2.5	0.5	389	13.0	4.9	0.2	0.1	231	175	395	ND
20	13.5	7.25	7.95	1010	1042	140	45.0	34	16.0	1.2	704	7.6	18.0	0.2	1.5	3840	114000	12400	ND
21	8.0	6.35	6.90	1100	1160	44	14.0	168	2.9	1.2	155	61.0	226.0	40.0	0.3	45	27	211	ND
22	8.0	6.90	7.60	800	838	103	28.0	42	1.9	1.0	397	93.0	29.0	4.0	0.1	71	377	8	ND
23	9.0	7.10	7.90	710	650	76	23.0	29	3.8	1.1	401	18.0	12.0	0.1	0.5	190	811	126	ND
24	15.0	7.50	8.00	410	415	40	15.0	24	5.7	0.6	213	23.0	6.4	14.0	<0.1	82	BQ	BQ	ND
25	14.0	7.10	7.83	625	610	62	24.0	21	4.6	1.2	175	74.0	49.0	25.0	<0.1	86	70	BQ	ND
26	16.0	7.15	7.90	640	608	60	27.0	29	3.8	1.2	265	84.0	13.0	9.3	0.1	118	41	19	ND
27	16.0	7.05	7.85	710	730	65	27.0	50	4.5	1.5	224	162.0	16.0	14.0	<0.1	20	16	BQ	ND
28	15.0	7.35	8.10	385	400	53	5.7	22	3.2	0.3	193	18.0	11.0	20.0	<0.1	141	BQ	BQ	ND
29	15.0	7.30	7.99	500	492	75	9.0	14	3.0	0.5	261	14.0	14.0	16.0	0.1	206	145	BQ	ND
30	14.0	6.85	7.70	1000	1050	176	14.0	29	4.6	0.7	347	180.0	71.0	0.3	0.1	197	904	52	ND
31	14.0	6.95	7.60	850	885	124	19.0	28	6.6	1.1	371	75.0	38.0	49.0	<0.1	213	22	BQ	ND

TABLE 6: Geochemical Results (continued)

SAMPLE NUMBER	TEMP (CEL)	pH FLD	pH LAB	COND FLD	COND LAB	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Sr mg/L	HCO_3 mg/L	SO_4 mg/L	Cl mg/L	NO_3 mg/L	NH_4 mg/L	Ba ug/L	Fe ug/L	Mn ug/L	H_2S mg/L
32	13.0	7.15	7.55	785	820	126	10.0	35	4.8	0.7	333	95.0	46.0	3.3	<0.1	204	45	140	ND
33	16.0	7.35	7.85	3700	3500	93	30.0	622	9.1	1.3	251	286.0	853.0	5.8	<0.1	38	BQ	BQ	ND
34	12.0	7.50	8.00	935	827	41	11.0	120	2.9	0.5	257	82.0	79.0	7.0	0.1	37	32	BQ	ND
35	15.0	7.45	7.85	600	580	57	28.0	29	1.7	0.7	324	23.0	14.0	13.0	0.1	136	BQ	BQ	ND
36	17.5	7.10	8.00	480	451	47	22.0	18	3.9	0.7	234	50.0	4.8	<0.1	0.2	72	166	BQ	ND
37	18.7	7.20	8.03	450	423	49	18.0	14	1.8	0.1	176	64.0	14.0	0.1	0.1	82	44	7	ND
38	20.0	7.35	7.60	780	790	51	24.0	87	5.3	0.8	320	34.0	86.0	<0.1	0.3	357	BQ	BQ	7.5
39	23.0	7.25	7.85	1200	1140	70	34.0	125	7.6	1.3	323	96.0	169.0	<0.1	0.4	52	122	BQ	3.5
40	14.0	6.80	7.65	820	820	118	14.0	38	6.9	0.7	352	71.0	45.0	27.0	0.1	178	BQ	BQ	ND
41	14.0	6.95	7.60	1040	1030	137	20.0	65	4.9	0.6	475	107.0	46.0	15.0	0.1	115	846	117	ND
42	14.0	6.95	7.90	950	923	142	15.0	42	5.0	0.8	476	96.0	22.0	0.6	0.3	122	3470	669	ND
43	13.0	6.80	7.60	1620	1481	184	43.0	88	7.4	2.1	392	379.0	100.0	0.2	1.0	39	616	2620	ND
44	13.0	7.05	7.80	840	778	95	32.0	18	0.9	0.3	386	21.0	29.0	36.0	0.2	556	BQ	BQ	ND
45	13.0	6.95	7.60	1900	1670	303	54.0	32	2.3	5.3	401	687.0	31.0	3.1	0.1	26	924	14	ND
46	15.0	6.95	8.01	2200	1960	78	12.0	319	6.8	0.5	250	59.0	474.0	6.0	<0.1	203	651	37	ND
47	13.0	6.60	6.85	1590	1520	227	30.0	47	1.4	0.9	352	140.0	134.0	188.0	0.1	192	BQ	BQ	ND
48	16.0	7.15	7.45	590	560	86	12.0	22	1.1	0.4	335	24.0	2.2	0.1	0.2	12	396	48	ND
49	21.0	7.25	7.85	685	725	106	16.0	22	2.7	1.0	385	30.0	17.0	0.1	1.1	805	9270	1790	ND
50	22.0	7.25	7.45	785	830	69	29.0	60	6.2	0.8	326	83.0	54.0	<0.1	0.3	108	40	BQ	2.0

BQ = BELOW QUANTIFIABLE LIMIT
ND = NOT DETECTED
CEL = DEGREES CELSIUS

FLD = FIELD VALUE
LAB = LAB VALUE
COND=SPECIFIC CONDUCTANCE IN umhos
IRON, MANGANESE, AND BARIUM ARE IN ug/L

DISCUSSION

Occurrence of TOC and TFP

The TOC concentrations (Table 3) ranged form 0.21 to 3.31 mg/L with a median value of 0.85 and a mean of 1.05 mg/L. Figure 5 shows the TOC concentrations on a map of Kansas. The highest values (i.e., those >2.0 mg/L) are located in the eastern third of the State. Another area of moderately high values (>1.0 mg/L) is located in the central part of the State.

TFP concentrations in micromoles per liter closely reflected the TOC concentrations in mg/L (r=0.95), as shown in Figure 6. Figure 6 also shows the TOC concentrations for each of five aquifer classifications, illustrating that the highest TOC and TFP concentrations (>1.5 mg/L) were found exclusively in the alluvial aquifers, including those of the Missouri, Neosho, Smoky Hill and Republican rivers. The glacial and Ogallala aquifers are the only non-alluvial aquifers with TOC concentrations greater than 1 mg/L. A lower concentration region with TOC levels between 0.2 and 0.9 mg/L includes the remaining samples, which are predominantly from non-alluvial sources.

River waters often carry large organic loads, and other investigations have shown that river waters generally have higher TOC concentrations than groundwaters (see Drinking

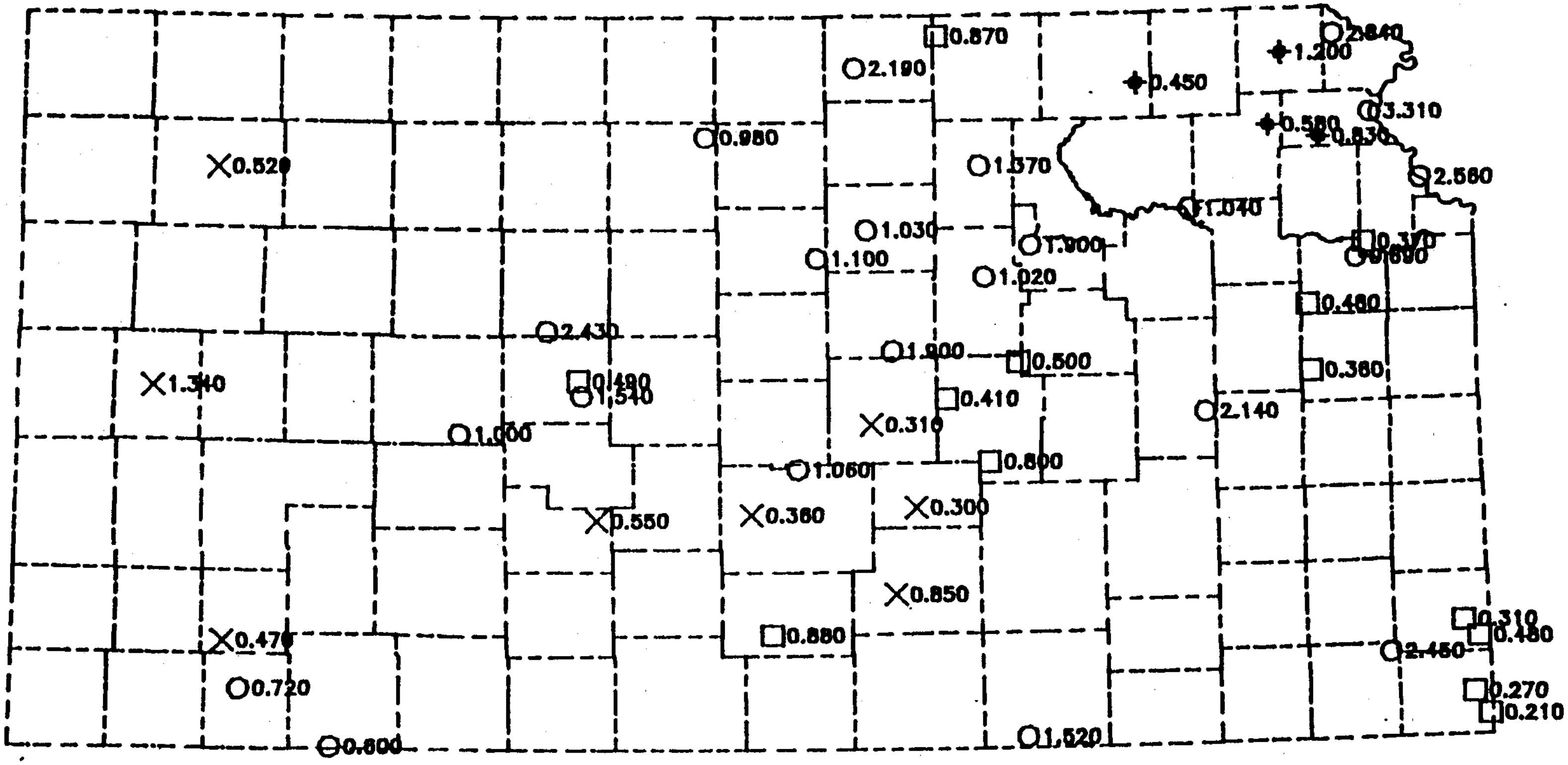

FIGURE 5: TOC Concentrations Plotted on a State of Kansas Map.

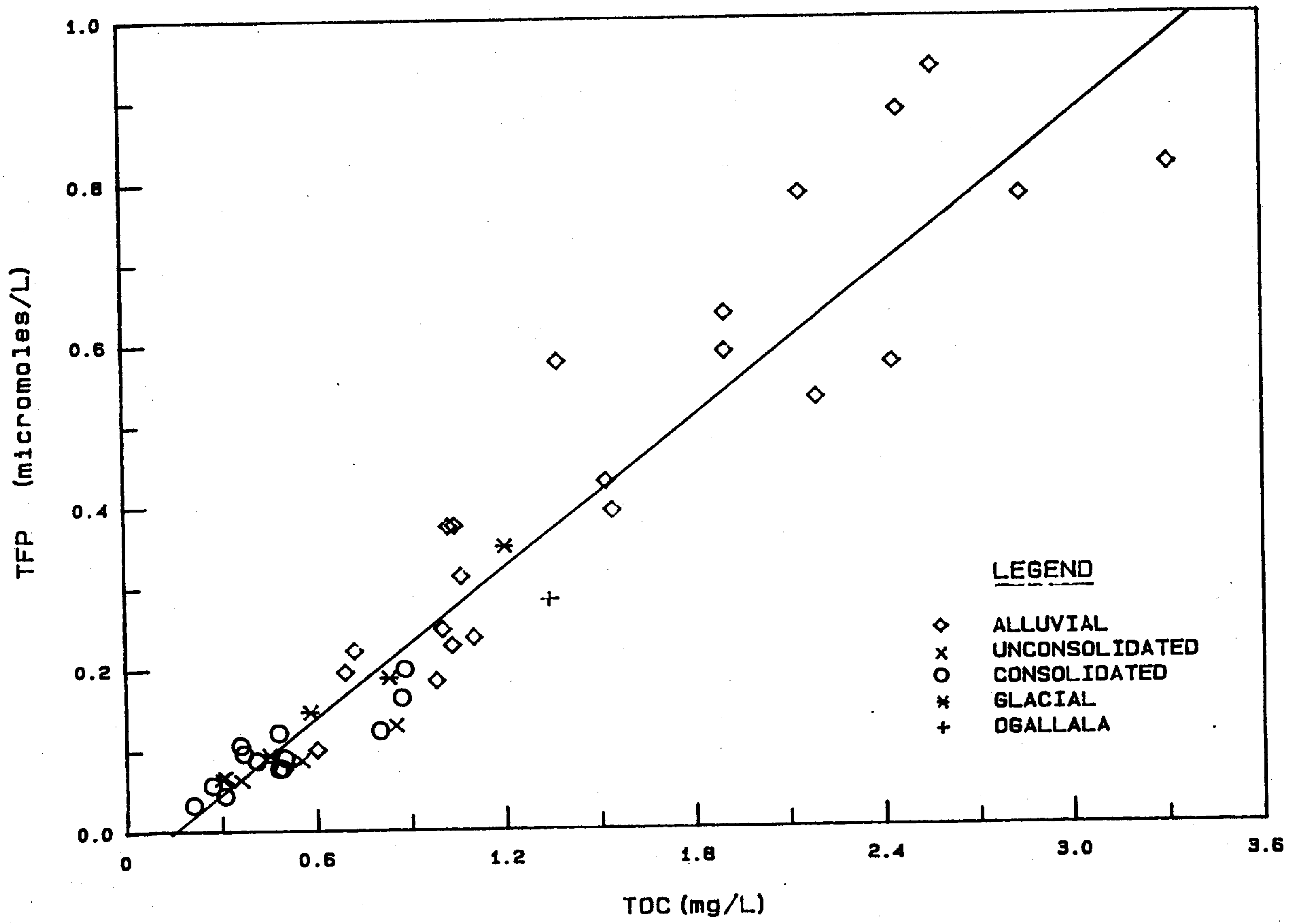

FIGURE 6: TFP as a Function of TOC and Aquifer Type
$y = -.0476 + .3138\ x$

Water Investigations). The recharge and discharge relationship of a river and its adjoining alluvium is probably a major factor in the amount of TOC in the water samples from alluvial sources. Therefore, alluvial aquifers which are at least partially recharged by river waters would be expected to have higher TOC levels. The alluvial deposits might also contain organic materials as a result of river deposition.

The TFPs ranged from 5.3 to 178 ug/L, with $CHCl_3$ ranging from <0.1 to 64.2 ug/L, $CHCl_2Br$ from 0.4 to 43.5 ug/L, $CHClBr_2$ from 1.4 to 58.2 ug/L, and $CHBr_3$ from <0.1 to 107 ug/L. Twenty-eight of the samples had $CHClBr_2$ as the highest THM, while 13 samples had $CHCl_3$ as the highest THM. Sample #47 had anomalously large concentrations of brominated THMs, presumably due to high concentrations of bromide in the raw water. Table 7 shows the mean and standard deviation of each THM species in untreated water supplies.

Figure 7 shows the TOC-TFP relationship with the private and public supply wells delineated. The spread of the differing well types indicates that there is no apparent relationship between the TOC level in a well and whether it is a private or public supply well.

TABLE 7: Mean and Standard Deviation of Individual THM Species in the Untreated Samples

Species	Mean*	SD.
$CHCl_3$	13.6	21.3
$CHCl_2Br$	11.7	9.6
$CHBr_2Cl$	13.3	11.6
$CHBr_3$	8.3	17.0

* 47 samples

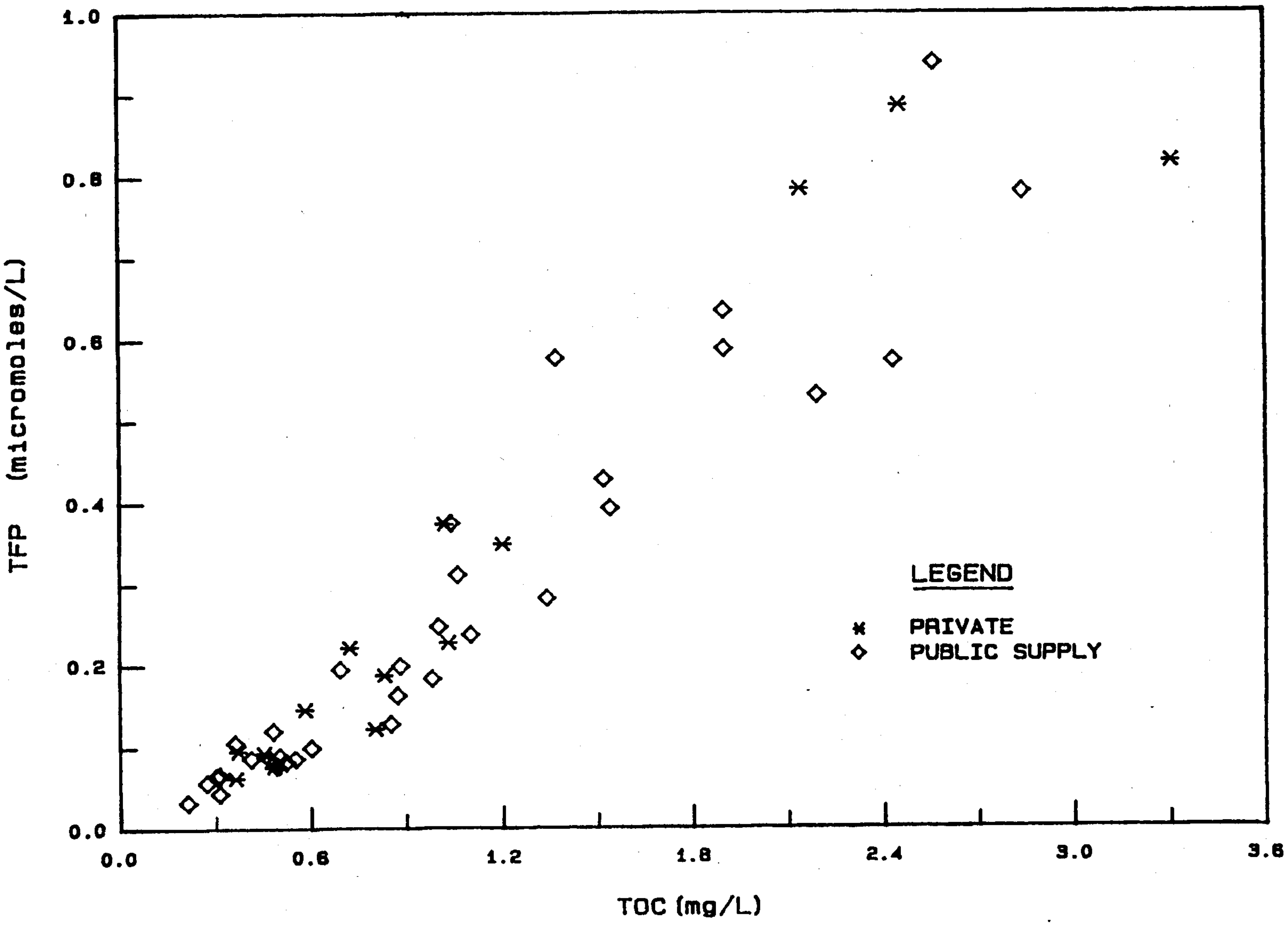

FIGURE 7: TFP as a Function of TOC and Well Type

TFP Yield

TFP yields ranged from 0.086 to 0.421 umoles/mg with a mean of 0.242 ± 0.07 umoles/mg. Figure 8 shows yield versus TOC concentration and illustrates that the alluvial aquifers had the highest yields. Yield values might be affected by the character of the TOC content (i.e., the type of organic precursor), other aquatic chemical or physical factors, or experimental factors; and yields are also known to be affected by the presence of bromide ion (see Trihalomethane Formation). Sample #47 had one of the six highest TFP yields of the study, and was dominated by brominated THMs (especially bromoform). Bromide can occur in water from natural sources (5 to 150 mg/L in rain and snow) and from anthropogenic sources. The oxidation of bromide ion to bromine and its subsequent reaction with organic compounds to produce THMs may be a factor in the high yield (0.367 uM/mg) and low percentage chlorine (19 percent) of this sample. The higher yields in the samples from alluvial sources may result from the type of organic precursor; these waters might contain high levels of fulvic acid for example.

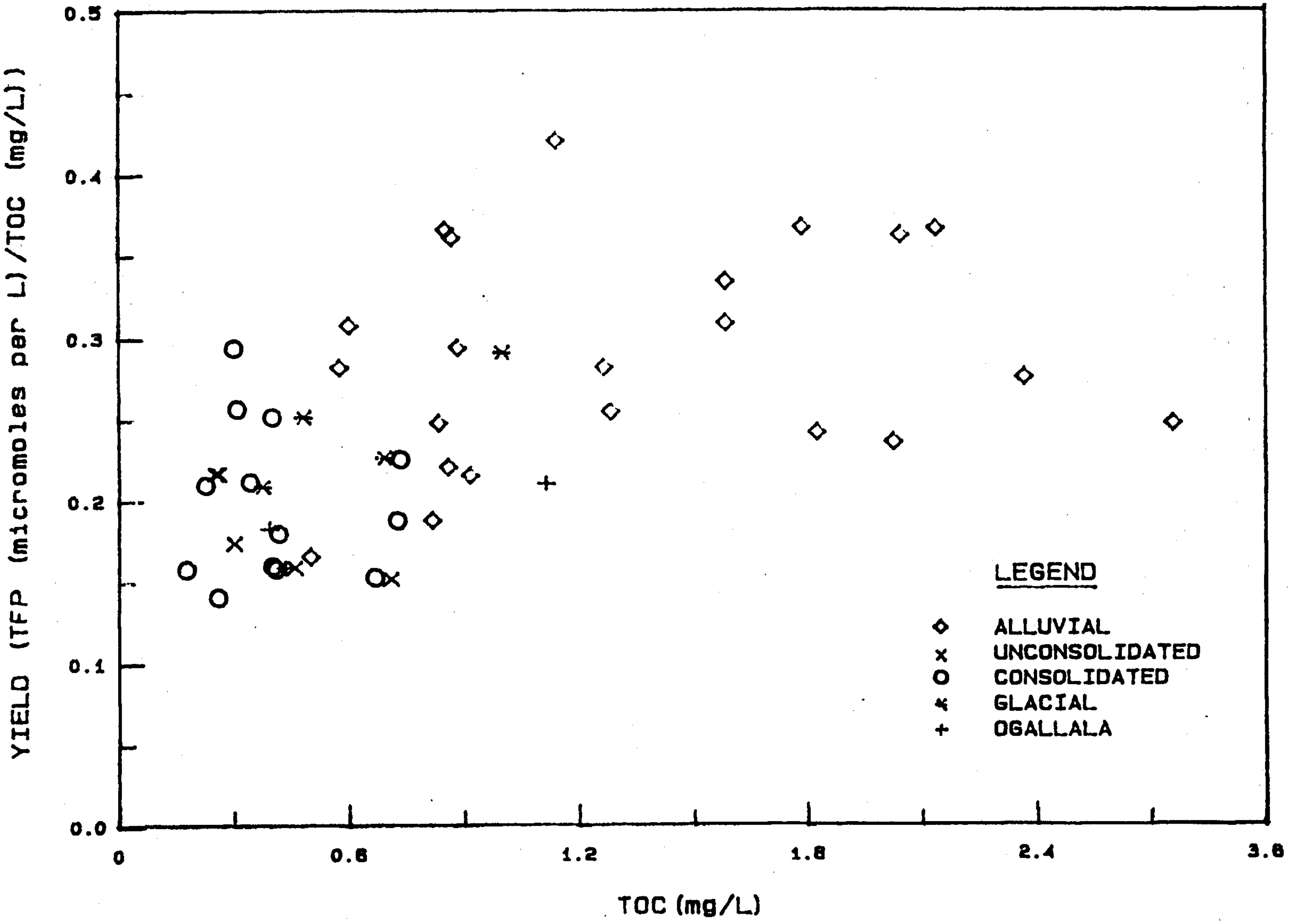

FIGURE 8. TFP Yield as a Function of TOC and Aquifer Type

Instantaneous and Terminal THMs in Public Water Supplies

The 31 samples from public water supplies were analyzed for terminal and instantaneous THM concentrations (Tables 4 and 5). Terminal THM concentrations ranged from 0.2 to 154 mg/L. Fifteen of these samples had terminal THM levels greater than 10 ug/L, but only one sample contained THMs in excess of the maximum contaminant level (MCL) of 100 ug/L. Field measurements showed chlorine levels to be between 0.2 and 4.0 mg/L; and the free and total chlorine concentrations were generally (except for samples #5 and #49) equal to each other, indicating that most of the residual was free. Free chlorine was detected in most of the samples when they were analyzed for terminal THM concentrations. Samples which did not contain free chlorine might have had higher THM concentrations if a higher chlorine dosage had been used.

Instantaneous THM concentrations ranged from 0.3 to 83.4 ug/L and five samples had levels greater than 10 ug/L. TOC concentrations in the finished waters ranged from 0.22 to 2.61 mg/L and were generally a little lower than the TOC concentrations in the raw-water samples.

Chlorine Demand

Chlorine demand ranged from <0.1 to 8.7 mg/L (see Table 3). Sample #38 was not included due to the possible interference by the high concentration of hydrogen sulfide. The chlorine demand in some samples may have been affected by the presence of free chlorine in the raw sample which was used to obtain the TFP values. The difficulties in obtaining raw water from certain public supply systems were discussed previously (see "Sampling Procedure"). Some samples, including samples #8, #25 and #27, already had chlorine in them at the time of sampling, and therefore had lower chlorine demand than they would have had if they had not been previously chlorinated.

Chlorine demands attributable to ammonium were calculated using the measured ammonium ion concentrations in order to compare them with the total chlorine demands. All samples but one (#43) had ammonium-related chlorine demands significantly lower than the total chlorine demand, indicating good agreement between the measurements of chlorine demand and ammonium ion concentration.

Figure 9 shows the relationship of chlorine demand to TOC. As TOC increases, more chlorine is expected to be consumed by reaction with organic matter and the chlorine demand should increase. This relationship is generally demonstrated on Figure 9; however, a group of consolidated aquifer samples illustrates the effects of other chlorine-demanding substances in the water. Samples #39 and #50 had high concentrations of hydrogen sulfide. Sample #5 had a detectable amount of hydrogen sulfide and an ammonium ion

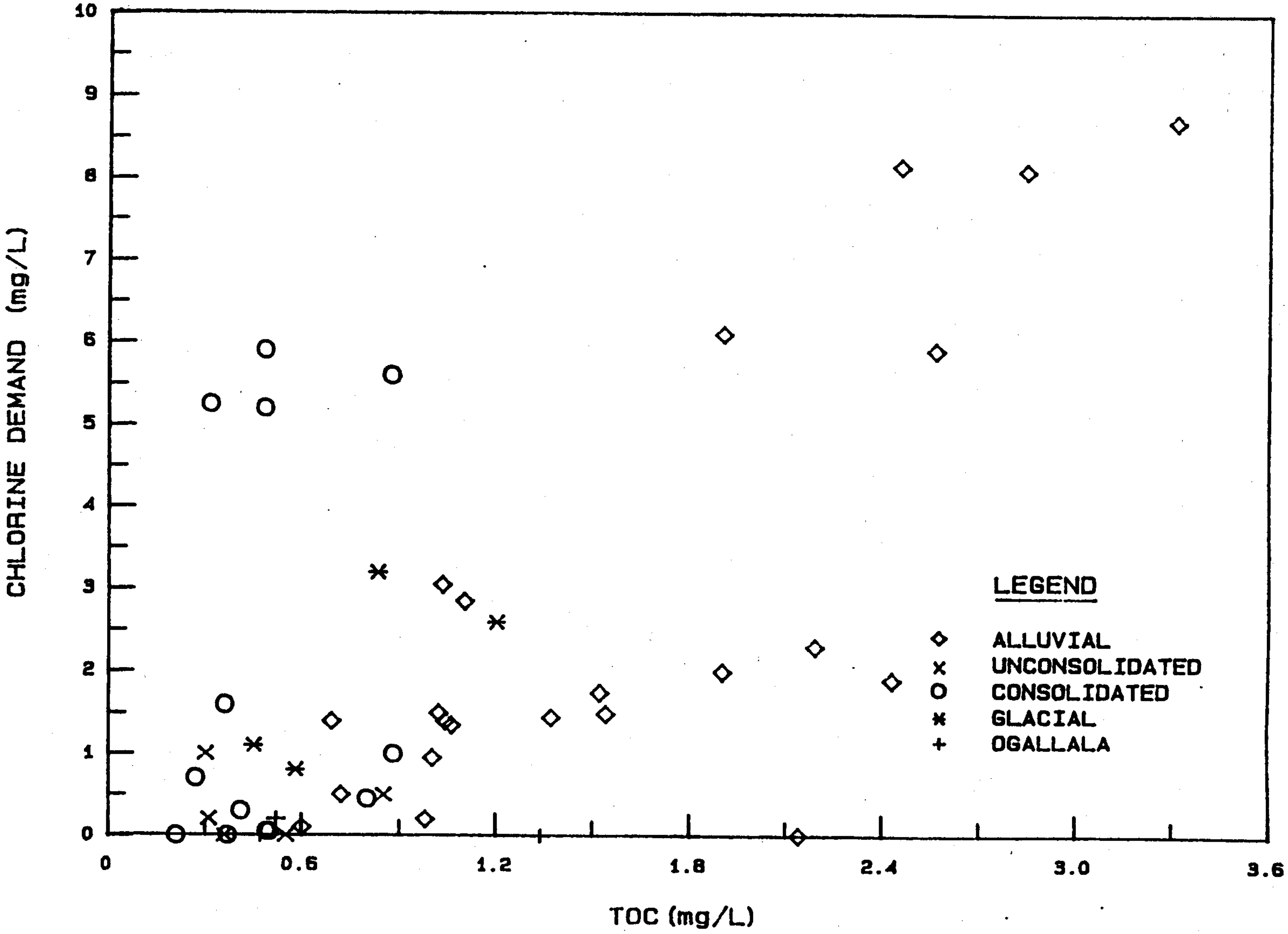

FIGURE 9. Chlorine Demand as a Function of TOC and Aquifer Type

concentration of 1.0 mg/L; and sample #18 had an ammonium ion concentration of 0.8 mg/L. Samples #32, #7 and #9 had high TOC levels in comparison to their chlorine demands. These samples were from wells in the Smoky Hill and Republican River alluviums. Possible reasons for the low chlorine demands might be the type of organic precursor or the lack of chlorine demand associated with low concentrations of certain inorganic species (iron, manganese and ammonium).

TOC Related to Geochemical Factors in the Water

TOC concentrations were statistically analyzed relative to various geochemical factors in order to attempt to discover any significant relationships that might exist. Table 8 shows the mean and standard deviation for each chemical constituent, as well as the correlation coefficient for each constituent in relation to TOC. Table 9 shows the means and standard deviations of ten parameters, including TOC, for the three major types of aquifers. The samples from the alluvial aquifers had the highest mean values for all parameters except temperature. The mean TOC concentration found in samples from the alluvial aquifers was over twice that of the unconsolidated aquifers and four times that of the consolidated aquifers. The samples taken from the glacial and Ogallala aquifers had a mean TOC concentration of 0.7 mg/L. The alluvial aquifer samples also had a notably higher mean TFP yield (0.288 ± 0.067 micromoles/mg) than both the unconsolidated (0.204 ± 0.041 micromoles/mg) and the consolidated aquifer samples (0.199 ± 0.047 micromoles/mg).

TABLE 8 Relationships of Chemical Constituents to TOC (47 Samples)

Chemical Constituent	Correlation Coefficient (r)	Range of Values	Mean	SD
Field Specific Conductance(umhos)	0.158	380-3700	900	442
TDS(mg/L)	0.201	191-1331	526	268
Ca(mg/L)	0.405	29-303	100	56
Mg(mg/L)	0.309	5.7-45	21	11
Hardness(Ca+Mg)	0.410	83.6-978	338	173
Na(mg/L)	0.125	14-622	60	71
K(mg/L)	0.464	0.9-12	4.6	3.2
Sr(mg/L)	0.135	0.1-5.3	1.0	0.9
SO_4(mg/L)	0.068	12-687	94	118
Cl(mg/L)	0.077	2.2-853	64	104
NO_3(mg/L)	0.138	<0.1-188	14	29
Ba(ug/L)*	0.610	12-868	188	194
H_2S(mg/L)	0.204	ND-7.5	---	---
HCO_3(mg/L)	0.564	86-704	339	111
NH_4(mg/L)	0.725**	<0.1-1.5	0.29	0.35
Fe(ug/L)*	0.647	BQ-9270	2970	1319
Mn(ug/L)*	0.444	BQ-2620	253	509

95% confidence level (r) >0.37
99% confidence level (r) >0.46
* Excluding sample #20
** With <0.1 values eliminated from the regression analysis
ND= not detected
BQ= below quantifiable limit

TABLE 9: Means and Standard Deviation of Ten Parameters for Three Aquifer Types

	Alluvial Aquifers 22 Samples		Unconsolidated Aquifers 12 Samples		Consolidated Aquifers 13 Samples		Total 47 Samples	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
TOC (mg/L)	1.59	0.76	0.65	0.34	0.48	0.22	1.05	0.77
TFP (uM)	.473	.253	.131	.092	.098	.046	.283	.253
TFP Yield (uM/mg C)	.288	.067	.204	.041	.199	.047	.242	.070
NH4 (mg/L)	.373	.436	.150	.124	.292	.287	.294	.347
Fe+Mn* (Mg/L)	2964	4365	244	326	547	1174	1571	3246
Hardness (Ca+Mg)	423	140	241	65	282	226	338	173
Total Dissolved Solids (mg/L)	613	246	437	239	477	309	526	268
Field Specific Conductance (umhos)	1130	677	777	495	826	447	900	442
Field pH	7.0	0.2	7.1	0.3	7.2	0.3	7.1	0.3
Temperature (degrees C)	14.2	2.0	13.1	2.9	16.6	3.3	14.6	2.9

* Sample #20 was not included

Hardness, Calcium and Magnesium

Hardness was relatively well correlated with TOC ($r = 0.41$), and calcium and magnesium (which comprise the hardness) were also significantly correlated with TOC ($r = 0.405$ and $r = 0.309$, respectively).

Sources of calcium in water include calcium carbonate ($CaCO_3$), which is present in Tertiary and Quaternary sediments as well as Cretaceous, Permian and Pennsylvanian limestones and shales. Water containing CO_2 from the air and from biological activity dissolves calcium carbonate to form calcium and bicarbonate ions. Another source of calcium is gypsum ($CaSO_4$-$2H_20$) which can occur in evaporite deposits of the Permian System.

Calcium concentrations ranged from 29 to 303 mg/L with most of the calcium concentrations above 100 mg/L for waters from alluvial aquifers. Sample #45, which had the highest concentration, was from a Permian aquifer. Magnesium concentrations ranged from 5.7 to 45 mg/L. The highest magnesium values occurred in several alluvial aquifers; and moderately high values were obtained for water samples from the glacial, Ogallala and Cambro-Ordovician aquifers. Sources of magnesium include those mentioned for calcium, as well as dolomite ($MgCa(CO_3)_2$), which is present in the Cambro-Ordovician rock sequence.

Although hardness is correlated with TOC for these samples, there is no evidence of a causal relationship.

Most likely, these variables are found to be associated simply because both are higher in waters of alluvial aquifers. In fact, one would expect to find lower concentrations of TOC with increased hardness because a higher concentration of divalent cations would promote coagulation and adsorption of the humic substances.

Iron, Manganese and Ammonium

Elevated levels of ammonium, iron (II) and manganese (II) indicate reducing conditions in an aquifer. Decomposition of organic matter can lead to anaerobic conditions, causing iron and manganese to be reduced and dissolved into solution. Due to the decreased energy available to microorganisms under anaerobic conditions, higher concentrations of TOC are expected to occur.

Figure 10 shows a plot of ammonium versus TOC. An apparent trend of increasing ammonium with increasing TOC can be observed, although a number of samples with low concentrations of ammonium had high (>1 mg/L) concentrations of TOC. A correlation coefficient of 0.725 was found for the 18 data points with ammonium >0.1 mg/L and a correlation coefficient of 0.5 was calculated for all 47 samples.

In Figure 11 total iron plus total manganese is plotted as a function of TOC for water samples from the alluvial aquifers. For the 8 samples having more than 1.0 mg/L iron plus manganese, a linear relationship is very apparent (r =

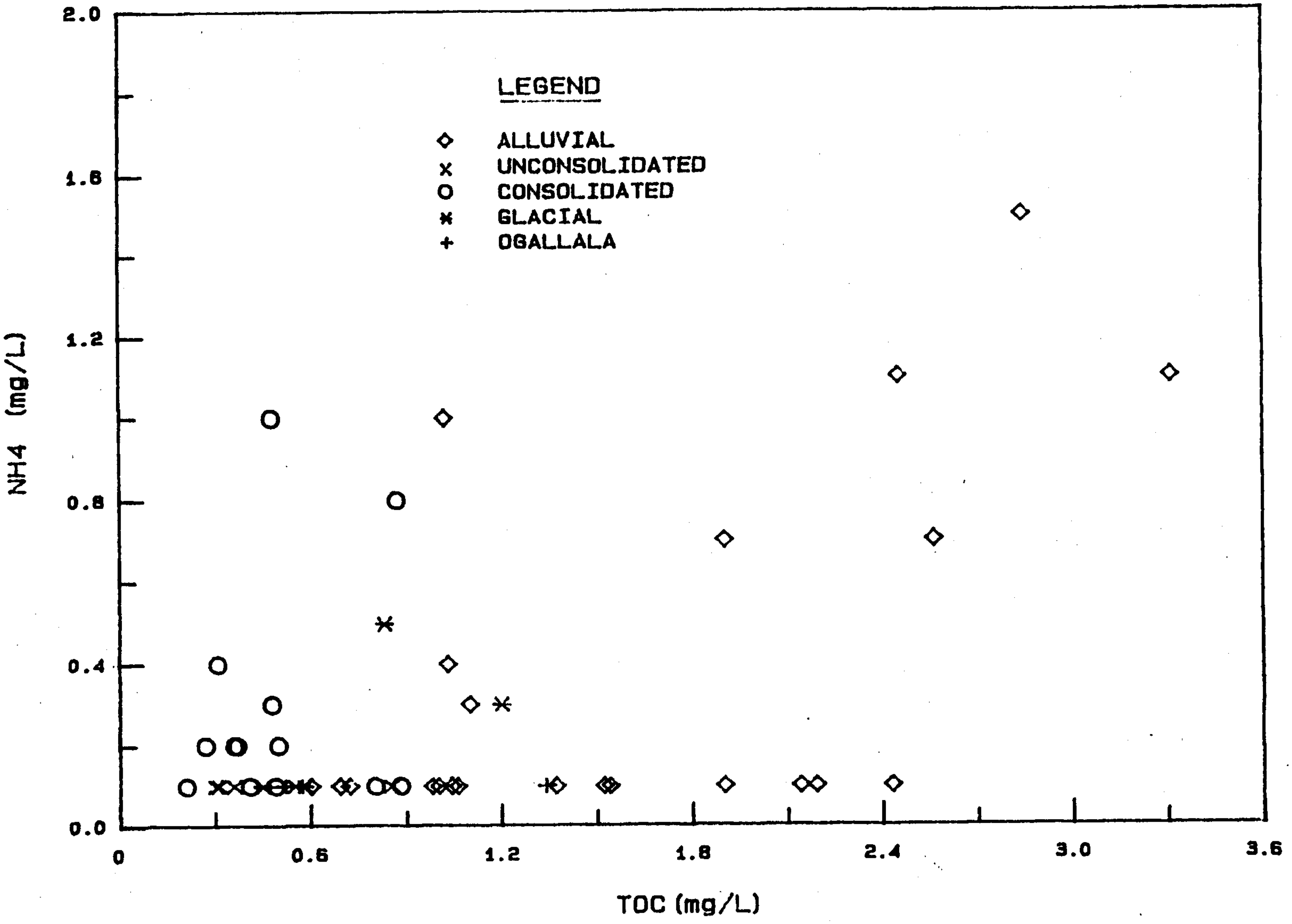

FIGURE 10. Ammonium as a Function of TOC and Aquifer Type

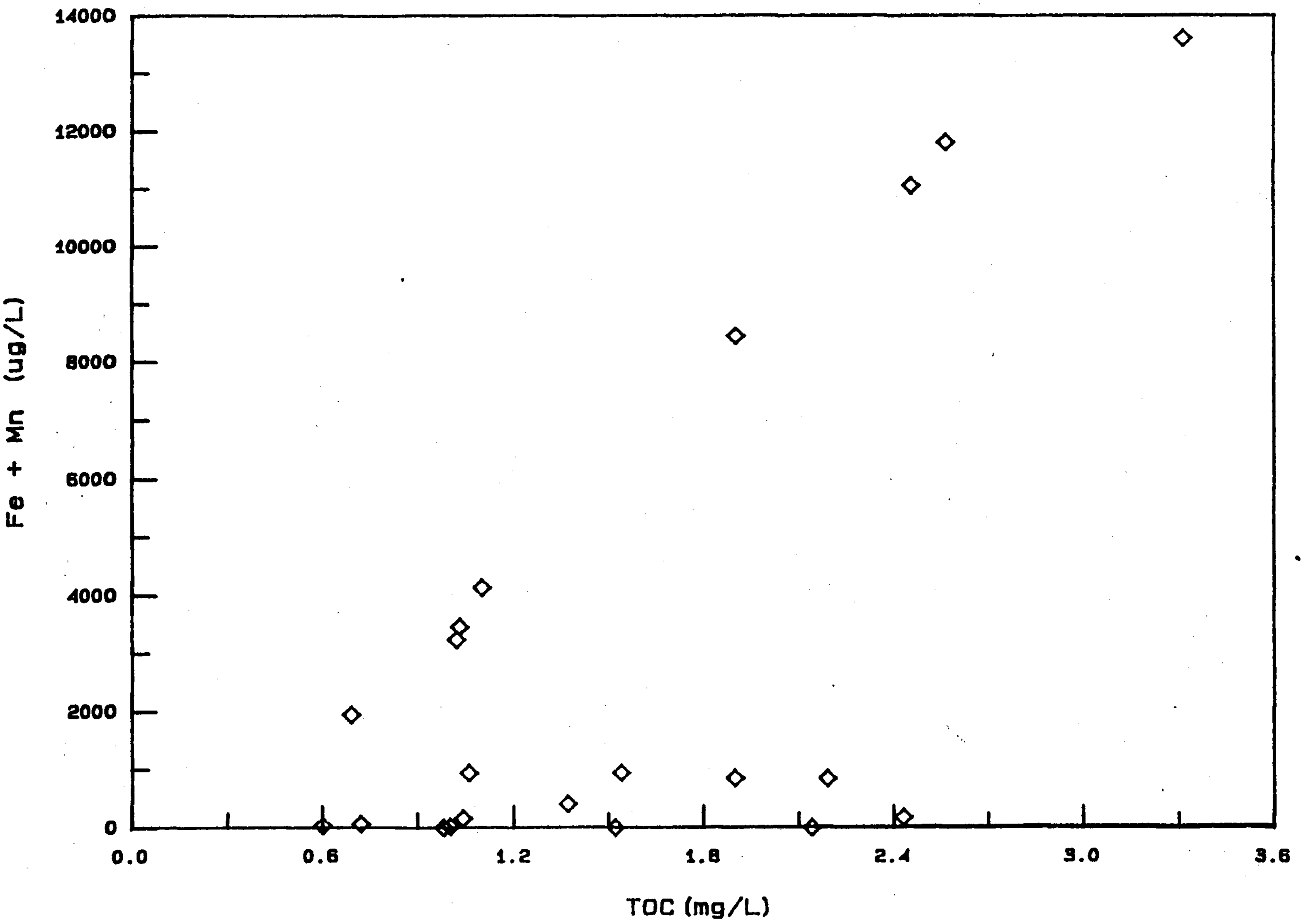

FIGURE 11. Fe + Mn as a Function of TOC for Alluvial Aquifers

0.99). Sample #20 (TOC=2.84 mg/L) is not included on this figure due to its anomalous high iron plus manganese concentration (>11,000 ug/L). Since the iron and manganese concentrations in this study were determined on unfiltered samples, the results include both particulate and dissolved species, and the form of these metals in a particular sample is not precisely known.

Organic matter has the ability to complex iron (II or III) and manganese, which causes these metals to go into solution. Humic materials can complex or chelate iron under conditions of pH and redox potentials where it would normally precipitate. Humic compounds of less than 700 molecular weight bind two to six times more than the heavier weight fractions. It is possible that the water samples from alluvial sediments with high iron and manganese concentrations had high levels of low molecular weight humic materials.

The role of bacteria might also be important in association with iron, manganese and ammonium levels, but it is not known how important bacteria are in this regard. Bacteria can grow using ammonium ion, Fe(II), and Mn(II) when oxygen is present, possibly producing TOC in the area of the well. Certain types of bacteria can oxidize dissolved ferrous iron and some species can directly reduce iron. These reducing bacteria may require organic matter as a carbon source (i.e., they may be heterotrophic).

The relationship of ammonium ion, iron and manganese to TOC is strongest in the alluvial aquifers, although some alluvial aquifers with high TOC levels do not have high iron, manganese or ammonium concentrations. Moderately high TOC levels (1.37 to 2.43 mg/L) in the Smoky Hill and Republican River alluviums were generally associated with ammonium concentrations of less than or equal to 0.1 mg/L, except sample #11 which had a concentration of 0.7 mg/L (TOC=1.90 mg/L). Figures 10 and 11 indicate that there are apparently two populations present in this study in which the relationship of iron, manganese, and ammonium ion with TOC levels differs. Closer examination of the alluvial aquifer samples revealed that they could be separated into two groups based on iron plus manganese concentrations greater than 1952 ug/L and ammonium ion concentrations greater than 0.1 mg/L. This difference is probably associated with anaerobic and oxygen-rich aquifer environments.

Sample #25, taken from the Ogallala aquifer, had a much greater TOC content than the other samples in the aquifer, but did not have a high ammonium concentration. Samples #18 and #23, from the glacial buried valley aquifers, both had TOC concentrations of 0.8 mg/L and ammonium concentrations of 0.5 and 0.8 mg/L, respectively. The occurrence of wood and other organic substances, accompanied by high ammonium ion concentrations in oxygen depleted zones of this aquifer are thought to be related to the elevated TOC levels observed in this area. In a previous investigation, Denne et al. (1984) found greater levels of ammonium ion and TOC in the glacial buried valley aquifers. These aquifers may not be homogeneous in the quality of waters which they contain.

Bicarbonate

Bicarbonate was found to be significantly correlated (r=0.564) to TOC for these groundwater samples. Bicarbonate is the dominant form of alkalinity in the water and its concentration in groundwater results principally from the dissolution of carbonate minerals in the sediment by water containing CO_2 from the air and the soil. To a lesser extent, the decay of organic matter will also cause an increase in both CO_2 and bicarbonate.

Figure 12 shows a plot of bicarbonate versus TOC. Bicarbonate concentrations ranged from 86 to 704 mg/L and were generally 200 mg/L and greater. Two Missouri River alluvium samples (#2 and #20) had the highest bicarbonate concentrations and also the highest TOC concentrations. However, the highest TOC levels in the glacial buried valley and Ogallala aquifers (see Figure 12) were accompanied by the lowest bicarbonate concentrations in these aquifers. There appears to be no causal relationship between TOC and bicarbonate, merely an association for the particular wells that were sampled (i.e., both tended to be high in waters from the alluvial aquifers).

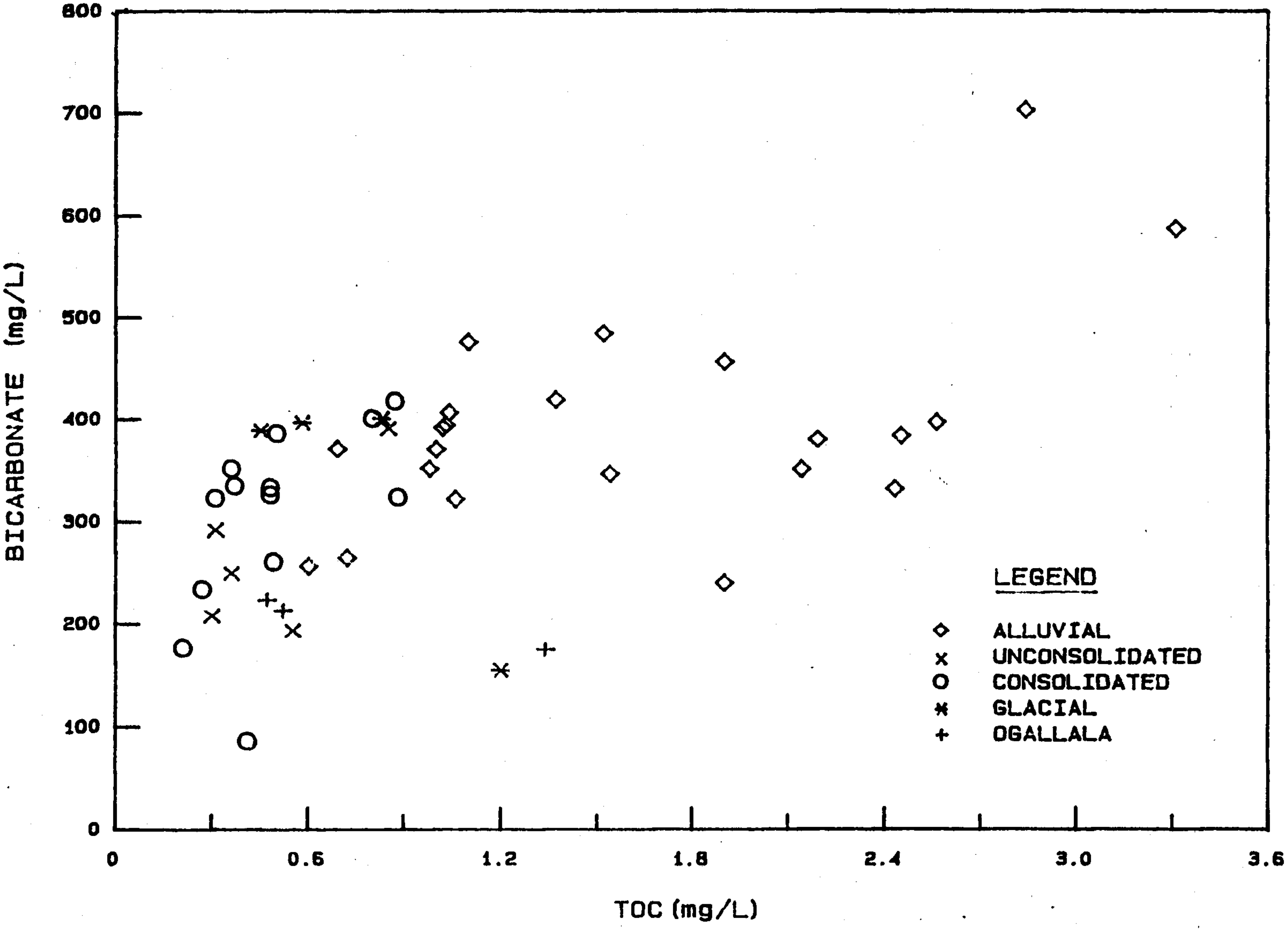

FIGURE 12. Bicarbonate as a Function of TOC and Aquifer Type

Sodium and Chloride

Sodium and chloride were not correlated with TOC. High sodium and chloride concentrations were generally coexistant. Chloride concentrations ranged from 2.2 to 853 mg/L, and there were 5 samples with values greater than 200 mg/L. Sodium concentrations ranged from 14 to 622 mg/L and 6 samples contained concentrations greater than 150 mg/L.

Elevated levels of sodium and chloride may have their origin in the dissolution of halite (NaCl) from evaporite deposits or other natural or oil field brines. In this study, high concentrations were generally associated with Permian rocks. Sodium levels can also be increased as a result of cation exchange reactions with clay minerals in which calcium and magnesium in solution displaces sodium in clay mineral structures. Areas where irrigation is prominent and evaporation is important may also increase sodium and chloride concentrations.

Potassium

Potassium concentrations ranged from 0.9 to 12.0 mg/L; and a significant relationship was found between potassium and TOC (r=0.464). This relationship might be explained by the presence of higher K concentrations in "fresher" (younger) waters affected by erosional and geochemical weathering processes. Increasing TOC levels in younger waters has been discussed (see Previous Investigations). Potassium is more readily absorbed by clay minerals of the sediments than sodium and is therefore less abundant in solution. There were 5 samples which had Na/K mass ratios greater than 70, indicating the presence of brines. Most of the samples were in the 5 to 25 Na/K mass ratio range, characteristic of aquifers close to recharge areas (Mandel and Shiftan, 1981).

Sulfate and Strontium

No relationship was found between sulfate and TOC or strontium and TOC. Sulfate concentrations ranged from 12 to 687 mg/L. Most concentrations above 100 mg/L were related to Permian age sediments and the presence of gypsum either underlying an alluvial aquifer or comprising a part of the aquifer itself. Sulfate in groundwater is derived from the solution of sulfate minerals and the oxidation of sulfide minerals.

Strontium concentrations ranged from 0.1 to 5.3 mg/L and were highly correlated with sulfate concentrations (r=0.82), indicating that the mineral source was celestite ($SrSO_4$), which is common in sediments. The highest strontium concentrations are from a Permian aquifer (sample #45) and aquifers in the Republican and Solomon River alluviums (#8 and #43) which are both underlain by Permian sediments.

Nitrate

There were 11 samples with nitrate concentrations equal to or greater than 20 mg/L, with the highest concentration being 188 mg/L (sample #47). Nitrate was not correlated with TOC, although the sample with the highest nitrate concentration had a high TOC level. Various nitrogen compounds are components of precipitation from thunder storms (traces only), are present in animal and human wastes, and are products of decay of animal and vegetable proteins. The well for sample #47 is located in an agricultural area, and the high nitrate level of the water may possibly be associated with nitrogen sources from farming activities.

Nitrate and TOC in aquifers may both originate from similar sources. In a study of nitrate levels in unconsolidated quaternary aquifers (Spruill, 1983), it was found that there was a significant relationship between nitrate levels and the depth of the well screen in relation to the water table. In other words, a shallow water table zone would be closest to the nitrate source areas, and therefore would experience higher concentrations of nitrate than deeper zones vertically removed from the nitrate sources. A similar relationship might exist in the case of TOC and the water table. Figure 13 shows a similar relationship to what was found in Spruill's study, although it includes alluvial aquifers, consolidated aquifers, and other aquifers under

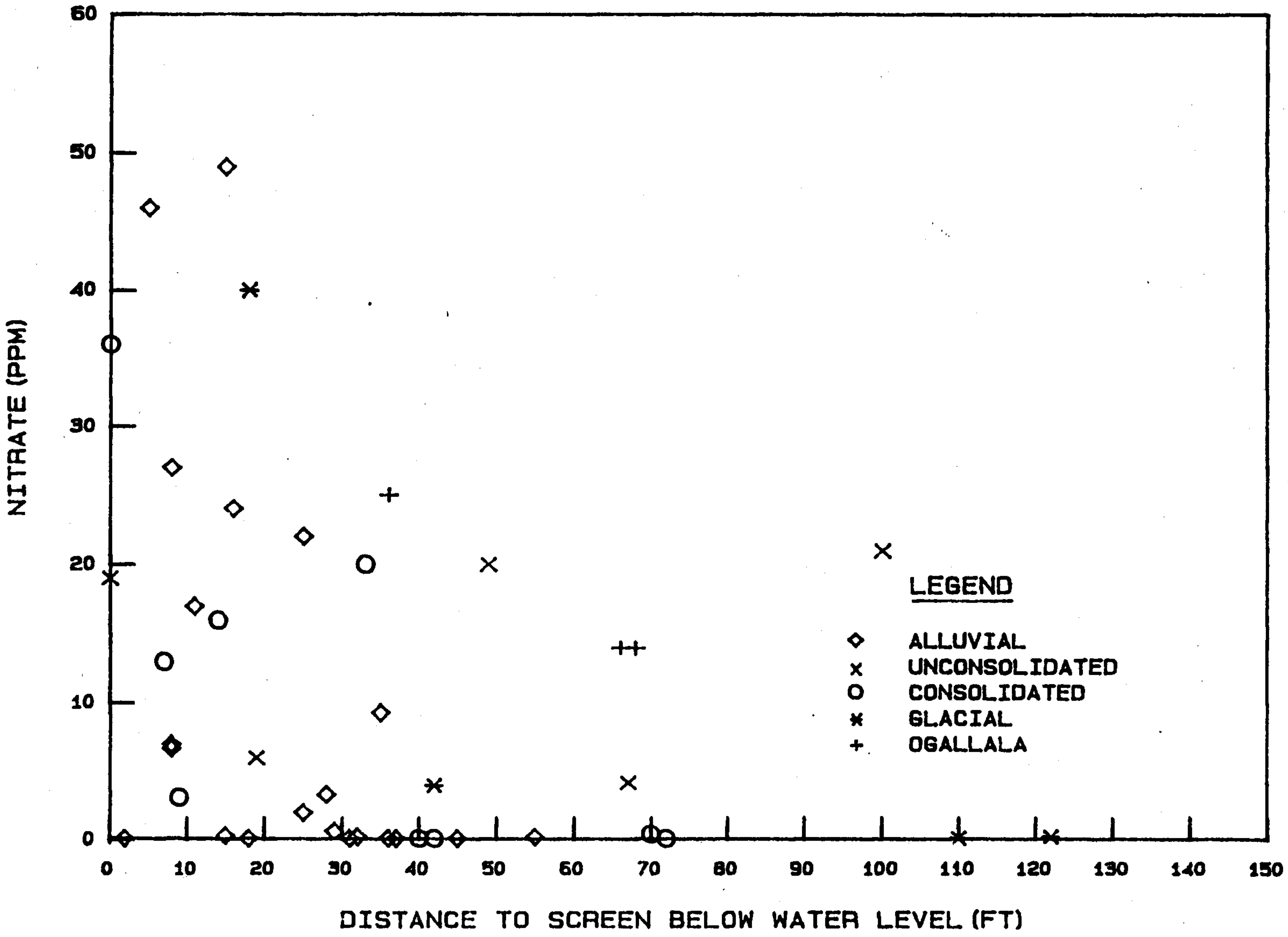

FIGURE 13. Nitrate versus Distance of Water Level Above Well Screen

confined conditions. The well of sample #47 and the Arbuckle (Cambro-Ordovician) wells are not included on this figure due to the extremely high nitrate concentration of sample #47 and the large depths of the Arbuckle wells. The depth of screen below water level in the high nitrate well (#47) was 1 foot; and the Arbuckle wells had nitrate concentrations between <0.1 and 0.4 mg/L, following the general trend of the data on Figure 13. TOC levels were also compared to the distance of the water level above the well screen (see Figure 14). All samples (12) with distance of the water level above the well screen greater than 61 feet had TOC levels equal to or less than 0.9 mg/L. However, many of the alluvial aquifers with the highest TOC levels diverge from the general trend of the data. This kind of relationship might have more significance if a particular aquifer were studied. The glacial buried valley and Ogallala aquifers on these figures have noticeable curvilinear trends.

Barium

Barium concentrations (total) ranged from 12 to 3840 ug/L. The highest values occurred in the Missouri River alluvium and in sample #49 from the Neosho River alluvium. A Permian aquifer (sample #44) had the highest value for the consolidated and unconsolidated aquifers. Barium in water has its source in sediments mainly from the mineral barite

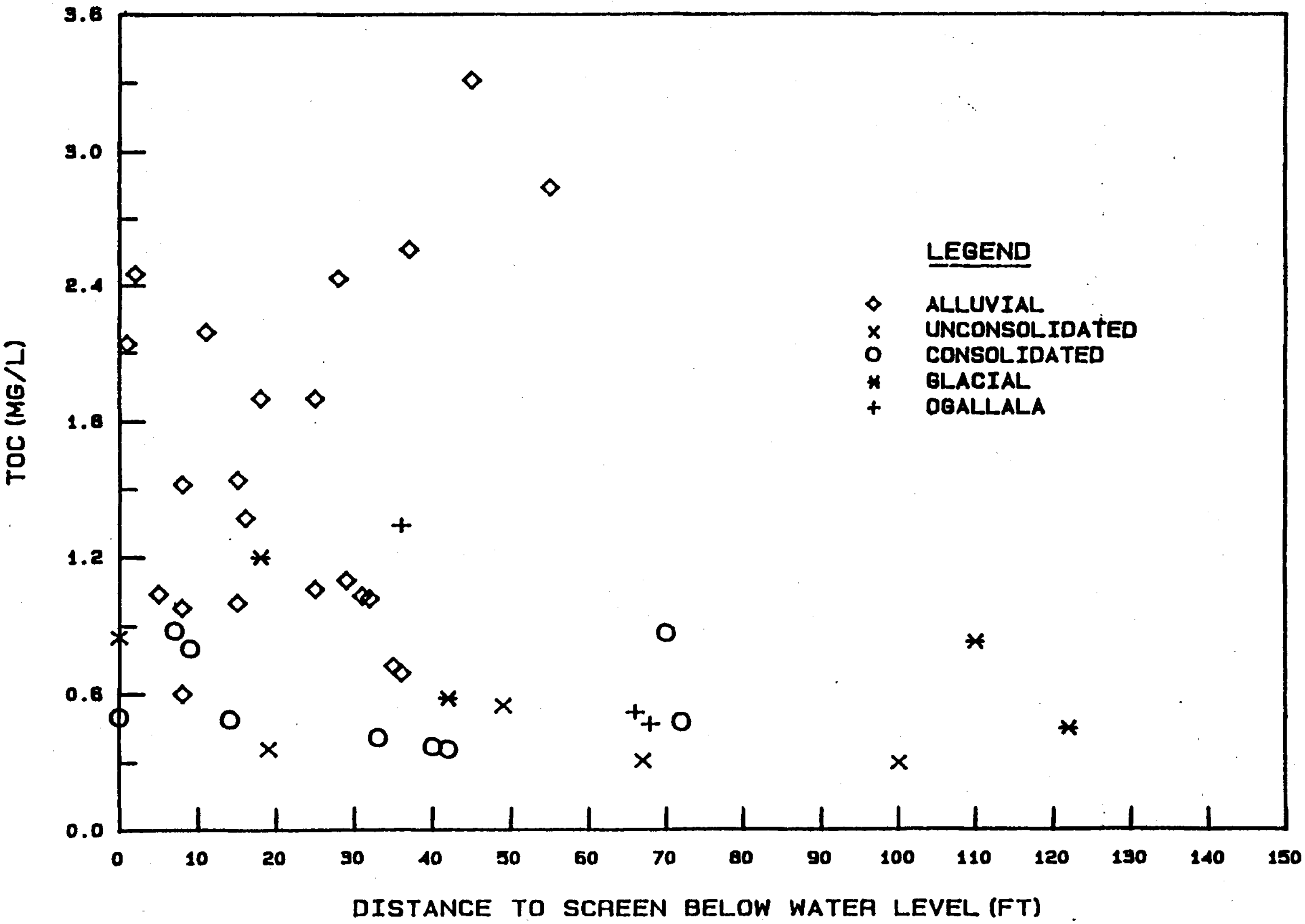

FIGURE 14. TOC versus Distance of Water Level Above Well Screen

($BaSO_4$). Another factor which influences the concentration of barium in water is adsorption by metal oxides or hydroxides. Barium was strongly correlated with TOC (r=0.519 and r=0.610 without sample #20) possibly suggesting some association with high concentrations of iron and manganese.

Hydrogen Sulfide

There was insufficient data to examine the relationship between TOC and hydrogen sulfide. Only four of the samples had detectable concentrations; three of these were from the Cambro-Ordovician aquifer system and one (#5) was from a Pennsylvanian aquifer, which locally contains the mineral pyrite. Since the occurrence of hydrogen sulfide gas is usually associated with reducing conditions in an aquifer (reduction of sulfate or dissolution of sulfide minerals) a relationship between TOC and sulfide might have been observed (as it was for other species)had more data been available.

Total Dissolved Solids and Specific Conductance

Total dissolved solids (TDS) and specific conductance were not found to relate to TOC in this study. High TDS concentrations and high specific conductance values were co-existant, and were generally related to high chloride and sodium concentrations.

Temperature and pH

Since the pH and water temperatures in this study did not vary significantly, a regression analysis was not done for TOC and these parameters. This study focused on a spring sampling period and the temperatures of the waters were generally related to the depth below land surface and the location of the aquifer. Investigations in which pH has been shown to be related to TFP have examined the pH during chlorination, which was held constant (at 8.2) in this study.

Water Type and TOC Occurrence

Water samples were assigned to water types according to their cation and anion contents in equivalents per liter. If a water sample contained 50 percent (% of a certain cation or anion out of the total amount of cations or anions in equivalents per liter) or more of a certain cation or anion, the sample was assigned to the water type of that particular cation or anion. "Mix" water types indicate that a particular cation and/or anion did not dominate these samples.

Most (27) of the samples had $CaHCO_3$ type waters, 15 of these being from alluvial aquifers (see Table 10). All of the Equus Beds aquifer samples, three glacial buried valley samples and two Pennsylvanian aquifer samples were $CaHCO_3$ type waters. Figure 15 shows a modified Piper diagram with most of the samples concentrated on the region of high HCO_3 and Ca+Mg+Sr. TOC levels ranged from 0.37 to 3.31 mg/L for $CaHCO_3$ type waters.

The five samples having Ca-Mix waters had TOC levels greater than 1.0 mg/L, ranging from 1.02 to 2.14 mg/L. Four of these samples were from alluvial aquifers and one was from the Ogallala aquifer. These waters contained elevated levels of sulfate, along with substantial amounts of HCO_3.

Samples (10) having Mix-Mix, Mix-HCO_3, $NaHCO_3$ and $CaSO_4$ water types show TOC concentrations close to or less than

TABLE 10: Classification of Samples by Water Type

$CaHCO_3$

Sample	Aquifer	TOC(mg/L)
1	A-Kansas	0.69
2	A-Missouri	3.31
3	A-Missouri	2.56
4	Pennsylvanian	0.36
6	A-Kansas	1.04
7	A-Smoky Hill	1.90
9	A-Republican	2.19
10	A-Solomon	1.03
11	A-Smoky Hill	1.90
13	Equus Beds	0.31
14	Equus Beds	0.30
15	Equus Beds	0.85
16	A-Arkansas	1.52
19	Glacial	0.45
20	A-Missouri	2.84
22	Glacial	0.58
23	Glacial	0.83
28	Big Bend	0.55
29	Dakota	0.49
31	A-Pawnee	1.00
32	A-Smoky Hill	2.43
37	Arbuckle	0.21
40	A-Solomon	0.98
42	A-Saline	1.10
44	Permian	0.50
48	Pennsylvanian	0.37
49	A-Neosho	2.45
	$CaSO_4$	
45	Permian	0.80

Ca-Mix

Sample	Aquifer	TOC(mg/L)
8	A-Republican	1.37
25	Ogallala	1.34
30	A-Walnut	1.54
43	A-Solomon	1.02
*47	A-Neosho	2.14
	Mix-Mix	
12	Dakota	0.41
27	Ogallala	0.47
39	Arbuckle	0.31
	$Mix-HCO_3$	
24	Ogallala	0.52
26	A-Cimarron	0.72
35	Permian	0.88
36	Arbuckle	0.27
50	Arbuckle	0.48
	$NaHCO_3$	
18	Dakota	0.87
	NaCl	
5	Pennsylvanian	0.48
*17	A-Arkansas	1.06
21	Glacial	1.20
33	A-Cimarron	0.60
46	Big Bend	0.36

A - designates Alluvial Aquifers
* Na/Cl(mg/L) is less than 0.65

the median concentration of 0.8 mg/L. Three of these samples were from the Arbuckle aquifer system, two were from Permian aquifers, two were from the Dakota aquifer, and two were from the Ogallala aquifer. There was only one alluvial sample (#26) which represented water of one of these types.

NaCl type waters had TOC concentrations ranging from 0.36 to 1.20 mg/L. Sample #21, from a glacial buried valley aquifer, is thought to be related to a fault system which allows upward movement of brines from underlying bedrock (Denne, 1983). The TOC concentration of this sample is probably related to the shallow depth of the well. The NaCl type water of sample #33 is associated with Permian rock, which underlies the Cimarron River alluvium in this area. Sample #5 (see Figure 15) shows geochemically evolved waters from a zone in this Pennsylvanian aquifer which has little recharge. Sample #46 was a NaCl type water accompanied by a high TDS concentration, perhaps influenced by sodic soils in this area.

Sample #17, from the Arkansas River alluvium, is probably affected by the poor quality of water in the Arkansas River in this area. This reach of the Arkansas River is reported to be seriously polluted by brines from salt plants and by other municipal and industrial wastes (Bayne, 1956). The Na/Cl ratio indicates that the high sodium and chloride levels in this sample may result from oil-gas brine contamination and not from natural halite brines. The Na-Cl ratio

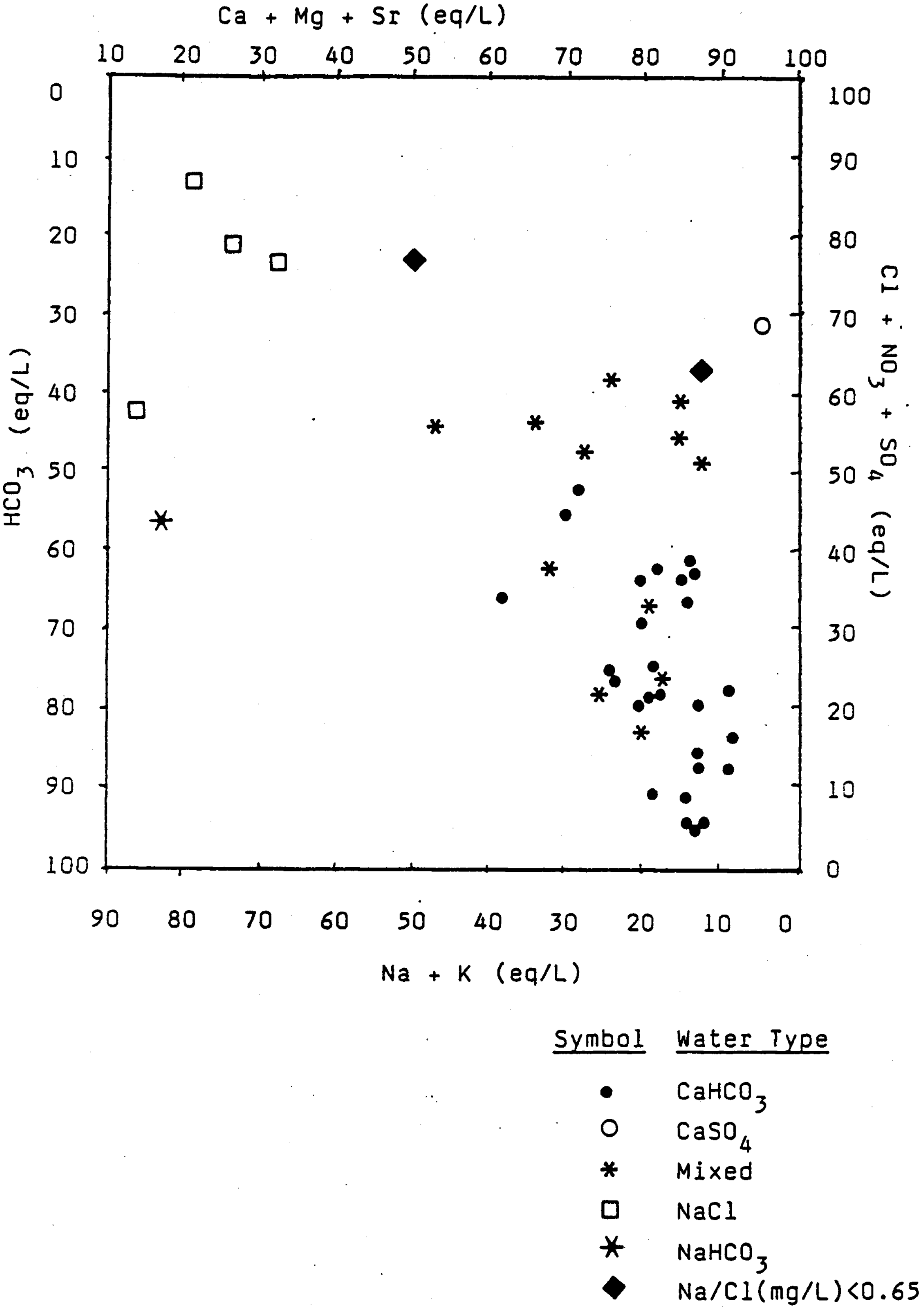

FIGURE 15: Modified Piper Diagram Showing Study Samples

of sample #47 also suggests oil-brine contamination; the elevated levels of nitrates present in the raw water and brominated THMs produced on chlorination in this sample have already been discussed. Both of these samples have TOC concentrations which are above the median for this study.

IMPLICATIONS FOR THM CONTROL IN KANSAS

The National Drinking Water Advisory Council recommended the implementation of the THM Maximum Contaminant Level (MCL) for utilities serving less than 10,000 persons should be at the discretion of the state agency having primacy because the states would be better able to evaluate potential THM problems associated with small supplies. The original MCL, set by the EPA, was based on health hazard and feasibility (related to the costs incurred by the implementation of alternative disinfection procedures). Any lowering of the THM standard would require justification by the EPA, including detailed studies showing danger to human health resulting from THMs in drinking water.

Approximately eleven percent of the study samples had TFPs greater than 100 ug/L (the present MCL for THMs). Eighty-nine percent of the samples had TFPs greater than 10 ug/L and 53 percent had TFPs greater than 25 ug/L, indicating that many water supply systems using groundwaters in Kansas might have difficulty in meeting a lower THM limit.

As discussed previously (see Discussion), the highest TFP concentrations were found in samples from the alluvial aquifers; hence it is clear that utilities using waters from alluvial sources would be the most greatly impacted by a lower THM limit. Since the state of Kansas is largely dependent on alluvial aquifers as sources for public water supplies, attention should be given to THM control and monitoring for finished waters from these aquifers.

There are four major alternatives to controlling THMs, including: 1) precursor removal; 2) use of an alternative disinfectant (eliminating the use of chlorine); 3) removal of THMs after they are formed; and 4) modification of the chlorination process to hinder the progress of the reaction (Randtke, 1984). According to Randtke (1984) and McCool (1986), the simplest and most effective means of controlling THM formation for most water treatment plants in Kansas is to modify the chlorination process and replace free chlorine with combined chlorine. In Kansas free chlorine residual of 0.2 mg/L or a combined residual of 1.0 mg/L is required throughout the finished water distribution system for disinfection purposes. Higher combined residuals are needed because combined residuals are not as strong a disinfectant as free chlorine. As discussed previously, ammonia or ammonium ion reacts with free chlorine to form combined chlorine; and combined chlorine residuals do not react with precursors to form high levels of THMs. Therefore, many surface water supplies in Kansas have begun to add ammonia to the water at the treatment plant in order to reduce THM formation (McCool, 1986). There are several other advantages (not including reduction of THMs) to using combined chlorine: 1) it is much more stable in the distribution system; 2) it can be used in higher concentrations than free chlorine, since it contributes less to taste and odor; and 3) it requires much lower dosages of chlorine for waters already containing substantial concentrations of ammonium (Randtke, 1984).

The use of combined chlorine in water supplies should be implemented with a basic knowledge of the ammonium and chlorine concentrations and how they relate to the breakpoint chlorination curve so that maximum disinfection can be achieved with minimum THM formation and a minimum of taste and odor problems. Also, any significant change in disinfection practice should be carefully monitored to insure that the microbial quality of the drinking water is not compromised.

SUMMARY AND CONCLUSIONS

The mean and median TOC concentrations obtained in this study of Kansas aquifers were 1.05 and 0.85 mg/L, respectively. The mean TFP yield was 0.242 ± 0.07 umoles/mg. Eighty-nine percent of the samples had TFPs greater than 25 ug/L, 53 percent had TFPs greater than 25 ug/L, and 10.6 percent had TFPs greater than 100 ug/L (the present MCL for THMs). Hence, utilities withdrawing water from many Kansas aquifers might have difficulty in meeting a MCL of 10 ug/L, and might have to resort to optional treatment methods (most probably the use of combined chlorine) to avoid THM formation in the event that the standard is substantially lowered.

The alluvial aquifers in general, and the Missouri, Neosho, Smoky Hill and Republican River alluvial aquifers in particular, were shown to have the highest TOC concentrations and the highest TFPs. The alluvial aquifers had a mean TOC concentration that was over twice that of the unconsolidated aquifers and four times the amount of the consolidated aquifers. The glacial buried valley and Ogallala aquifers had the highest TOC and TFP levels of the non-alluvial aquifers. The precursors in the alluvial aquifers also produced higher TFP yields.

Certain geochemical factors may be related to high TOC concentrations in groundwater. The presence of high ammonium concentrations accompanied by high iron and manganese concentrations is a warning sign for the occurrence of high organic levels in Kansas groundwaters. However, two sample populations were discernable in this study and moderately high TOC concentrations were present in a number of samples with low ammonium, iron and manganese, indicating that TOC levels are not necessarily dependent on these conditions. Hardness, bicarbonate, barium and potassium were also found to correlate with TOC, although it should be noted that the alluvial aquifers had the highest levels of all of these constituents, as well as TOC. Hence, there may not be a causal relationship between these variables and TOC.

Over half of the samples were $CaHCO_3$ type waters and over half of these came from alluvial aquifers. There were five samples of NaCl type waters and one of $CaSO_4$ type water. The analyses of two samples suggest the possibility of oil-brine contamination.

More attention should be focused on the Ogallala and glacial buried valley aquifers and their potential to produce THMs. Previous investigations of the glacial aquifers have demonstrated higher TOC levels and further study of the Ogallala aquifer might also reveal higher levels. A more detailed study could consider spatial and seasonal variations of climate, vegetation and soil as related to TOC levels, especially for the alluvial aquifers. Singer (1981) noted changes in the TOC levels of river waters across the state of North Carolina in relation to vegetation and accumulation of humic materials as the surface waters flow toward the coast. Further study of the alluvial aquifers could be conducted to provide information concerning anaerobic and oxygen-rich environments in these aquifers and how TOC levels might be related.

The results of this study indicate that a lowering of the THM standard will require that attention be given to TOC and TFP levels in public supply systems which utilize groundwaters from alluvial aquifers. These aquifers are extensively used for public water supplies in highly populated areas of northeastern Kansas and areas of central Kansas serving small and large communities. Since alluvial aquifers are able to yield larger quantities of water (and better qualities in some cases) than alternative unconsolidated or consolidated aquifers in many areas of Kansas, they will undoubtedly continue to be used as valuable water resources. In conclusion, it is evident that care should be used in the development of alluvial aquifers for public water supplies and that continuing study of the health effects of THMs and alternative water treatment methods which lower THM formation levels should be reviewed by utilities making use of alluvial aquifers in Kansas.

REFERENCES

Amy, G.L, P.A. Chadik, P.H. King, and W.J. Cooper 1984. Chlorine Utilization during Trihalomethane Formation in the Presence of Ammonia and Bromide. Environmental Science & Technology, V.18, no.9, pp. 781-786.

Barcelona, M.J. 1984. TOC Determinations in Groundwater. Groundwater, Vol.22, no.1, pp. 18-24.

Bayne, C.K. 1956. Geology and Ground-water Resources of Reno County, Kansas. Kansas Geological Survey Bulletin, pp. 120, 130.

Bayne, C.K. 1962. Geology and Ground-water Resources of Cowley County, Kansas. Kansas Geological Survey Bulletin, pp. 158, 219.

Briley, K.F., R.F. Williams, K.E. Longley and C.A. Sorber 1983. THM Production from Algal Precursors. Water Chlorination; Environmental Impact and Health Effects, Vol.3, R.L. Jolley et al., eds. Ann Arbor Science Publishers, Ann Arbor, MI., pp. 128-132.

Byrne, F.E. 1959. Geology and Construction Materials of Marion County Kansas. U. S. Geological Survey Bulletin 1060-B, pp. 63-95.

Christman, R.F., D.L. Norwood, D.S. Millington and J.D. Johnson 1983. Identity and Yields of Major Halogenated Products of Aquatic Fulvic Acid Chlorination. Environmental Science & Technology, Vol. 17, no.11, pp. 625-628.

Cooper, W.J., L.M. Meyer, C.C. Bofill and E. Cordal 1983. Quantitative Effects of Bromide on the Formation and Distribution of Trihalomethanes in Groundwater with a High Organic Content. Water Chlorination; Environmental Impact and Health Effects. Vol.3, R. L. Jolley et al., eds., Ann Arbor Publishers, Ann Arbor, MI., pp. 285-296.

Davis, J.C. 1973. Statistics and Data Analysis in Geology. John Wiley and Sons, Inc., New York, NY., 646 pp.

Denne, J.E., L.R. Hathaway and S.P. McCool 1984. Ammonium Ion, Humic Materials, and Trihalomethane Potential in Northeastern Kansas Ground Waters. Groundwater. Vol.22, no.6, pp. 755-763.

Denne, J.E. 1983. personal communication. Kansas Geological Survey, Lawrence, Ks.

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

Fader, S.W. 1974. Groundwater in the Kansas River Valley: Junction City to Kansas City, Kansas. Kansas Geological Survey Bulletin 206, part 2, 12 pp.

Federal Register, Vol.44, no.231, 1979. National Interim Primary Drinking Water Regulations; Control of Trihalomethanes in Drinking Water, pp. 68624-68642.

Fleishacker, S.J. and S.J. Randtke 1983. Formation of Organic Chlorine in Public Water Supplies. *Journal American Water Works Assoc., Vol.75*, no.3, pp. 132-138.

Gibb, J.P. and M.J. Barcelona 1984. Sampling for Organic Contaminants in Groundwater. *Journal American Water Works Assoc., Vol.76*, no.5, pp. 48-51.

Harper, F. 1984. History and Implementation of Total Organic Halogen Methodology as an Indicator of Groundwater Quality. *Groundwater Monitoring Review., Vol.4*, no.1, pp. 46-48.

Helgesen, J.O., D.G. Jorgensen, R.B. Leonard and D.C. Signor 1982. Regional Study of the Dakota Aquifer. *Groundwater., Vol.20*, no.4, pp. 410-414.

Hem, J.D. 1985. Study and Interpretation of the Chemical Characteristics of Natural Water. Third Edition, U.S. Geological Survey Water Supply Paper 2254. U.S. Government Printing Office. 263 pp.

Jolley, R.L. and J.H. Carpenter 1983. A Review of the Chemistry and Environmental Fate of Reactive Oxidant Species in Chlorinated Water. *Water Chlorination: Environmental Impact and Health Effects, Vol.4*, R.L. Jolley *et al.*, eds., Ann Arbor Science Publishers, Ann Arbor, MI., pp. 3-34.

Junk, G.A., R.F. Spalding and J.J. Richard 1980. Areal, Vertical and Temporal Differences in Ground Water Chemistry: II. Organic Constituents. Journal Environmental Quality, Vol.9, no.3, pp.479-483.

Kume J. and J.M. Spinozola 1985. Geohydrology of Sandstone Aquifers in Southwestern Kansas. Kansas Geological Survey Irrigation Series 8, 49 pp.

Lane, C.W. 1960. Geology and Groundwater Resources of Kingman County, Kansas. Kansas Geological Survey Bulletin, pp. 144, 174.

Latta, B.F. 1949. Ground-Water Conditions in the Smoky Hill Valley in Saline, Dickinson and Geary Counties, Kansas. Kansas Geological Survey Bulletin 84, 152 pp.

Leenheer, J.A., R.L. Malcolm, P.W. Mckinley and L.A. Eccles 1974. Occurrence of Dissolved Organic Carbon in Selected Ground-Water Samples in the United States. Journal Research U.S. Geological Survey., Vol.2, No.3, pp. 361-369.

Macfarlane, P.A., D. Whittemore and L.R. Hathaway 1981. A Report to the Kansas Department of Health and Environment on the Chemical Quality in the Lower Paleozoil Aquifers in Southeast Kansas and Adjoining Areas of Missouri and Oklahoma. Kansas Geological Survey Open-File Report 81-16, 68 pp.

Mandel, S. and Z.L. Shiftan 1981. Groundwater Resources. Academic Press, New York, NY., 269 pp.

McCool, S.P. 1986. Rechlorination of Combined Chlorine Residual. The Kansas Lifeline, Kansas Rural Water Association Publication, 3 pp.

McLaughlin, T.G. 1949. Geology and Ground-Water Resources of Pawnee and Edwards Counties, Kansas. Kansas Geological Survey Bulletin 80, 189 pp.

Minear, R.A. and J.C. Bird 1983. Trihalomethanes: Impact of Bromide Ion Concentration on Yield, Species distribution, rate of formation and influence of other variables. Water Chlorination: Environmental Impact and Health Effects, Vol.3, R.L. Jolley et al, eds., Ann Arbor Science Publishers, Ann Arbor, MI., pp. 151-160.

Montgomery, R.H., J.C. Loftis and J. Harris 1987. Statistical Characteristics of Ground-Water Quality Variables. Groundwater., Vol.25, no.2, pp. 176-184.

Moore, D.F. 1940. Ground-Water Resources of Kansas. Kansas Geological Survey Bulletin 27, 112 pp.

O'Connor, H.G. 1960. Geology and Ground-Water Resources of Douglas County, Kansas. Kansas Geological Survey Bulletin 148, 200 pp.

O'Connor, H.G. and P.K. Chaffee 1983. Time-Series Water-Quality Sampling: A Tool for Determining Aquifer-Baseline Quality, Contaminant Sources and Remedial Policies. Kansas Geological Survey Open-File Report 85-12, 51 pp.

O'Connor, H.G. 1987. personal communication. Kansas Geological Survey, Lawrence, KS.

Oliver, B.G. 1983. Effect of Temperature, pH and Bromide Concentration on the Trihalomethane Reaction of Chlorine with Aquatic Humic Material. Water Chlorination: Environmental Impact and Health Effects, Vol.3, R.L. Jolley et al., eds., Ann Arbor Science Publishers, Ann Arbor, MI., pp. 141-149.

Oliver, B.G. and E.M. Thurman 1984. Influence of Aquatic Humic Substance Properties on THM Potential. Water Chlorination: Environmental Impact and Health Effects, Vol.4, Book 1, R.L. Jolley et al., eds., Ann Arbor Science Publishers, Ann Arbor, MI., pp. 231-238.

Pettyjohn, W.A. and A.W. Hounslow 1983. Organic Compounds and Groundwater Pollution. Groundwater Monitoring Review, Vol.3, no.4, pp. 41-47.

Prescott, G.C., Jr., J.R. Branch and W.W. Wilson 1954. Geology and Ground-Water Resources of Wichita and Greeley Counties, Kansas. Kansas Geological Survey Bulletin 108, 133 pp.

Randtke, S.J. 1984. Treatment Alternatives for Controlling Trihalomethanes. Transactions of the 34th Annual Sanitary Engineering Conference, University of Kansas, p. 27.

Randtke, S.J. 1986. Laboratory report and personal communication. University of Kansas, Lawrence, KS.

Randtke, S.J., F. de Noyelles, Jr. and C.E. Burkhead 1987. Trihalomethane Precursors in Kansas Lakes: Sources and Control: Report of Year 1 Results. The Kansas Water Resources Research Institute, University of Kansas, Lawrence, KS., p. 34.

Rook, J.J. 1974. Formation of Haloforms During Chlorination of Natural Waters. Water Treatment and Examination, Vol.23, pp. 234-243.

Rook, J. J. 1976. Haloforms in Drinking Water. Journal American Water Works Association, Vol.68, No.3, pp. 168-172.

Schnoor, J.L., J.L. Nitzshcke, R.D. Lucas and J.N. Veenstra 1979. Trihalomethane Yields as a Function of Precursor Molecular Weight. Environmental Science & Technology, Vol.13, no.9, pp. 1134-1138.

Spruill, T. B. 1983. Relationship of Nitrate Concentrations to Distance of Well Screen Openings Below Casing Water Levels. Water Resources Bulletin, Vol. 19, No. 6, pp. 977-981.

Standard Methods for the Examination of Water and Wastewater, 16th edition, 1985. American Public Health Association (APHA), Water Pollution Control Federation (WPCF) and American Water Works Association (AWWA), eds., APHA pub., Washington, D.C..

Steeples, D.W. and R. Buchanan 1983. Kansas Geomaps. Kansas Geological Survey, Educational Series 4, 30 pp.

Symons, J.M., T.A. Bellar, J.K. Carswell, J. DeMarco, K.L. Kropp, G.G. Robeck, D.R. Seeger, C.J. Slocum, B.L. Smith and A.A. Stevens 1975. National Organics Reconnaissance Survey for Halogenated Organics. Journal American Water Works Assoc., Vol.67, No.11, pp. 634-647.

Veenstra, J.N. and J.L. Schnoor 1983. Seasonal Patterns and Molecular Weight Variations of THM Precursors in the Iowa River. Water Chlorination: Environmental Impact and Health Effects, Vol.3, R.L. Jolley et al., eds., Ann Arbor Science Publishers, Ann Arbor, MI., pp. 115-127.

Ward, J.R. 1975. Geohydrology of Nemaha County Northeastern Kansas. Kansas Geological Survey, Groundwater Series 2, 19 pp.

Westrick, J.J., J.W. Mello and R.F. Thomas 1984. The Groundwater Supply Survey. Journal American Water Works Association, Vol.76, no.5, pp. 52-59.