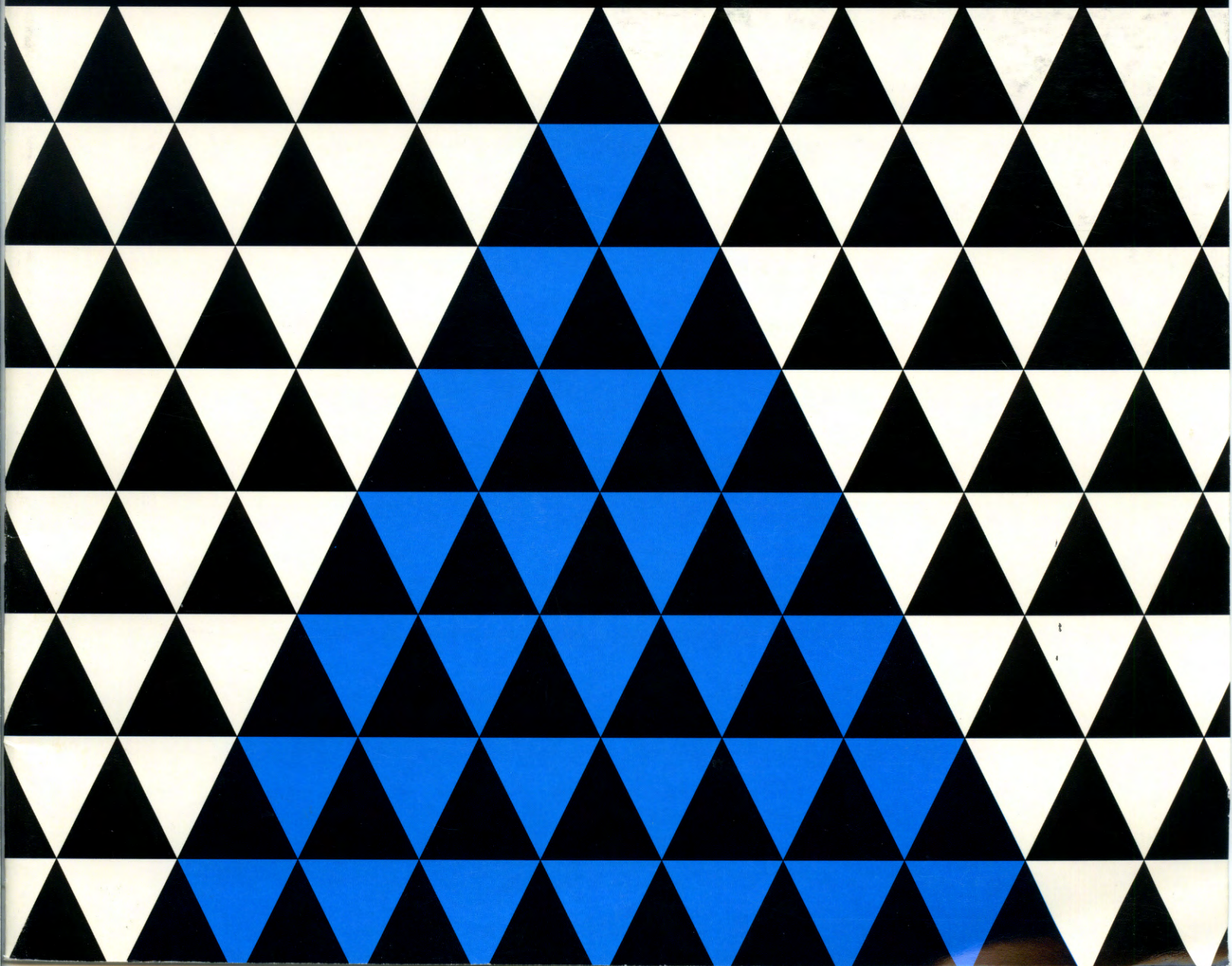


A survey of organic carbon
and trihalomethane formation potential
in Kansas ground waters

*Rachel E. Miller, Stephen J. Randtke,
Lawrence R. Hathaway, and Jane E. Denne*

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by

Rachel E. Miller,¹
Stephen J. Randtke,²
Lawrence R. Hathaway,³
and
Jane E. Denne⁴

¹Graduate Research Assistant, Kansas Geological Survey;
now with the Kansas Department of Health and Environment

²Professor of Civil Engineering, The University of Kansas

³Senior Scientist, Kansas Geological Survey

⁴Research Associate, Kansas Geological Survey; now with the
U.S. Environmental Protection Agency

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Executive summary

Drinking-water standards promulgated by the U.S. Environmental Protection Agency (EPA) underscore the importance of detailed water-quality data for sources used in conjunction with public water supplies. It has been recognized that reaction of the chlorine (used as a disinfectant) with organic matter present in surface waters can lead to formation of trihalomethanes (THMs) in concentrations which may exceed the 100 $\mu\text{g/L}$ maximum contaminant level (MCL) established by the EPA. However, relatively little consideration has been given to ground-water sources with regard to the organic carbon content of the waters, the potential for THM formation, or the presence of ammonium ion (NH_4^+), which both consumes chlorine and serves to reduce THM formation. The successful operation of water-treatment plants for public supplies is dependent upon many factors, such as operator skill and the condition of the equipment, but of similar importance is a detailed knowledge of water quality for the sources being employed.

A survey of Kansas ground waters to determine their concentrations of total organic carbon (TOC) and trihalomethane-formation potential (TFP) was conducted in the spring of 1986. Wells were carefully selected, based on well logs made during construction, to represent particular geologic intervals. Thirty-four samples were collected from public water supply wells and 16 samples were collected from private water wells. Samples from 11 alluvial aquifers, four unconsolidated aquifers in Quaternary and Tertiary formations, and four consolidated aquifers in Cretaceous, Permian, Pennsylvanian, and Cambrian–Ordovician rocks were taken.

The mean and median TOC concentrations were 1.03 ± 0.76 and 0.84 mg/L , while the mean and median TFP concentrations were 46.7 ± 39.5 and $30.6 \text{ } \mu\text{g/L}$, respectively. The mean TFP yield was $0.242 \pm 0.07 \text{ } \mu\text{mol}$ per mg of TOC, and the TFP concentration in micromoles per liter was very strongly correlated ($r = 0.953$) with TOC. Only 8% of the samples had a TFP concentration exceeding the present MCL for THMs of 100 $\mu\text{g/L}$, but 56% exceeded 25 $\mu\text{g/L}$ and 90% exceeded 10 $\mu\text{g/L}$, suggesting that many Kansas water-supply systems using ground water might have difficulty meeting a substantially lower THM standard.

The average instantaneous THM (ITHM) concentration was only 6.95 $\mu\text{g/L}$, while the average terminal (TTHM) concentration was 35.6 $\mu\text{g/L}$. Hence, only a small fraction of the THM concentration to which consumers might be exposed is formed prior to distribution. For the 21 TTHM samples having a free chlorine residual at the end of the incubation period, TTHM was strongly correlated with both TOC ($r = 0.819$) and TFP ($r = 0.926$), suggesting that either of these might be a good surrogate measure for TTHM.

TOC (and TFP) appeared to be unrelated to aquifer (well screen) depth, but both were clearly much higher in the alluvial aquifers, all of which were located at relatively shallow depths. TOC also appeared to be unrelated to the inorganic constituents present in the samples, with the exception of a subset of samples from alluvial aquifers having high concentrations of NH_4^+ ($>0.1 \text{ mg/L}$) and Fe + Mn ($>1.0 \text{ mg/L}$). For these samples, TOC was strongly correlated with both NH_4^+ ($r = 0.676$) and Fe + Mn ($r = 0.991$). These relationships merit further investigation, since all of the constituents involved pose problems for water-treatment plants.

In Kansas, efforts to control THMs in public water supplies from ground-water sources should focus primarily on alluvial aquifers, especially those having high concentrations of TOC, NH_4^+ , Fe, and Mn. TOC and TFP may be useful surrogates for TTHM and could be used as a basis for exemptions from monitoring requirements. Use of combined chlorine appears to be the simplest and most effective means of limiting THM formation, but the necessary precautions must be taken to ensure that the microbial quality of the drinking-water supply is not compromised.

Introduction

Reasons for investigating TOC and THM formation potential in Kansas ground waters

Since the discovery of trihalomethanes (THMs) in drinking water by Rook (1974), concern has existed over the presence and possible carcinogenicity of these compounds in public water supplies. THMs are 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). These and other halogenated byproducts 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 ($\mu\text{g/L}$) for public water supplies serving over 10,000 persons (Federal Register, 1979). Consideration is presently being given to lowering of the standard, perhaps to as low as 10 $\mu\text{g/L}$, in the future; new standards for a variety of disinfection byproducts are due to be released in the near future.

Although much attention has been given to the control of THMs in surface-water supplies, ground waters in most areas of the United States, including Kansas, have not been extensively studied in this respect. Surface waters, including rivers and lakes, generally contain more organic matter than ground waters, and are therefore more likely to produce high THM concentrations. However, certain ground-water sources have been found to produce THM concentrations above the maximum contaminant level (MCL) of 100 $\mu\text{g/L}$ (Symons et al., 1975). The successful operation of water-treatment plants for public supplies is dependent upon many factors, such as operator skill and the condition of the equipment, but of similar importance is a detailed knowledge of water quality for the sources being employed. Ground waters also may contain significant concentrations of ammonium (NH_4^+), sulfide, iron (Fe), and manganese (Mn), all of which interfere with the production of a free chlorine residual. Ammonium also can be beneficial because it reacts with chlorine to form monochloramine. In sufficient concentrations, monochloramine is an adequate disinfectant for most ground-water supplies, but it does not form THMs and it greatly reduces formation of other halogenated byproducts.

Research objectives

Because the total organic carbon (TOC) concentrations in uncontaminated Kansas ground waters were largely unknown and because the potential for Kansas

ground waters to form THMs had not been systematically investigated, the major goal of this study was to provide and to evaluate this information. Other objectives of the study were 1) to statistically examine the geological and geochemical characteristics of Kansas aquifers in relation to TOC concentrations and THM formation potential (TFP) 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 lower THM standard.

Related research

Formation of THMs and other halogenated byproducts

In his 1974 study, Rook found a good correlation between THM formation and color. The coloration in the surface waters he studied was due to naturally occurring humic substances (humic and fulvic acids). Rook proceeded to prove that humic substances could be precursors by injecting peat into water samples, chlorinating them, and obtaining positive results upon analysis for THMs. Since that time many investigators have examined the factors influencing the formation of THMs and other halogenated byproducts, including temperature, pH, ammonium, bromide, and the concentrations of chlorine and precursor material (TOC).

The rate and extent of THM formation are generally found to increase with increasing temperature, pH, TOC, chlorine, and bromide. The same is true for other halogenated byproducts except that most increase with a decrease in pH. Monochloramine, formed by the reaction of chlorine with ammonium, does not form THMs at low dosages under laboratory conditions; however, small amounts of THMs are likely to be formed upon chlorination of treated-water supplies because of the manner in which the chlorine is added. THM concentrations also can be reduced by avoiding prechlorination, avoiding higher concentrations of chlorine than are necessary for good disinfection, and removing precursor materials prior to chlorination. For more detailed information, the reader may consult Symons et al. (1975, 1981), Randtke (1984), Amy et al. (1984), and numerous other published works on this subject.

THM precursors and TOC in ground waters

Leenheer et al. (1974) examined the concentration of naturally occurring dissolved organic carbon (DOC) at 100 uncontaminated sites dispersed over 27 states. A variety of aquifer materials were represented, including Pleisto-

cene deposits (sand and gravel), Cretaceous rock, Mississippian rock (sandstone), river alluvium, limestone, crystalline rock, dolomite, and basalt. DOC values ranged from < 0.1 to 15.0 mg/L; the median value was 0.7 mg/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. DOC concentrations appeared to be related to those of the source water. For example, a site in Miami, Florida, apparently received its high DOC concentrations from infiltration of surface waters high in DOC. Increasing DOC was directly correlated with increasing specific conductance and alkalinity; however, no correlation was found with pH and well depth.

In the National Organics Reconnaissance Survey for Halogenated Organics (NORS), water samples were collected from 80 public water supplies and analyzed for TOC and six organic chemicals, including the four principal THMs (Symons et al., 1975). The waters sampled included ground waters, lakes, streams, and reservoirs. THM formation was found to be strongly correlated with TOC, which ranged from < 0.05 to 12.2 mg/L, with a median of 1.5 mg/L. Raw-water samples were classified into six divisions according to TOC concentration. The 16 ground-water sources sampled were found to have a lower average THM concentration than surface-water sources except in the upper division (TOC > 5 mg/L). This reflected the average TOC concentrations from the different sources: 1.85 ± 2.79 mg/L for the 16 ground-water samples, 3.33 ± 2.02 mg/L for the 26 lake and reservoir samples, and 3.98 ± 3.23 mg/L for the 39 river samples. River-water sources had the highest average THM concentration in four of the six divisions. Twenty-four of 39 river-water samples were in the upper three divisions (TOC > 3 µg/L), compared to only three of 16 ground waters and 10 of 25 impounded waters. TOC concentrations were not correlated with UV absorption or fluorescence.

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 ground-water regimes. Ground-water 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 ground water 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. In 34 of 35 cases, DOC concentrations decreased with depth. River DOC concentrations were higher than those of the adjacent ground water regardless of season. DOC levels in ground waters were highest in September and levels in river waters were highest in April.

Junk et al. (1980) concluded that the most probable mechanism of DOC removal with increasing depth was 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 ground water.

Oliver and Thurman (1984) studied the TFP associated with the fulvic- and humic-acid fractions of various aquatic humic materials. They found that, in general, ground-water fulvic acids had the lowest TFPs, with surface-water fulvic acids having greater TFPs, and marsh/bog fulvic acids having the largest TFPs. Since ground water 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. In comparing fulvic acids with humic acids, they found that 18–52% more THMs were produced by humic acids from the same source. 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. They also found a strong correlation between color and TFP.

In 1981 and 1982, the EPA conducted a survey of public ground-water supplies with 466 randomly selected and 479 selected by State agencies (Westrick et al., 1984). 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; however, this was probably due to a higher percentage of the larger systems chlorinating their water. Median values of the individual THMs were generally low, ranging from 1.2 to 5.1 µg/L, but the maximum values were 430 µg/L for chloroform, 110 µg/L for bromodichloromethane, 63 µg/L for dibromochloromethane, 4.2 µg/L for dichloriodomethane, and 110 µg/L for bromoform. Chloroform and bromodichloromethane had their highest median and maximum concentrations in the state-selected sites serving more than 10,000 persons.

In January of 1984, seven wells were sampled in a glacial buried-valley aquifer system in northeastern Kansas (Denne et al., 1984). The TOC levels ranged from 0.9 to 2.4 mg/L with a mean concentration of 1.4 mg/L. Two of the samples were found to have THM levels of 81 and 61 µg/L when quenched seven days after collection. In another study of the same glacial buried valley system, Denne et al. (1987) found an average DOC of 2.65 mg/L and an average TFP of 123 µg/L. DOC decreased with depth to the tan/gray contact (where the color of the sediments changed from tan to gray), but increased with depth below the tan/gray contact. DOC and TFP were strongly correlated with Fe, Mn, and NH_4^+ .

O'Conner and Chaffee (1985) investigated areas in Kansas where poor well construction, poor well-plugging procedures, and high well densities might affect water quality and TOC levels. Time-series sampling of 10 wells in the Lincolnville area of Marion County, Kansas, was conducted over a 1-yr period. The wells were screened in Permian-age aquifer units, 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 were 3.04 and 3.26 mg/L for the two sampling periods.

ACKNOWLEDGMENTS—Anne Melia assisted extensively in the analysis of samples for TOC and THM formation

potential. Information helpful in contacting public water utilities was obtained from the Kansas Department of Health and Environment. Peter A. Macfarlane generously helped to supply well logs and to collect samples from the Cambrian–

Ordovician aquifers. The use of Kansas Geological Survey (KGS) vehicles for sample collection, KGS monies for travel, and a General Research Fund Allocation (3070–XX–0038) from the University of Kansas made this study possible.

Sampling-site selection

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). 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 working file because there were no recent water-well records (1974–present) for this aquifer in the main well-log file. Because of the great depths (and accompanying high construction costs) of these wells, few have been drilled in recent years. 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 well-construction methods and materials. Each well was chosen to reflect a particular geologic interval or aquifer. The screened interval was examined to

TABLE 1—SAMPLING SITES, AQUIFERS, AND WELL CONSTRUCTION.

No.	County	Legal Location	Geologic Source	Well Type ¹	Casing Material ²	Total Depth (ft)	Grouted Interval (ft)	Screened Interval ³ (ft)	Screened Material ⁴	Water Level (ft)	Est. Yield gpm
1	Douglas	12S20E17ABA	Kansas R. Alluv.	PWS	STL	78	0-20	58-78	MCS,GR,B	22	350
2	Buchanan (MO)	55N37W19CCA (in MO)	Missouri R. Alluv.	IND	STL	80		60-80	MCS,GR		
3	Leavenworth	9S23E08DAA	Missouri R. Alluv.	PWS	STL	69	0-20	49-69	CMS,GR	13	2000
4	Franklin	18S18E06ACC	Pennsylv. Tonganoxie	PWS	PLAS	210	3-51	141-200	SS	99	19
5	Douglas	14S17E36DDD	Pennsylv. Tonganoxie	PWS	STL	500	0-420	OH420-500	SS,SH	348	30
6	Pottawatomie	10S12E15ABB	Kansas R. Alluv.	PWS	PLAS	47	0-20	26-47	MCGR	21	1200
7	Geary	11S05E35B	Republican R. Alluv.	PWS	STL	65	0-20	42-62	MCS,GR	17	1500
8	Clay	8S03E07BAA	Republican R. Alluv.	PWS	STL	55	0-20	38-53	CS,GR,FS	22	700
9	Republic	3S04W17DAD	Republican R. Alluv.	PWS	AS-CE	42	0-20	29-42	GR	18	400
10	Ottawa	11S04W01CBB	Solomon R. Alluv.	PR	PLAS	59	3-13	56-59	FCS,GR	25	50
11	Saline	16S03W25DAB	Smoky Hill R. Alluv.	PWS	STL	53	5-25	43-53	MCS	25	90
12	Marion	18S01E33DDD	Cretaceous Dakota	PWS	STL	68	5-20	58-68	FMSS	25	125
13	McPherson	20S04W01DDD	Equus Beds	PWS	STL	215	0-20	138-178 194-204	MCS,GR MCS,GR	71	2500
14	Harvey	24S01W06CBC	Equus Beds	PWS	STL	150	1-20	123-148	FCS	23	600
15	Sedgwick	28S03W01DDD	Equus Beds	PR	PLAS	45	3-14	35-45	MCS	25	
16	Cowley	35S04E01AA	Arkansas R. Alluv.	PWS	STL	30	0-12	18-30	MCS	10	300
17	Reno	22S07W10CAA	Arkansas R. Alluv.	PWS	STL	53	0-20	38-53	MCS,GR	13	800
18	Washington	1S01E07AAA	Cretaceous Dakota	PWS	PLAS	285	0-20	265-285	SS	195	100

TABLE 1 (continued)—SAMPLING SITES, AQUIFERS, AND WELL CONSTRUCTION.

No.	County	Legal Location	Geologic Source	Well Type ¹	Casing Material ²	Total Depth (ft)	Grouted Interval (ft)	Screened Interval ³ (ft)	Screened Material ⁴	Water Level (ft)	Est. Yield gpm
19	Marshall	4S10E17AB	Glacial	PR	PLAS	185	0-20	175-185	GR,SH	53	90
20	Doniphan	1S19E09DBD	Missouri R. Alluv.	PWS	PLAS	73	4-22	68-72	S,GR,B	13	75
21	Brown	3S16E01DAC	Glacial	PR	PLAS	58	0-10	38-58	S,GR,SH	20	15
22	Jackson	6S16E21BCB	Glacial	PR	PLAS	145	0-10	132-142	CS,MGR	90	50
23	Atchison	6S18E27DAD	Glacial	PR	PLAS	200	0-15	190-200	CS,FGR	80	100
24	Thomas	8S34W12DBA	Ogallala	PWS	STL	261	0-20	200-220 225-235 241-261	FS,MGR S,GR FS,GR	134	
25	Wichita	18S37W14DD	Ogallala	PWS	STL	172	0-20	154-172	MCS,GR,CL	118	260
26	Seward	32S33W27ABC	Cimarron R. Alluv.	PR	PLAS	100	0-10	60-100	MCS	25	50
27	Haskell	30S34W13DAB	Ogallala	PWS	STL	430	0-20	329-379 401-426	FMCS,GR FMCS	261	2000
28	Edwards	24S16W2ODD	Big Bend	PWS	PLAS	100	0-20	70-100	S,GR,CL	21	500
29	Rush	18S17W03BCC	Cretaceous Dakota	PWS	PLAS	100	5-25	60-100	SS,LS	46	50
30	Rush	18S17W22DA	Walnut Ck Alluv.	PWS	STL	58	0-20	48-58	S,GR	33	200
31	Ness	20S23W24ADD	Pawnee R. Alluv.	PR	PLAS	65	4-15	55-65	S,SH	41	80
32	Ellis	15S18W30D	Smoky Hill R. Alluv.	PWS	PLAS	47	0-20	37-47	FMS,GR,CGR	9	300
33	Meade	35S29W13BBC	Cimarron R. Alluv.	PR	PLAS	42	0-10	36-42	MS	7	25
34	Meade	35S29W10CCB	Pleist.?	PR			(no log)				
35	Kingman	30S08W05ABD	Permian Harper Silts	PR	PLAS	74	5-15	62-74	SH	55	15
36	Cherokee	33S25E18DAA	Cam-Ord	PWS	STL	900		OH575-900		145	
37	Cherokee	34S25E13CCC	Cam-Ord	PWS	STL	1260		OH514-1260			
38	Crawford	30S25E28DDA	Cam-Ord	PWS	STL	1050	0-550	OH550-1050		217	
39	Crawford	30S24E02DDD	Cam-Ord	PWS	STL	1113	0-723	OH723-1113		274	1000
40	Osborne	6S11W28ACD	Solomon R. Alluv.	PWS	PLAS	68	0-34	42-68	S	34	800
41	Lincoln	12S06W15ABD	Saline R. Alluv.	PWS			(no log)				
42	Lincoln	12S06W15BCD	Saline R. Alluv.	PWS	PLAS	55	0-22	47-55	CS,GR,SH	18	200
43	Dickinson	13S03E17AB	Smoky Hill R. Alluv.	PWS	STL	58	7-20	43-58	MCS,GR	11	2000
44	Marion	17S04E12CCC	Permian Nolans	PR	PLAS	93	0-10	65-93	LS,SH	65	55
45	Marion	22S03E04AAB	Permian Wellington	PWS	PLAS	60	0-20	23-53	LS,SH	14	100
46	Reno	24S09W16ACB	Big Bend	PR	PLAS	72	0-10	52-72	CL,S,GR	33	
47	Lyon	19S13E29CCC	Neosho R. Alluv.	PR	PLAS	29	4-10	11-29	CL,SLT, GR,SH	10	25
48	Leavenworth	12S20E15ADA	Pennsylv. Tonganoxie	PR	PLAS	160	0-10	120-160	SS	80	50
49	Labette	31S21E16BDD	Neosho R. Alluv.	PWS	STL	33	0-20	26-31	MCS,GR	24	20
50	Crawford	30S25E28DDA	Cam-Ord	PWS	STL	1050	0-550	OH550-1050		217	2250

¹ PWS = Public Water Supply; PR = Private; IND = Industrial² PLAS = Plastic; STL = Steel; AS-CE = Asbestos-Cement³ OH = Open Hole⁴ B = Boulders; C = Coarse; CL = Clay; F = Fine; GR = Gravel; LS = Limestone; M = Medium; S = Sand; SH = Shale; SLT = Silt; SS = Sandstone

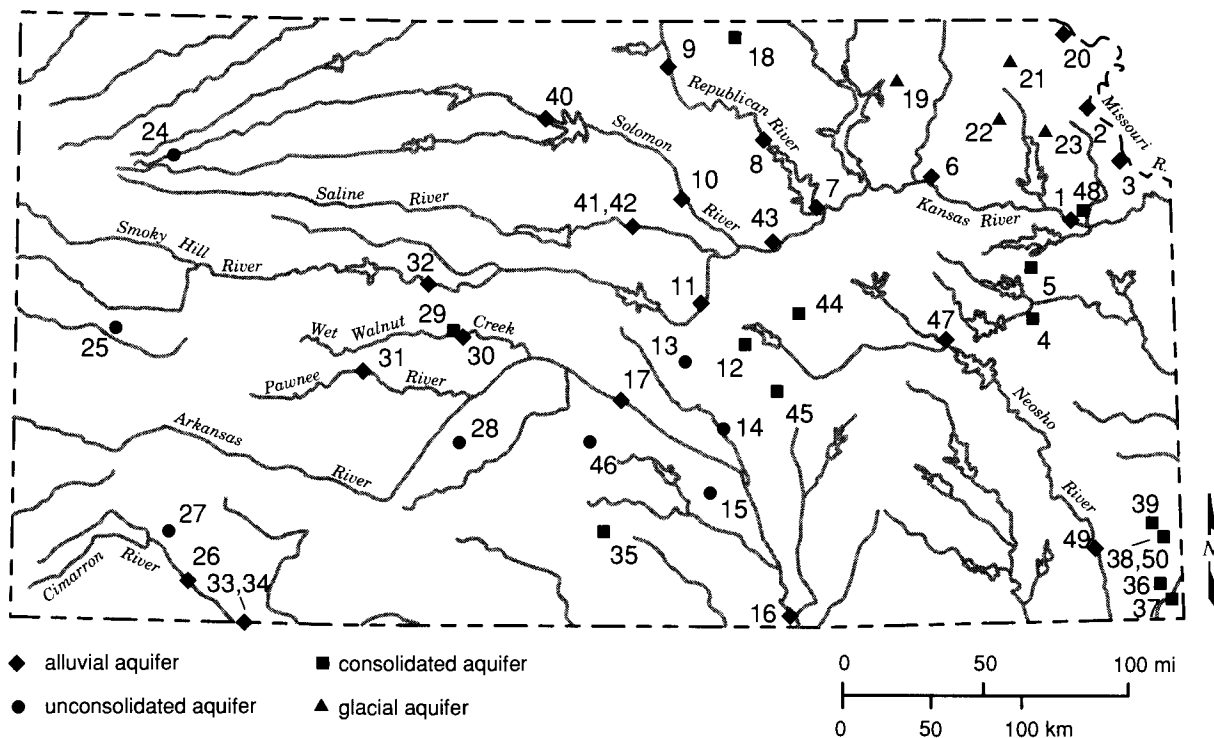


FIGURE 1—SAMPLING SITE LOCATIONS (see table 1 for well descriptions; base map from Steeples and Buchanan, 1983).

determine the aquifer's representation. Wells constructed in such a way that they might also draw water from aquifers other than the aquifer of interest were eliminated as possible sampling sites. As can be seen, fairly detailed information was available for 48 of the 50 wells chosen.

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 (gpm) 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 ground water. 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, feedlots, or areas with a high density of water wells, especially those of older construction.

The possible leaching of chlorinated organic substances from well casing and construction materials has recently been pointed out by Gibb and Barcelona (1984). Polyvinyl chloride (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.

Geological description of aquifers and sampling sites

The geochemical character of freshwater 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 ft (60 m) in depth. The consolidated aquifers are composed of sandstone, limestone, or sandy dolomite, and the wells tapping them can be in excess of 1,000 ft (300 m) in depth in areas of southeastern Kansas. Climatic and geographic

changes within the state also affect the recharge and discharge relationships of the aquifers.

Figure 1 shows the principal drainageways of the state, as well as the locations of the 50 sampling sites employed in this study. The major alluvial aquifers are associated with river systems in the northeastern, 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. Several consolidated aquifers serve as important sources of potable water. The Dakota Sandstone aquifer, which is present in the Cretaceous geologic sequence, 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 freshwater supplies in the Arbuckle (Cambrian–Ordovician) aquifer are used as the sole source of water by communities in southeastern Kansas. A generalized map depicting the nonalluvial aquifers of Kansas is shown in fig. 2.

The 50 sites selected in the present study include 23 wells in 11 different alluvial aquifer systems, four wells in glacial buried-valley aquifers, three wells in the Ogallala aquifer, three wells in the Equus Beds aquifer, two wells in the Big Bend aquifer, three wells in the Dakota aquifer of Cretaceous age, three wells in Permian-age aquifers, three wells in Pennsylvanian-age aquifers, five wells in Cambrian–Ordovician-age aquifer units, and one well believed completed in material of Pleistocene age (in Meade County). Thirty-four of the sites are public-supply wells, 15 are private domestic wells, and one is an industrial

well. Samples were collected at all 50 sites, but lack of well logs at sites 34 and 41 and analytical problems associated with the high sulfide level at site 38 restricted use of data from these three sites in some of the statistical analyses performed.

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 (fig. 1). The Kansas River continues eastward into the Missouri River, which forms the northeastern state border. The principal 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 ft (30 m). The major water-bearing formation and the formation

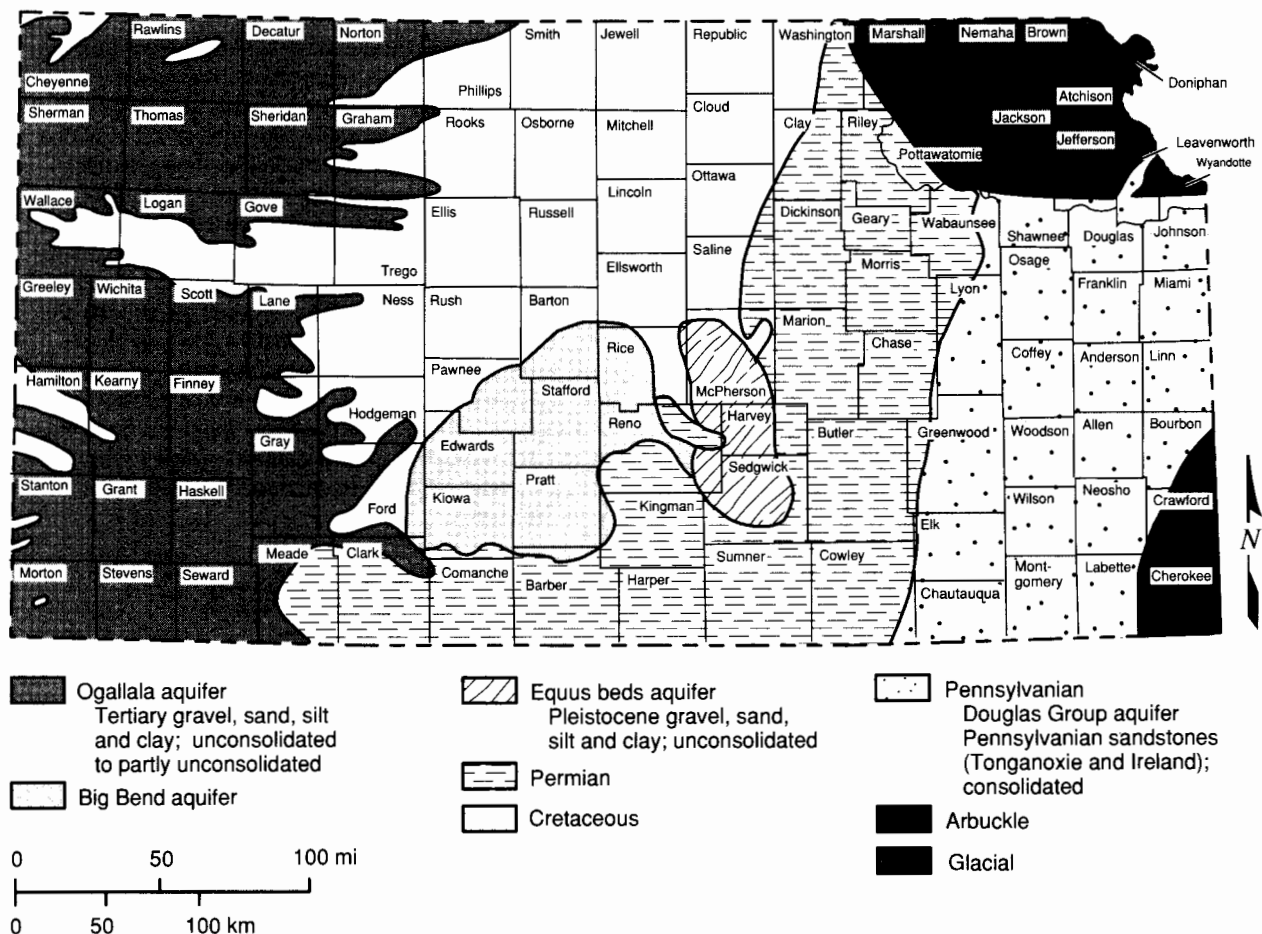


FIGURE 2—GENERALIZED DOMAINS OF NON-ALLUVIAL AQUIFER MATERIALS.

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 ground water exists in equilibrium with the river water and the surrounding ground water. 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 sets of samples (sites 2, 3, and 20) were taken from wells located in the Missouri River alluvium. Site 20 in Doniphan County has a reported yield of 75 gpm and is screened in 4 ft (1 m) of aquifer material consisting of gravel, gray sand, and boulders. Site 3 in Leavenworth County has a maximum yield of 2,000 gpm. This well has 20 ft (6 m) of screened aquifer materials consisting of medium- and coarse-grained sand with traces of gravel. The third site, site 2, is a well located in southwestern Buchanan County, Missouri. This well is screened in about 20 ft (6 m) 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 wells (sites 1 and 6) located in the Kansas River alluvium were sampled. At site 1 in northeastern Douglas County, the well is located in Newman Terrace deposits. It is screened in 20 ft (6 m) of medium- to coarse-grained sand, gravel, and rough boulders. At site 6 in Pottawatomie County, the well is screened in 21 ft (6.5 m) of medium to coarse brown gravel. The bedrock at site 1 is shale of Pennsylvanian age, whereas at site 6 a shale of Permian age forms the bedrock unit.

The Republican River enters the state in north-central Kansas and flows southeastward to join the Kansas River at Junction City. 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 sets of samples (sites 7, 8, and 9) were taken from wells located in the Republican River alluvium. The log for the well at site 9 in Republic County indicates 13 ft (4 m) of screened alluvial gravel overlying bedrock of the Cretaceous System (Greenhorn) and Carlile formations. The well at site 8 in Clay County is screened in 15 ft (4.5 m) of fine to coarse sand and gravel underlain by rock of Permian age (Sumner). The screened interval at site 7 has 20 ft (6 m) of medium to coarse sand and gravel and is underlain by Permian-age (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 44–65 ft (13.5–19.5 m) 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). Two samples (sites 10 and 40) were taken from wells tapping the Solomon River alluvium. The well at site 40 in Osborne County is located on the North Fork about 6 mi (10 km) above the point where the two forks join. It is screened in 26 ft (7.9 m) of sand and is underlain by a Cretaceous-age gray shale at a depth of 68 ft (21 m). At site 10 in Ottawa County, the well is screened in 3 ft (0.9 m) of fine to coarse sand and gravel overlying bedrock of Cretaceous age.

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 20–92 ft (6–28 m) 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 sets of samples (sites 41 and 42) were taken from wells in the Saline River alluvium in Lincoln County. A record of the well log could not be found for site 41, which is an old well. The well that produced the samples for site 42 is screened in 8 ft (2.4 m) of sand and gravel, which is underlain by Cretaceous-age (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. Cedar Bluff Reservoir and Kanopolis Lake are contained along its length. The Smoky Hill River alluvium has a thickness of 30–90 ft (9–27 m). The upper 8–45 ft (2.4–13.4 m) is composed of silt, sandy silt, and fine sand and is underlain by poorly sorted sand and gravel (Latta, 1949). Wells at three sites (11, 32, and 43) are situated in the Smoky Hill River alluvium. At site 11 in Saline County, the well is screened in 10 ft (3.0 m) of medium to coarse sand which is underlain by Permian-age (Sumner) gray shale. In Ellis County, the well at site 32 is screened in 10 ft (3.0 m) of fine to medium sand and gravel with coarse gravel underlain by Cretaceous-age (Greenhorn) black shale. The well at site 43 in Dickinson County is screened in 15 ft (4.6 m) of medium to coarse sand and gravel underlain by Permian-age (Gearyan) red shale.

The Arkansas River cuts across the western two-thirds of Kansas, entering 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 sets of water samples, sites 16 and 17, were taken from wells in 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 generally are used for drinking water because better qualities and quantities of water may be obtained from the Ogallala, Big Bend, and Dakota aquifers. The well at site 17 in Reno County is screened in 15 ft (4.6 m) of medium to coarse sand and gravel. In this area the Arkansas River cuts through Quaternary- (Big Bend), Cretaceous-, and Permian-age sediments. In Cowley County at site 16, the well is screened in 12 ft (3.7

m) of medium to coarse sand underlain by Permian-age (Gearyan) shale.

The Pawnee River and Wet Walnut Creek are tributaries to the Arkansas River in western Kansas. A set of water samples was taken from the Pawnee River alluvium at site 31 in Ness County. This well is screened in 10 ft (3.0 m) of sand underlain by Cretaceous (Carlile or Greenhorn) black shale. Water samples from the Wet Walnut Creek alluvium were obtained from the well at site 30 in Rush County. The screened interval of this well is set in 10 ft (3.0 m) of sand and gravel.

The Cimarron River originates in extreme southwestern Kansas and flows southeastward into Oklahoma. Samples were collected from two sites (26 and 33) having wells into the Cimarron River alluvial aquifer. At site 26 in Seward County, the well is screened in 40 ft (12 m) of medium to coarse sand. In the region of this site, the river cuts through Ogallala-, Pleistocene-, Cretaceous-, and Permian-age sediments. In Meade County at site 33, the well is screened in 6 ft (1.8 m) of medium sand.

The Neosho River extends from Morris County southeastward to Cherokee County where it bends southward into Oklahoma. Council Grove Lake and John Redmond Reservoir are located along its length. Samples were collected from two sites (47 and 49) where wells derive water from the Neosho River alluvial aquifer. The well at site 49 in Labette County is screened in 5 ft (1.5 m) of medium to coarse sand and gravel underlain by Pennsylvanian-age (Marmaton or Cherokee) bedrock. At site 47 the well is screened in 18 ft (5.5 m) of clay, silt, gravel, and shale, and is underlain by Pennsylvanian (Wabaunsee Group) bedrock.

Unconsolidated aquifers

The Ogallala aquifer is the principal water supply in the High Plains region. High-yielding irrigation wells tap this aquifer throughout western Kansas. The Ogallala Formation originated predominantly from deposits by streams flowing eastward from the Rocky Mountains area during Tertiary time (Moore, 1940). The thickness of the Ogallala deposits varies; thicknesses of less than 200 ft (60 m) are typical 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 gradations occur 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. Wells at three sites (24, 25, and 27) derive water from the Ogallala aquifer. At site 24 in Thomas County, the well is screened in fine sand and medium gravel and has a total depth of 261 ft (79 m). In Wichita County at site 25, the well is screened in 18 ft (5.5 m) of medium to coarse sand and gravel and is 172 ft (52.4 m) in total

depth. The well at site 27 in Haskell County has a depth of 430 ft (130 m) and is screened in 75 ft (23 m) of sand with traces of gravel.

The well at site 34 in Meade County is believed to be completed in Pliocene–Pleistocene-age materials, but no well log was found for this site.

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 ground water in the south-central area of Kansas, although some areas have had oil-brine contamination (Williams and Lohman, 1949).

The Equus beds are composed of streamborne 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 ft (0–88 m) in thickness (Williams and Lohman, 1949). Three sites (13, 14, and 15) are located in the region of the Equus Beds aquifer. The well at site 13 in McPherson County is screened in 50 ft (15 m) of sand and gravel, with a total depth of 215 ft (65.5 m). In Harvey County the well at site 14 is screened in 25 ft (7.5 m) of fine to coarse sand. Its total depth is 150 ft (45 m). At site 15 in Sedgewick County, the well has a total depth of 45 ft (13 m) and is screened in 10 ft (3 m) of medium to coarse sand.

A major ground-water 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 ft (91 m; Bayne, 1956). Most of the public and private water supplies in the aquifer area are obtained from the Big Bend aquifer, although saline ground waters 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 (sites 28 and 46) completed in the Big Bend aquifer were sampled. The well at site 46 in Reno County has a total depth of 72 ft (22 m) and is screened in 20 ft (6 m) of sand and gravel. At site 28 in Edwards County, the well has a total depth of 100 ft (30 m) to shale bedrock and is screened in 30 ft (9 m) 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 glaciofluvial deposits are an important ground-water 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 or its meltwater deposited sediments in Pleistocene age or older stream valleys. The valley sediments can be up to 400 ft (120 m) in thickness and 3 mi (5 km) in width (Denne et al., 1984).

Glacial sediments predominantly are 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 ft (12 m). 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 may be 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.

Water samples were collected from three wells (sites 19, 22, and 23) associated with the major buried-valley system. Site 19 in Marshall County has 182 ft (55 m) of glaciofluvial sediments, and the well is screened in 10 ft (3 m) of gravel. The well at site 22 in Jackson County is constructed in 145 ft (44.2 m) of glacial-related sediments and is screened in 10 ft (3 m) of coarse sand and medium and pea gravel. Further east along the course of the buried valley in Atchison County, the well at site 23 is situated in 200 ft (60 m) of glacial material and screened in 10 ft (3 m) of coarse sand and pea gravel. A fourth well which taps a glacial aquifer, site 21 in Brown County, also was sampled. At this site the glacial sediments are only 45 ft (14 m) thick and are not part of the major buried valley to the south. The well is screened in 7 ft (2 m) of sand and gravel and 13 ft (4.0 m) of the underlying shale bedrock.

Consolidated aquifers

The Dakota Formation of the Lower Cretaceous System is composed of sandstone (some conglomeratic) separated by layers of siltstone, mudstone, shale, and clay (Leonard et al., 1983). The sandstone is iron rich, and saltwater occurs in parts of this formation (Moore, 1940). It has a wide outcrop area in the north-central region of Kansas (fig. 2). 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 ft (176 m; 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 2,200 gpm (Kume and Spinozola, 1985). Three sets of

water samples (sites 12, 18, and 29) were taken from wells screened in the Dakota Sandstone aquifer of the Cretaceous System. The well at site 18 is 285 ft (86.9 m) deep and is screened in 20 ft (6 m) of sandstone. This well is located in Washington County near the Nebraska border in a Dakota Formation outcrop area. At site 12 in Marion County, the well is situated in an outcrop island of the Dakota Formation. The well has a depth of 68 ft (21 m) and is screened in 10 ft (3 m) of tan, fine- to medium-grained sandstone. The well at site 29 in Rush County is 100 ft (30 m) deep and screened in 40 ft (12 m) of loose sandstone and limestone. This well is found in a small area of the Cretaceous System adjacent to the Wet Walnut Creek alluvium.

Two wells (sites 44 and 45) were sampled which have screened sections in Lower Permian rocks. The Lower Permian Series comprises more than 1,900 ft (580 m) of evaporite-bearing siltstones, sandstones, and shales in the upper portion and a little less than 800 ft (240 m) of alternating limestone, shale, and minor amounts of gypsum in the lower part (Zeller, 1968). Ground waters in Permian-age deposits vary widely in quality and quantity depending on the location and aquifer material. In Marion County, the Winfield Limestone, the Nolans Limestone, 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 ft (102 m) 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 ft (7.6 m) 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 ft (1 m) in thickness (Zeller, 1968). The upper limestone is yellowish tan and is dolomitic with a thickness of 6–10 ft (2–3 m). The Nolans Limestone is 22–40 ft (6.5–12 m) 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, where it also crops out in the southern region. Thin shale beds alternating with beds of white, pink, or gray gypsum can be as great as 20 ft (6 m) in thickness (Byrne, 1959). The limestone of the Wellington weathers blocky and cavernous to porous (Byrne, 1959).

At site 44 in northeastern Marion County, the well is constructed to a total depth of 93 ft (28 m) and is screened in 28 ft (8.5 m) of limestone and shale which are probably part of the Nolans Limestone (O'Connor, 1987). The well at site 45 in the southern part of Marion County is 60 ft (18 m) deep and screened in 30 ft (9 m) of limestone and shale of the Wellington Formation.

One set of samples, site 35 in Kingman County, was taken from a well which is screened in the "red beds" section of the Nippewalla 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). The well at this site in southwestern Kingman County is 74 ft (23 m) deep and is screened in 12 ft (3.7 m) of shale in the Harper Siltstone.

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 Stranger Formation occupies an erosional river valley cut into older rocks of the Stranger and Stanton formations. The valley is 14–20 mi (22–32 km) 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 ft (37 m) in thickness. The sandstone is light to dark gray and contains fine to very fine, angular to subangular quartz and is up to 70 ft (21 m) 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 0.5 mi (0.8 km) wide, and the Ireland Sandstone can reach a thickness of 115 ft (35.0 m). 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 percentage 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 becomes more mineralized farther from the recharge area. There is recharge to the Tonganoxie Sandstone from the Ireland Sandstone where they are interconnected. Discharge occurs from the Tonganoxie into alluvial deposits of the Wakarusa and Kansas River valleys (O'Connor, 1960). Wells in Douglas Group sandstones yield 5–100 gpm.

Three sets of water samples (sites 4, 5, and 48) were taken from wells in the Douglas Group sandstones. The well at site 4 in Franklin County is screened in 59 ft (18 m) of white sandstone and has a depth of 210 ft (63.5 m). In Douglas County at site 5, the well has a total depth of 500 ft (152 m), including 80 ft (24 m) of uncased open hole at its base. The aquifer material at this location consists of sandstone and shale. The well at site 48 in southwestern Leavenworth County is 160 ft (48.5 m) deep and is screened in 40 ft (12 m) of sandstone.

The Arbuckle aquifer refers to the lower Paleozoic units of Cambrian–Ordovician age located in southeast Kansas and adjoining areas of Oklahoma, Arkansas, and Missouri. The Mississippian and Cambrian–Ordovician 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 1,000 ft (300 m) in depth and are usually com-

pleted as open bore holes. The first freshwater 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 freshwater of the Arbuckle is widely used for public supplies and industry (Macfarlane et al., 1981). Recharge into the Cambrian–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 Cambrian–Ordovician aquifers produce oil west of Crawford and Cherokee counties, and water in these units increases 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 1,200 to 2,800 ft (360–850 m) and are composed of limestone, dolomite, sandstone, and shale. The Cambrian–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 ft (0–91 m). A particular layer of sandstone from 5 to 10 ft (1.5–3 m) in thickness has been informally named the "Swan Creek." The Roubidoux Formation is composed of white sandstone; gray, medium-grained, sandy dolomite; and chert dolomite. It is generally around 140 ft (42 m) 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 sets of water samples (sites 36, 37, 38, 39, and 50) were taken from wells deriving water from the Cambrian–Ordovician aquifer system. Sites 38 and 50 are in close geographic proximity in southeastern Crawford County. These two wells have 500 ft (152 m) of open bore hole drilled into the Cotter and Jefferson City dolomites, the Roubidoux Formation, and the Gasconade Dolomite. At site 39, about 6.5 mi (10 km) northwest of sites 38 and 50 in Crawford County, the well has a total depth of 1,113 ft (339 m) and 390 ft (119 m) of open bore hole in the Lower Ordovician section including the Cotter, Jefferson City, Roubidoux, and Gasconade. Site 36 in east-central Cherokee County has a well with a total depth of 900 ft (274 m) and 325 ft (99 m) of open hole which includes the Jefferson City Dolomite and the Roubidoux Formation. The well at site 37 in southeastern Cherokee County has a total depth of 1,260 ft (384 m) and 746 ft (227 m) of open hole in the Cotter, Jefferson City, Roubidoux, Gasconade, and a small section of the Eminence.

Sampling procedure and analytical methods

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 polyethylene bottle for determination of pH, specific conductance, and major anions and cations; one 250-mL polyethylene bottle acidified with 2 mL of redistilled 6 N hydrochloric acid and filled to 200 mL for analysis of trace metals, nitrate, and ammonium; and one 250-mL glass bottle (with a TeflonTM-lined cap) for the determination of TOC and TFP.

Finished water samples also were 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 g 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

(H₂S) was determined using a hydrogen sulfide kit (CHEM_{et}, CHEMetrics Inc., Calverton, VA) employing a colorimetric method with a detection limit of 0.1 mg/L. 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, 1986, but samples from sites 48 through 50 were collected from June 5 to July 17, 1986. Following collection, 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 Environmental Health Laboratory housed in Learned Hall at the University of Kansas for analysis of TOC, THM, and TFP. The polyethylene bottles were taken to the Analytical Services Laboratory of the Kansas Geological Survey housed in Moore Hall. All samples were refrigerated while awaiting analysis.

Although most of the samples were fairly clear, three (5, 20, and 49) contained dark-colored suspended solids and were filtered through a glass-fiber filter (934 AH) to remove particulate organic matter prior to determination of TOC and TFP. Table 2 shows TOC concentrations determined for six samples under various suspended solids conditions. Samples 5 and 20 contained 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 11) were similar for filtered and unfiltered portions. Because it was thought that the TOC associated with the solids in these samples had probably been absorbed from solution after oxidation and precipitation of iron, these samples were not filtered prior to TFP analysis.

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.

Analytical methods

TOC

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 (1985). Samples were acidified to pH < 2, purged with nitrogen to remove CO₂ and shaken well prior to injection. TOC concentrations were determined for all raw-water samples and 26 of the 31 finished-water samples. 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 $\pm 2\%$ for concentrations greater than 1.0 mg/L.

TFP

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 61-mL bottles dosed with free chlorine in 5-mg/L increments, and incubated head-space free 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 (1985), 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 mg/L of THMs, and analysis of independent quality-control samples always produced results within $\pm 3\%$ of the stated value. More detailed descriptions of the analytical procedure for TFP are given by Randtke et al. (1987) and Denne et al. (1987).

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

Instantaneous and terminal THM concentrations

Samples analyzed to determine the THM concentration at the time of sampling (instantaneous THMs) were dechlorinated at the time of collection, immediately placed on ice and then refrigerated at 4°C (39°F) in the laboratory for up to two 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.

Samples analyzed to determine the THM concentration in the finished water after a four-day (96-hr) incuba-

tion period (terminal THM) were incubated at 25°C (77°F), extracted, and analyzed for THMs. TOC was not determined for these samples.

Specific conductance

A portion of each unacidified sample (collected in a 500-mL polyethylene bottle) was allowed to come to room temperature in the laboratory. Specific conductance measurements were then made using a Lab-Line Lectro Mho-Meter, Mark IV unit. These values were used later as guides in the determination of dissolved-concentration levels of major cation and anion constituents of the water samples.

pH and bicarbonate

Measurements of sample pH and alkalinity, herein expressed as mg/L bicarbonate (HCO⁻), were obtained using a Fisher Titrimeter II Titration System. The alkalinity was derived from the volume of 0.02 N H₂SO₄ necessary to bring a room-temperature 50-mL aliquot of sample to pH 4.5 according to the procedure described in Standard Methods (1985).

Sulfate, chloride, nitrate, and ammonium

A Technicon Auto Analyzer II continuous-flow system was used in the analysis of sulfate (SO₄⁻²), chloride (Cl⁻), nitrate (NO₃⁻) and ammonium (NH₄⁺). SO₄⁻² and Cl⁻ were determined on room-temperature aliquots of unacidified samples, using the methylthymol blue and ferric thiocyanate methods, respectively. NO₃⁻ and NH₄⁺ were determined, using the cadmium reduction-diazotization and indophenol methods, respectively, on room-temperature aliquots of acid-preserved samples neutralized to pH 6 prior to analysis. These automated procedures were based on chemistries developed for the Auto Analyzer II system and supplied by Technicon Industrial Systems.

Metals

Concentrations of major [calcium (Ca), magnesium (Mg), and sodium (Na)] and minor [potassium (K) and strontium (Sr)] metallic constituents and selected trace metals [barium (Ba), iron (Fe), and manganese (Mn)] were determined using a Jarrell-Ash Model 975 Plasma Atomcomp inductively coupled argon-plasma optical-emission spectrophotometer (ICP). Room-temperature aliquots of unacidified samples were used in the determinations of Ca, Mg, Na, K, and Sr, whereas room-temperature aliquots of the acid-preserved samples were employed for the determinations of Ba, Fe, and Mn.

Results and discussion

Analytical results

Table 3 shows the concentrations of TFP and TOC in the untreated samples. The concentrations of the four individual THM species are given in $\mu\text{g/L}$ and then summed to give TFP in $\mu\text{g/L}$ and micromoles per liter (μM). The percentage chlorine (%Cl) is the percentage of the halogen atoms in the THMs composed of chlorine, the balance being bromine. The yield, in μmol of TFP per mg of TOC, is a calculated value. The chlorine demand is the amount of free chlorine consumed during the 96-hr incubation period in the subsample used for TFP analysis.

In table 3, as well as tables 4–6, a number of the values reported are below the detection limit. In computing the mean, sample standard deviation (SD), geometric mean (G. Mean), and median for a constituent, values less than the detection limit were assumed equal to one half of the detection limit. Geometric means and medians are

reported because the concentrations of many constituents were not normally distributed.

Table 4 shows the terminal THM concentrations of the finished water samples collected from public-water supplies (i.e. those using chlorine to disinfect the water). A majority 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.

Table 6 gives the results of the geochemical analyses. The laboratory pH was generally higher than the field pH, as would be expected with the escape of CO_2 . A large difference between field and laboratory conductance might indicate precipitation of minerals from the water after sampling, but the values were generally close. Ionic balances were computed for these results, and the greatest deviation from electroneutrality (the difference between meq/L of anions and meq/L of cations divided by their sum) was 1.87%.

TABLE 3—TFP AND TOC IN UNTREATED GROUND-WATER SAMPLES.

Sample	CHCl ₃ $\mu\text{g/L}$	CHCl ₂ Br $\mu\text{g/L}$	CHClBr ₂ $\mu\text{g/L}$	CHBr ₃ $\mu\text{g/L}$	TFP			TOC mg/L	Yield $\mu\text{moles/mg}$	Chlorine Demand mg/L
					$\mu\text{g/L}$	μM	%Cl			
1	8.9	12.0	8.7	1.3	30.9	0.195	71	0.69	0.282	1.71
2	85.2	14.1	3.4	<0.1	102.7	0.816	95	3.31	0.247	10.61
3	91.2	22.8	7.2	<0.1	121.2	0.938	93	2.56	0.366	7.20
4	9.0	3.7	1.6	<0.1	14.3	0.106	88	0.36	0.294	1.95
5*	1.7	2.2	9.0	12.7	25.6	0.121	31	0.48	0.252	7.20
6	7.5	16.2	28.5	19.4	71.7	0.375	47	1.04	0.361	1.71
7	36.1	32.2	24.4	4.9	97.6	0.635	74	1.90	0.334	2.44
8†	27.9	21.9	30.7	15.8	96.3	0.577	64	1.37	0.421	1.77
9	26.7	28.4	23.3	5.6	83.9	0.530	71	2.19	0.242	2.81
10	8.3	13.4	13.1	3.7	38.4	0.228	63	1.03	0.221	3.72
11	37.0	28.6	18.7	3.3	87.7	0.588	78	1.90	0.309	7.44
12	3.4	4.5	4.5	2.4	14.8	0.087	62	0.41	0.212	0.37
13	3.2	2.5	3.0	2.7	11.4	0.067	62	0.31	0.217	0.24
14	4.0	3.2	2.3	0.2	9.7	0.065	77	0.30	0.217	1.22
15	4.3	7.3	7.6	3.0	22.2	0.129	60	0.85	0.152	0.61
16	27.3	20.1	14.2	2.5	64.1	0.429	78	1.52	0.282	2.14
17	4.1	13.6	24.9	19.1	61.6	0.312	42	1.06	0.294	1.65
18	9.5	8.7	5.6	1.0	24.8	0.163	76	0.87	0.188	6.83
19	6.1	3.9	3.9	<0.1	14.0	0.094	78	0.45	0.209	1.34
20*	64.2	29.2	12.7	0.8	106.9	0.780	87	2.84	0.275	9.88
21	1.2	5.3	27.0	44.9	78.4	0.349	21	1.20	0.291	3.17
22	3.4	6.7	12.4	4.4	26.9	0.146	52	0.58	0.252	0.98
23	9.1	10.2	8.7	2.0	30.0	0.188	70	0.83	0.227	3.90
24	2.8	4.4	4.8	2.3	14.3	0.083	60	0.52	0.159	0.24
25†	3.5	11.5	22.2	19.6	56.8	0.283	39	1.34	0.211	<0.06
26	6.5	12.6	15.3	4.6	38.9	0.222	58	0.72	0.308	0.61
27†	<0.1	3.3	7.6	7.4	18.3	0.086	30	0.47	0.183	<0.06
28	4.5	5.3	3.8	<0.1	13.5	0.087	74	0.55	0.159	<0.06
29	3.1	4.1	4.3	1.4	12.9	0.078	64	0.49	0.158	0.06
30	4.3	18.4	33.1	21.6	77.5	0.393	42	1.54	0.255	1.83
31	3.6	13.4	19.7	10.4	47.1	0.248	47	1.00	0.248	1.16
32	35.7	27.5	19.4	3.4	86.0	0.573	77	2.43	0.236	2.32
33	1.1	4.3	8.5	5.9	19.8	0.100	41	0.60	0.166	0.12
34	3.4	5.2	5.4	1.9	15.8	0.093	62	0.50	0.186	<0.06
35	11.0	10.7	7.9	1.0	30.6	0.199	74	0.88	0.226	1.22

TABLE 3 (continued)—TFP AND TOC IN UNTREATED GROUND-WATER SAMPLES.

Sample	CHCl ₃ μg/L	CHCl ₂ Br μg/L	CHClBr ₂ μg/L	CHBr ₃ μg/L	TFP			TOC mg/L	Yield μmoles/mg	Chlorine Demand mg/L
					μg/L	μM	%Cl			
36	3.6	3.1	1.6	<0.1	8.3	0.057	80	0.27	0.210	0.85
37	1.5	2.1	1.7	<0.1	5.3	0.033	71	0.21	0.158	<0.06
38‡	<0.1	0.4	1.4	3.9	5.8	0.025	16	0.29	0.086	>24.40
39	0.3	1.3	3.6	4.0	9.2	0.044	31	0.31	0.141	7.63
40	4.2	10.7	12.7	5.7	33.4	0.184	54	0.98	0.188	0.24
41	9.6	17.9	22.3	9.4	59.2	0.334	57	1.27	0.263	0.61
42	7.4	12.4	15.6	6.4	41.8	0.238	58	1.10	0.216	3.48
43	5.9	15.0	29.3	23.2	73.5	0.374	42	1.02	0.366	7.93
44	0.4	6.5	7.2	3.1	17.3	0.090	46	0.50	0.180	0.06
45	3.4	6.8	8.1	3.4	21.8	0.123	57	0.80	0.153	0.55
46	1.3	3.7	4.6	1.9	11.4	0.063	53	0.36	0.174	<0.06
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	9.94
50	2.3	3.9	5.2	2.2	13.6	0.077	57	0.48	0.160	6.34
Mean	13.5	11.7	13.3	8.2	46.7	0.281	61	1.03	0.242	2.69
SD	20.9	9.5	11.5	16.7	39.5	0.250	18	0.76	0.070	3.09
G. Mean	5.4	8.5	9.2	2.2	32.5	0.192	58	0.81	0.232	0.95
Median	4.3	10.2	8.7	3.3	30.6	0.188	62	0.84	0.227	1.65

* This sample was filtered through a glass-fiber filter (934 AH) to remove suspended solids.

† Free chlorine was detected in the untreated sample (this was not checked in samples 1–23 or 36–50, except for sample 8).

‡ No free chlorine residual was detected following chlorination, perhaps due to the high concentration of H₂S. Therefore, the TFP and chlorine demand data for this sample were excluded from all statistical summaries and correlations.

** Not determined

TABLE 4—TERMINAL TRIHALOMETHANE CONCENTRATIONS IN FINISHED WATER SAMPLES.

Sample	CHCl ₃ μg/L	CHCl ₂ Br μg/L	CHClBr ₂ μg/L	CHBr ₃ μg/L	Term. THM			Yield* μmoles/mg	Free Chlorine Remaining
					μg/L	μM	%Cl		
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	—	<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	—	<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	—	<0.005	no
20	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	—	<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	—	<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

TABLE 4 (continued)—TERMINAL TRIHALOMETHANE CONCENTRATIONS IN FINISHED WATER SAMPLES.

Sample	CHCl ₃ μg/L	CHCl ₂ Br μg/L	CHClBr ₂ μg/L	CHBr ₃ μg/L	Term. THM			Yield* μmoles/mg	Free Chlorine Remaining
					μg/L	μM	%Cl		
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
Mean	7.6	6.4	6.9	4.7	25.5	0.154	54	0.136	—
SD	18.8	9.5	7.9	7.2	34.4	0.237	25	0.118	—
G. Mean	0.6	1.4	1.8	0.9	6.1	0.037	47	0.044	—
Median	0.5	1.5	3.3	1.9	9.1	0.046	52	0.136	—

* Based on the TOC concentration of the sample analyzed for instantaneous THMs (except for samples 49 and 50, in which case the yield was based on the TOC value of the raw water sample).

† The detection of free chlorine in this sample may have been an artifact. It is more likely that this sample contained combined chlorine and enough iodide ion to cause monochloramine to be mistaken for free chlorine (see table 5).

TABLE 5—INSTANTANEOUS THM AND TOC CONCENTRATION IN FINISHED WATER SAMPLES.

Sample	CHCl ₃ μg/L	CHCl ₂ Br μg/L	CHClBr ₂ μg/L	CHBr ₃ μg/L	Inst. THM			TOC mg/L	Yield μmoles/mg	Free Cl ₂ (Field) mg/L
					μg/L	μM	%Cl			
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	—	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	—	2.48	<0.001	0.2
11	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	—	1.93	<0.002	0.2
12	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	—	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	—	0.64	<0.005	0.2
20	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	—	2.08	<0.001	1.0
24	<0.1	<0.1	<0.1	<0.1	<0.4	<0.003	—	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	—	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	—	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
Mean	2.7	1.8	1.5	0.9	6.9	0.045	58	1.13	0.032	1.6
SD	8.4	5.1	2.6	1.6	16.0	0.112	28	0.81	0.048	1.3
G. Mean	0.2	0.3	0.4	0.2	1.4	0.009	49	0.81	0.011	1.0
Median	<0.1	0.2	0.4	<0.1	1.3	0.007	52	1.00	0.015	1.3

* Raw water TOC (other TOC values were determined on the treated sample taken for analysis of instantaneous THMs).

† The total residual chlorine concentration was greater than the free chlorine concentration (the total concentration is shown in parentheses).

TABLE 6—RESULTS OF THE GEOCHEMICAL ANALYSIS.¹

No.	Temp °C	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 ²⁻ mg/L	Cl ⁻ mg/L	NO ₃ ⁻ mg/L	NH ₄ ⁺ mg/L	Ba μg/L	Fe μg/L	Mn μg/L	H ₂ S mg/L
01	12	6.95	7.40	740	663	106	14	15	1.6	0.5	371	36	5.2	0.1	0.1	490	1530	422	ND
02	15	6.95	7.50	940	908	123	35	29	5.4	0.9	588	15	6.6	<0.1	1.1	868	12900	713	ND
03	15	7.05	7.60	830	810	90	28	46	5.9	0.7	398	96	14	<0.1	0.7	674	11100	706	ND
04	16	7.05	7.60	550	562	90	13	16	1.1	0.8	352	12	2.2	<0.1	0.2	131	664	24	ND
05	19	7.70	8.00	1450	1300	20	8.2	251	2.7	1.0	333	19	248	<0.1	1.0	31	4300	36	1.0
06	11	6.95	7.45	950	1020	142	26	33	5.3	2.3	407	94	56	46	0.1	193	152	9	ND
07	15	7.05	7.90	660	685	69	17	43	11.0	0.6	241	95	40	2.0	0.1	371	93	769	ND
08	16	6.95	7.60	1450	1430	207	42	52	11.0	2.7	420	382	45	24	0.1	55	BQ	411	ND
09	14	7.15	7.60	1030	1098	138	17	68	12.0	0.7	381	154	74	17.0	0.1	207	311	545	ND
10	14	6.85	7.45	720	750	103	16	34	4.1	0.4	395	64	16	0.1	0.4	168	2630	837	ND
11	14	7.10	7.70	960	1000	140	28	34	6.0	1.6	457	119	43	0.1	0.7	108	7520	937	ND
12	15	6.35	6.80	310	333	30	6.9	24	2.1	0.2	86	46	19	20	<0.1	158	BQ	16	ND
13	14	7.10	7.65	530	570	89	9.0	17	2.5	0.4	292	21	26	4.2	<0.1	188	BQ	BQ	ND
14	14	7.10	7.60	380	412	58	7.5	18	1.2	0.3	208	20	6.1	21	<0.1	122	BQ	BQ	ND
15	14	7.15	7.60	850	909	94	14	84	1.0	0.4	391	46	73	19	<0.1	130	BQ	BQ	ND
16	16	7.05	7.50	780	830	124	26	18	1.3	2.4	485	54	13	6.7	0.1	218	BQ	BQ	ND
17	15	7.05	7.85	2250	2350	167	37	263	7.1	1.3	322	188	487	22	<0.1	65	947	BQ	ND
18	14	7.25	7.85	1130	1180	29	7.7	229	6.1	0.4	418	116	102	0.4	0.8	24	127	25	ND
19	15	7.15	7.80	620	602	82	14	29	2.5	0.5	389	13	4.9	0.2	0.1	231	175	395	ND
20	14	7.25	7.95	1010	1042	140	45	34	16.0	1.2	704	7.6	18	0.2	1.5	3840 ²	14000 ²	12400 ²	ND
21	8	6.35	6.90	1100	1160	44	14	168	2.9	1.2	155	61	226	40	0.3	45	27	211	ND
22	8	6.90	7.60	800	838	103	28	42	1.9	1.0	397	93	29	4.0	0.1	71	377	8	ND
23	9	7.10	7.90	710	650	76	23	29	3.8	1.1	401	18	12	0.1	0.5	190	811	126	ND
24	15	7.50	8.00	410	415	40	15	24	5.7	0.6	213	23	6.4	14	<0.1	82	BQ	BQ	ND
25	14	7.10	7.85	625	610	62	24	21	4.6	1.2	175	74	49	25	<0.1	86	70	BQ	ND
26	16	7.15	7.90	640	608	60	27	29	3.8	1.2	265	84	13	9.3	0.1	118	41	19	ND
27	16	7.05	7.85	710	730	65	27	50	4.5	1.5	224	162	16	14	<0.1	20	16	BQ	ND
28	15	7.35	8.10	385	400	53	5.7	22	3.2	0.3	193	18	11	20	<0.1	141	BQ	BQ	ND
29	15	7.30	8.00	500	492	75	9.0	14	3.0	0.5	261	14	14	16	0.1	206	145	BQ	ND
30	14	6.85	7.70	1000	1050	176	14	29	4.6	0.7	347	180	71	0.3	0.1	197	904	52	ND
31	14	6.95	7.60	850	885	124	19	28	6.6	1.1	371	75	38	49	<0.1	213	22	BQ	ND
32	13	7.15	7.55	785	820	126	10	35	4.8	0.7	333	95	46	3.3	<0.1	204	45	140	ND
33	16	7.35	7.85	3700	3500	93	30	622	9.1	1.3	251	286	853	5.8	<0.1	38	BQ	BQ	ND
34	12	7.50	8.00	935	827	41	11	120	2.9	0.5	257	82	79	7.0	0.1	37	32	BQ	ND
35	15	7.45	7.85	600	580	57	28	29	1.7	0.7	324	23	14	13	0.1	136	BQ	BQ	ND
36	18	7.10	8.00	480	451	47	22	18	3.9	0.7	234	50	4.8	<0.1	0.2	72	166	BQ	ND
37	19	7.20	8.05	450	423	49	18	14	1.8	0.1	176	64	14	0.1	0.1	82	44	7	ND
38	20	7.35	7.60	780	790	51	24	87	5.3	0.8	320	34	86	<0.1	0.3	357	BQ	BQ	7.5
39	23	7.25	7.85	1200	1140	70	34	125	7.6	1.3	323	96	169	<0.1	0.4	52	122	BQ	3.5

TABLE 6 (continued)—RESULTS OF THE GEOCHEMICAL ANALYSIS.¹

No.	Temp °C	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 ²⁻ mg/L	Cl ⁻ mg/L	NO ₃ ⁻ mg/L	NH ₄ ⁺ mg/L	Ba μg/L	Fe μg/L	Mn μg/L	H ₂ S mg/L
40	14	6.80	7.65	820	820	118	14	38	6.9	0.7	352	71	45	27	0.1	178	BQ	BQ	ND
41	14	6.95	7.60	1040	1030	137	20	65	4.9	0.6	475	107	46	15	0.1	115	846	117	ND
42	14	6.95	7.90	950	923	142	15	42	5.0	0.8	476	96	22	0.6	0.3	122	3470	669	ND
43	13	6.80	7.60	1620	1481	184	43	88	7.4	2.1	392	379	100	0.2	1.0	39	616	2620	ND
44	13	7.05	7.80	840	778	95	32	18	0.9	0.3	386	21	29	36	0.2	556	BQ	BQ	ND
45	13	6.95	7.60	1900	1670	303	54	32	2.3	5.3	401	687	31	3.1	0.1	26	924	14	ND
46	15	6.95	8.00	2200	1960	78	12	319	6.8	0.5	250	59	474	6.0	<0.1	203	651	37	ND
47	13	6.60	6.85	1590	1520	227	30	47	1.4	0.9	352	140	134	188	0.1	192	BQ	BQ	ND
48	16	7.15	7.45	590	560	86	12	22	1.1	0.4	335	24	2.2	0.1	0.2	12	396	48	ND
49	21	7.25	7.85	685	725	106	16	22	2.7	1.0	385	30	17	0.1	1.1	805	9270	1790	ND
50	22	7.25	7.45	785	830	69	29	60	6.2	0.8	326	83	54	<0.1	0.3	108	40	BQ	2.0
Mean	14.8	7.08	7.69	956	942	100	21	72	4.7	1.0	340	97	80	13.6	0.3	186	1258	240	—
SD	2.9	0.25	0.28	584	546	55	11	105	3.2	0.8	110	118	150	28.3	0.3	191	2887	495	—
GM	14.5	7.07	7.68	842	837	87	19	43	3.7	0.8	321	59	33	1.8	0.2	122	139	21	—
Med.	14.5	7.10	7.68	810	824	90	19	34	4.4	0.8	350	68	30	4.1	0.1	131	122	14	—

¹Notation: Fld = Field value; Lab = Lab value

Cond = Specific conductance in μmhos/cm

BQ = Below quantifiable limit (26 μg/L for Fe and 4 μg/L for Mn)

SD = Standard Deviation

GM = Geometric Mean

Med. = Median

²Sample 20 contained a substantial amount of sediment, and the acidified sample had to be filtered prior to analysis for Ba, Fe, and Mn. The high values for these constituents probably reflect dissolution of particulate matter and not the presence of dissolved minerals. These values were discarded in all statistical summaries and correlations.

TOC and TFP

The raw-water TOC concentrations (table 3) ranged from 0.21 to 3.31 mg/L with a median value of 0.84 and a mean of 1.03 mg/L. Fig. 3 shows the statewide distribution of TOC concentrations greater than and less than 1.0 mg/L. Values greater than 1 mg/L were found throughout the state but primarily in alluvial aquifers. All of the consolidated aquifers sampled had TOC concentrations below 1 mg/L. The highest values (i.e. those > 2.0 mg/L) were found exclusively in the eastern third of the state.

The TFPs (table 3) ranged from 5.3 to 178 mg/L, with a median value of 30.6 µg/L, a mean of 46.7 µg/L, and a geometric mean of 32.5 µg/L. On the average, only about 61% of the THM-halogen atoms were chlorine, illustrating the importance of bromide in THM formation in Kansas. For 29 of the 50 samples, either CHClBr_2 or CHCl_2Br was the most abundant THM species, with another five samples dominated by CHBr_3 . Sample 47 had anomalously high concentrations of brominated THMs, presumably due to an unusually high concentration of bromide in the raw water.

Of the 50 samples analyzed, only four (8%, all in Missouri or Neosho River alluvium) had TFPs exceeding the current MCL for THMs of 100 µg/L. However, 28 (56%) had TFPs exceeding 25 µg/L, and 45 (90%) had TFPs exceeding 10 µg/L. Hence, if the MCL were set at a substantially lower level, a significant number of water utilities relying on ground water as a source of supply might have difficulty complying with the new MCL.

TOC and TFP (µM) were very strongly correlated ($r = 0.953$), as shown in fig. 4 and table 7. This was expected based on the results of many previous investigations of THM formation in surface waters; this relationship is reflected in the relatively low standard deviation in TFP yield ($\pm 25\%$, as shown in table 3). This demonstrates that TOC would be an excellent surrogate measure for THM formation, which might prove particularly useful in monitoring and regulatory efforts.

Fig. 4 and table 7 also show the TOC and TFP concentrations for each of the three major aquifer types. The highest concentrations (TOC values > 1.5 mg/L and TFP values > 50 µg/L) were found exclusively in alluvial aquifers, including those of the Missouri, Neosho, Smoky Hill, and Republican rivers. Only two nonalluvial aquifer samples had TOC concentrations greater than 1 mg/L; one was from a glacial buried-valley aquifer and one was from the Ogallala Formation. The remaining nonalluvial aquifer samples had TOC concentrations ranging from 0.2 to 0.9 mg/L, a range which includes only three alluvial aquifer samples.

As shown in table 7, the mean TOC and TFP concentrations were substantially higher for the alluvial aquifer samples than for the samples from consolidated and unconsolidated aquifers. River waters often carry large organic loads, and other investigations (see Introduction) have shown that river waters generally have higher TOC concentrations than ground waters. The recharge and discharge relationship of a river and its adjoining alluvium is probably a major factor in the amount of TOC in

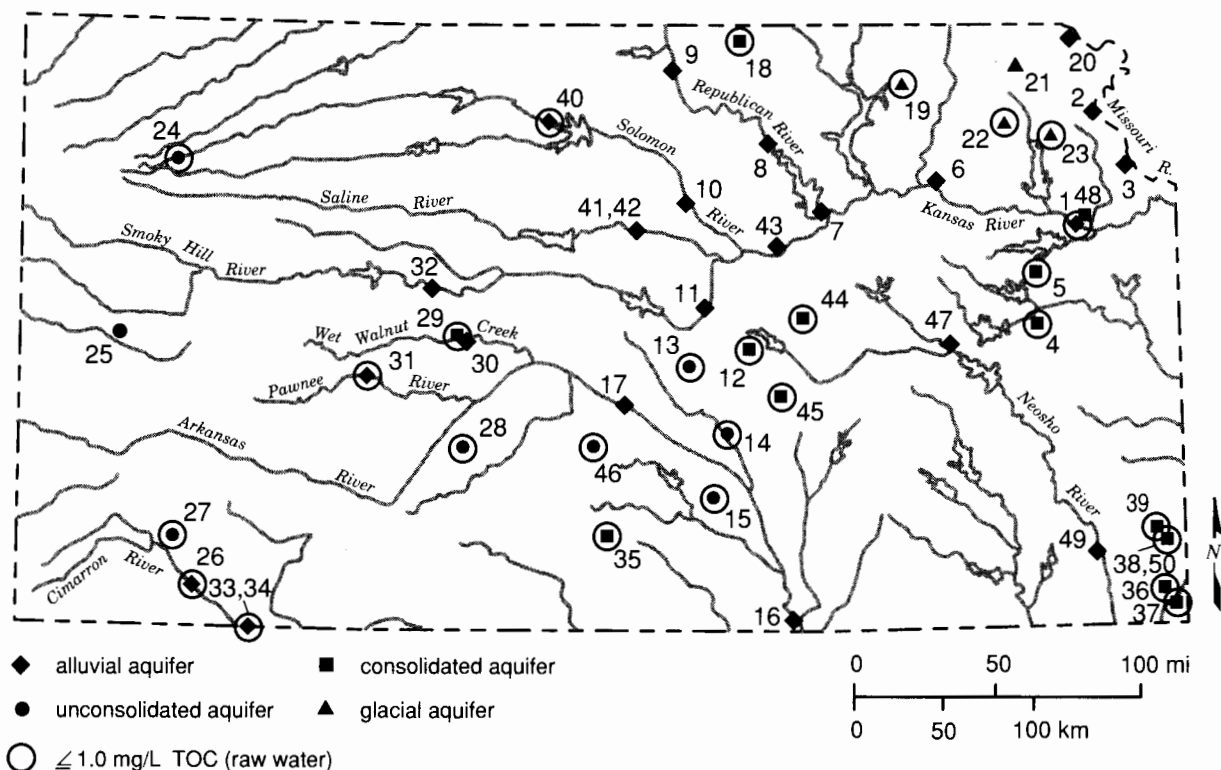


FIGURE 3—STATEWIDE DISTRIBUTION OF TOC CONCENTRATIONS (base map from Steeples and Buchanan, 1983).

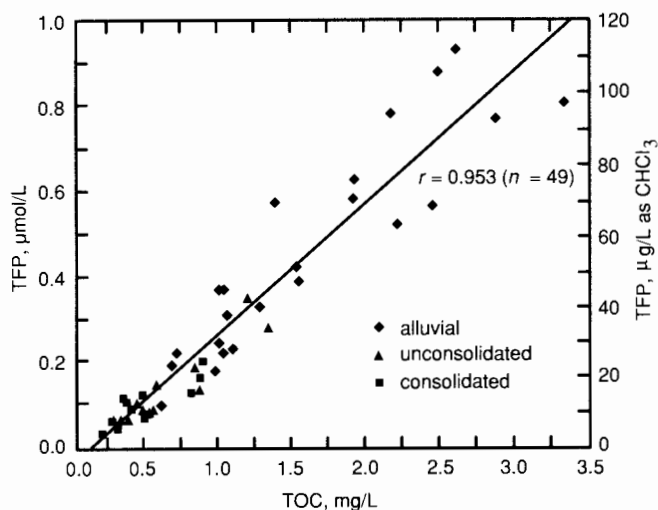


FIGURE 4—TFP AS A FUNCTION OF TOC AND AQUIFER TYPE.

samples from alluvial sources. Alluvial aquifers which are at least partially recharged by river waters would be expected to have higher TOC levels. Organic materials deposited along with the alluvial sediments might also impart a significant amount of TOC to alluvial waters.

Table 7 also presents some statistical information regarding TFP yields, which were, on the average, about 50% higher in the alluvial aquifers in comparison to the nonalluvial aquifers. The TFP yields did not vary much, suggesting that the organic matter in Kansas ground waters has somewhat similar characteristics from place to place. When grouped by aquifer type, TFP yields were not

correlated with TOC concentration; the weak correlation ($r = 0.531$) for the entire sample set is an artifact resulting from the combining of different sample populations.

Chlorine demand

Chlorine demand, determined simultaneously with TFP, averaged 2.69 mg/L and ranged from < 0.1 mg/L to 10.6 mg/L, excluding sample 38 (table 3). As shown in table 7, the average chlorine demand was significantly higher for the alluvial aquifer samples than for the samples from consolidated and unconsolidated aquifers. TOC and TFP appear to be weakly correlated with chlorine demand for the grouping of all samples and for samples from alluvial aquifers (table 7), but this is an artifact caused by a cluster of alluvial aquifer samples which contained both high amounts of TOC (and TFP) and high concentrations of ammonium, iron, and manganese.

To determine how well the measured chlorine demand values would compare to those expected on the basis of the chemical constituents present in the samples, the chlorine demand for each sample was calculated using the formula: $5.91(\text{NH}_4^+) + 0.63(\text{Fe}) + 1.29(\text{Mn}) + 8.34(\text{H}_2\text{S}) + \text{TOC}$, where all concentrations are expressed as mg/L. (The first four terms are based on stoichiometry, assuming all of the Fe and Mn present in divalent form.) The average calculated chlorine demand was 6.1 mg/L, substantially higher than the average measured chlorine demand. There are several reasons why this should be so: 1) a few of the raw-water samples, including samples 8, 25, and 27, already had some chlorine in them at the time they were collected; 2) Fe and Mn were not necessarily

TABLE 7—STATISTICAL SUMMARY OF TOC AND TFP DATA BY AQUIFER TYPE.¹

Parameter	All Samples	Alluvial Aquifers (23)	Consolidated Aquifers (14)	Unconsolidated Aquifers (12)
TOC, mg/L	1.03 ± 0.76	1.59 ± 0.76	0.48 ± 0.22	0.65 ± 0.34
TFP, μg/L	46.7 ± 39.5	76.2 ± 37.6	16.3 ± 7.4	25.6 ± 21.1
TFP, μM	0.28 ± 0.25	0.47 ± 0.25	0.10 ± 0.05	0.14 ± 0.09
TFP Yield, μmoles/mgC	0.24 ± 0.07	0.29 ± 0.07	0.20 ± 0.05	0.20 ± 0.04
Percent Cl	61 ± 18	62 ± 19	63 ± 19	56 ± 18
Cl ₂ demand	2.69 ± 3.09	3.70 ± 3.42	2.76 ± 3.19	0.99 ± 1.29
Correlation coefficients:				
TFP, μg/L vs TOC	0.887	0.766	0.875	0.902
TFP, μM vs TOC	0.953	0.911	0.887	0.934
TFP yield vs TOC	0.531	0.187	-0.072	0.360
Cl ₂ demand vs TOC	0.597	0.737	0.095	0.358
Cl ₂ demand vs TFP, μg/L	0.565	0.708	0.201	0.476
Calculated demand vs actual demand	0.853	0.965	0.848	0.906

¹ Excluding THM and Cl₂ data for sample 38, excluding sample 34 from the aquifer types, and excluding Cl₂ demand for samples 47 and 48.

present in a reduced state, because oxygen introduced into the samples during pumping and handling could have oxidized the Fe and Mn prior to chlorination; and 3) some of the H₂S may have escaped by volatilization. Nevertheless, the measured and calculated chlorine demands were strongly correlated for all samples ($r = 0.853$) and for each aquifer type (table 7).

Instantaneous and terminal THM concentrations

Samples from the 31 public water-supply wells were analyzed for terminal and instantaneous THM concentrations (THM and ITHM, respectively), and the results are shown in tables 4 and 5. Additional statistical information is presented in table 8, which includes a separate category for the 21 samples that had a free chlorine residual remaining at the end of the TTHM incubation period (the TTHM results for the other samples were questionable).

The finished-water TOC concentrations were determined on 26 of the 31 ITHM samples. As shown in table 8, the average finished-water and raw-water TOC concentrations were quite similar and raw-water TOC was strongly correlated with finished-water TOC, as would be expected. The raw-water TOC concentration for these samples averaged 1.04 ± 0.74 mg/L, in very close agreement with the raw-water TOC concentration of 1.03 ± 0.76 mg/L for all 50 samples. Hence these samples are a very representative subset.

The average ITHM concentration for all 31 samples was only $6.95 \mu\text{g/L}$, and the average ratio of ITHM to TFP was only 11%. Similarly, for the 21 TTHM samples having a free chlorine residual, the average ratio of ITHM to TTHM was only 19%. Hence, the concentration of THMs in the finished water generally represented only a small fraction of the THM concentration to which the consumers have been exposed. ITHM concentrations were only weakly correlated with TOC ($r = 0.433$), reflecting the strong influence of other factors, such as temperature, reaction time, pH, and chlorine dosage, on the initial rate of THM formation.

The mean TTHM concentration was $35.6 \pm 37.0 \mu\text{g/L}$. Since the TTHM incubation conditions (4 days at 25°C [77°F]) were probably, in most cases, a bit more severe than those actually present in the distribution system, the TTHM values represent a conservative estimate of the THM concentrations actually present in the distribution system.

The TTHM concentrations were strongly correlated with TOC ($r = 0.819$) and very strongly correlated with TFP ($r = 0.926$), as would be expected when the THM formation reaction is allowed to go to completion in the presence of excess free chlorine. Hence, TOC and TFP appear to be useful as predictors of distribution system THM concentrations. However, the average ratio of TTHM to TFP (based on 21 samples) was only 78%. The

difference is readily attributable to the more extreme conditions (pH and chlorine dosage) of the TFP analysis. A pH of 8.2 was used for the TFP analysis, whereas the average pH of the raw water was 7.1 (table 5), and the average free chlorine residual in the TFP samples was undoubtedly a bit higher than in the TTHM samples. Clearly, it would be better to simulate conditions in the distribution system if the goal is to predict the distribution system THM concentrations; however, the TFP analysis provides a superior basis for comparisons among water sources, which was a major goal of this study.

TOC as a function of depth

TOC is generally expected to decrease with depth due to adsorption and biodegradation of organic matter as the water percolates downward through the sediments. Also, wells screened closer to the ground level are generally more susceptible to contamination by high-TOC surface water percolating into the shallow ground water through cracks, fissures, permeable deposits, or poorly constructed wells. Therefore, the data were examined to see if there might be a relationship between TOC concentration and the depth of the top of the well screen, the mid-depth of the well screen, or the depth of the top of the well screen below the water table. A statistical summary of this examination is presented in table 9, and fig. 5 shows TOC, as a function of aquifer type, versus the depth of the top of the well screen.

As shown in table 9, TOC was weakly correlated with depth when considering all of the samples or only those from consolidated aquifers, but there was no correlation between TOC and depth for the alluvial aquifers. This was

TABLE 8—STATISTICAL SUMMARY OF ITHM AND TTHM DATA.

Parameter	All (31) Samples	Selected Samples ¹
Raw water TOC, mg/L	1.04 ± 0.74^2	0.93 ± 0.69^2
Finished water TOC, mg/L	1.09 ± 0.77^2	0.86 ± 0.67^2
ITHM, $\mu\text{g/L}$	6.95 ± 16	9.78 ± 18.9
TTHM, $\mu\text{g/L}$	—	35.6 ± 37.0
ITHM/TTHM	—	0.19 ± 0.15
ITHM/TFP	0.11 ± 0.13^3	0.15 ± 0.14^3
TTHM/TFP	—	0.78 ± 0.41^3
Correlation coefficients:		
ITHM vs TOC ⁴	0.433	0.658
TTHM vs TOC ⁴	—	0.819
TTHM vs TFP	—	0.926 ³
TOC, Finished vs Raw	0.822^2	0.944^2

¹ Those 21 samples, excluding sample 5, for which the TTHM sample had a free chlorine residual at the end of the incubation period.

² Excluding samples 1, 3, 4, 49, and 50, for which finished water TOC was not determined.

³ Excluding sample 38

⁴ Finished water TOC

true whether the depth was measured to the top of the screen, to mid-depth, or from the water table to the top of the screen. A close examination of fig. 5 reveals that the weak correlations for the consolidated aquifers are really artifacts due to a data cluster associated with the very deep open-hole wells (the six deepest wells). Similarly, the weak correlations for all of the samples are attributable to the combining of two different populations; the alluvial aquifers had, on the average, much higher TOC values than the other types and their top-of-screen depths were all less than 80 ft (24 m). The curvilinear relationship shown in fig. 5 suggests that an exponential curve might better fit the data, and indeed the correlation coefficient for a semilogarithmic plot was higher (-0.593), but this too is attributable to the combining of two different populations of aquifers. Thus, it can be concluded that there is a general trend of decreasing TOC with depth, but only because alluvial aquifers tend to be shallow and high in TOC.

Aquifer classification by water type

Fig. 6 is a modified Piper diagram summarizing the geochemical composition of the samples. Water-type assignments were made according to dominant contributions ($>50\%$) of particular ions to the total milliequivalents per liter of cations or anions in solution. Samples not dominated by a particular cation or anion were designated as "Mix" types. A majority (27) of the samples were Ca-HCO_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 also were Ca-HCO_3 type waters.

There does not appear to be any significant relationship between TOC and water type. The five Ca-Mix waters had TOC levels greater than 1.0 mg/L , ranging from 1.02 to 2.14 mg/L , but four of these samples were

from alluvial aquifers. The Mix-Mix , Mix-HCO_3 , and Ca-SO_4 waters all had TOC concentrations close to or less than the median concentration (0.8 mg/L), but only one of these samples came from an alluvial aquifer. Na-Cl type waters had TOC concentrations ranging from 0.36 to 1.20 mg/L .

Summary of geochemical data by aquifer type

A simple statistical analysis of the geochemical data according to aquifer type is presented in table 11. Inspection of the means and medians reveals that the mean and median concentration of every constituent was higher in the alluvial aquifers than in the consolidated and unconsolidated aquifers, with only three minor exceptions: 1) the mean and median pH values were slightly lower for the alluvial aquifers (meaning that the hydrogen ion concentration was actually higher); 2) the median NO_3^- concentration was highest for the unconsolidated samples; and 3) the median ammonium concentration was highest for the

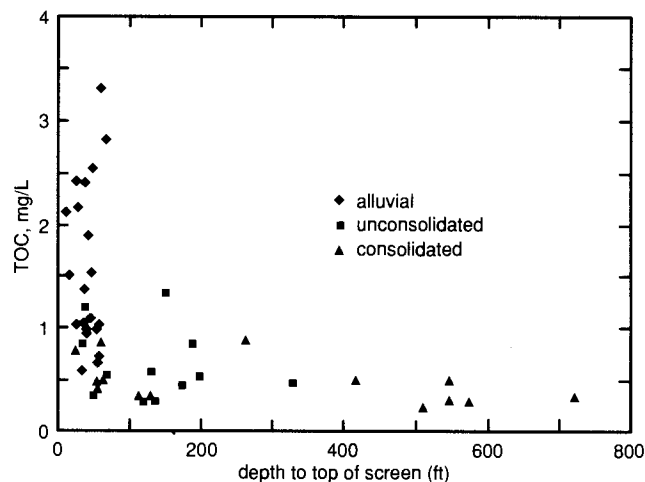


FIGURE 5—TOC AS A FUNCTION OF DEPTH TO THE TOP OF THE WELL SCREEN.

TABLE 9—CORRELATION OF TOC AND WELL DEPTH.

	Linear Regression Correlation Coefficient ¹			
	All Samples	Alluvial Aquifers	Consolidated Aquifers	Unconsolidated Aquifers
TOC vs depth to top of screen	-0.455(48)	-0.008(22)	-0.540(14)	-0.215(12)
TOC vs mid depth of well screen	-0.443(48)	-0.060(22)	-0.582(14)	-0.249(12)
TOC vs depth from water table to top of screen	-0.377(46)	+0.014(21)	-0.550(13)	-0.414(12)

¹ The number of samples included in the correlation is shown in parentheses (the necessary data were unavailable for several wells).

consolidated aquifers. Hydrogen sulfide was excluded from the data summary, because only four samples contained a detectable amount, but all four came from deep open-hole wells in consolidated aquifers.

Specific conductance, calcium, bicarbonate, sulfate, chloride, barium, iron, and manganese were, on the average, present in substantially higher concentrations in the alluvial aquifers. Hence, these parameters would be expected to be correlated (associated) with TOC even where no causal relationship exists. For this reason, it was necessary to examine the relationship between TOC and the inorganic constituents for each individual type of aquifer, as described in the following section.

The consolidated-aquifer samples were, on the average, quite similar to the unconsolidated samples; however, the consolidated aquifer samples had slightly higher concentrations of the majority of constituents, especially bicarbonate, sulfate, and iron.

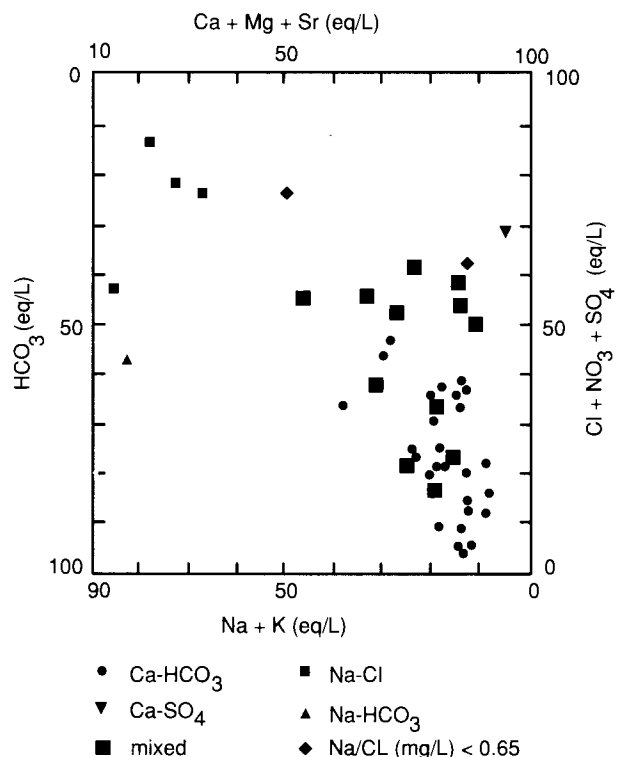


FIGURE 6 (right)—MODIFIED PIPER DIAGRAM SHOWING STUDY SAMPLES.

TABLE 10—Classification of aquifers by water type.

Sample	Aquifer*	TOC(mg/L)	Sample	Aquifer	TOC(mg/L)
Ca-HCO₃ Type Waters			Ca-Mix Type Waters		
1	Kansas(A)	0.69	8	Republican(A)	1.37
2	Missouri(A)	3.31	25	Ogallala(U)	1.34
3	Missouri(A)	2.56	30	Walnut(A)	1.54
4	Pennsylvanian(C)	0.36	43	Solomon(A)	1.02
6	Kansas(A)	1.04	47**	Neosho(A)	2.14
7	Smoky Hill(A)	1.90			
9	Republican(A)	2.19	Mix-Mix Type Waters		
10	Solomon(A)	1.03	12	Dakota(C)	0.41
11	Smoky Hill(A)	1.90	27	Ogallala(U)	0.47
13	Equus Beds(U)	0.31	39	Arbuckle(C)	0.31
14	Equus Beds(U)	0.30			
15	Equus Beds(U)	0.85	Mix-HCO₃ Type Waters		
16	Arkansas(A)	1.52	24	Ogallala(U)	0.52
19	Glacial(U)	0.45	26	Cimarron(A)	0.72
20	Missouri(A)	2.84	35	Permian(C)	0.88
22	Glacial(U)	0.58	36	Arbuckle(C)	0.27
23	Glacial(U)	0.83	38	Arbuckle(C)	0.29
28	Big Bend(U)	0.55	50	Arbuckle(C)	0.48
29	Dakota(C)	0.49			
31	Pawnee(A)	1.00	Na-HCO₃ Type Waters		
32	Smoky Hill(A)	2.43	18	Dakota(C)	0.87
37	Arbuckle(C)	0.21	34	Pleistocene(U)	0.50
40	Solomon(A)	0.98			
42	Saline(A)	1.10	Na-Cl Type Waters		
44	Permian(C)	0.50	5	Pennsylvanian(C)	0.48
48	Pennsylvanian(C)	0.37	17**	Arkansas(A)	1.06
49	Neosho(A)	2.45	21	Glacial(U)	1.20
Ca-SO₄ Type Waters			33	Cimarron(A)	0.60
45	Permian(C)	0.80	46	Big Bend(U)	0.36

* A = alluvial, C = consolidated, U = unconsolidated

** The ratio of Na to Cl in mg/L is less than 0.65.

Correlation of TOC and inorganic constituents

The data were statistically analyzed to reveal any significant geochemical relationships that might exist between TOC and various inorganic constituents. As shown in table 12, only a few of the correlations were statistically significant, and most of the statistically significant correlations were artifacts due to the combining of different populations (e.g., TOC versus Ca, Mg, hardness, K, and HCO_3^- for all 50 samples) or to the presence of outliers (e.g., TOC versus HCO_3^- or Ba for the alluvial aquifers and TOC versus NO_3^- for the unconsolidated aquifers). Upon closer inspection, the only potentially significant relationships were those involving NH_4^+ , Fe, and Mn.

Figs. 7 and 8 show NH_4^+ and Fe + Mn, respectively, as a function of TOC concentration for the alluvial aquifers. In each case, there is a subset of samples having an elevated concentration of NH_4^+ or Fe + Mn in which the concentration is linearly related to TOC. The correlation of Fe + Mn with TOC was especially strong ($r = 0.991$) for alluvial aquifer samples having a concentration of Fe + Mn greater than 1,000 $\mu\text{g/L}$ (table 12 and fig. 8). Interestingly, the subsets of samples high in NH_4^+ and high in Fe + Mn are virtually identical, i.e. each of the alluvial aquifer samples having an NH_4^+ concentration greater than 0.1 mg/L also had an Fe + Mn concentration greater than 1,000 $\mu\text{g/L}$. Also, for the alluvial aquifer samples having > 0.1 mg/L of NH_4^+ , NH_4^+ is linearly correlated to both Fe + Mn ($r =$

0.893) and to TOC ($r = 0.845$) when sample 43 is excluded as an outlier. Sample 43 had a high NH_4^+ concentration (1.0 mg/L) relative to its TOC concentration of 1.02 mg/L and, unlike the other high ammonium samples, it contained much more Mn than Fe. Sample 20 was not plotted in fig. 8, due to its excessive concentrations of Fe and Mn, but this sample had the highest concentration of NH_4^+ (1.5 mg/L) among all the samples.

These results reveal two distinct populations of alluvial aquifers: one having elevated concentrations of NH_4^+ , Fe, and Mn, and the other having low concentrations of these constituents. Presumably, the former population is associated with reducing (anoxic or anaerobic) conditions, under which iron and manganese were solubilized and the NH_4^+ released by biological activity could not be oxidized to nitrate. The TOC values of both populations vary over about the same range, but those for the population having high concentrations of NH_4^+ , Fe, and Mn are linearly related to those constituents. There are several possible explanations for this relationship:

1) Under more reducing conditions, higher concentrations of TOC may occur due to the decreased energy available to the microorganisms metabolizing the organic matter;

2) Increased TOC may be associated with the active microbial populations metabolizing Fe, Mn, and NH_4^+ ; and

3) Higher concentrations of TOC may correspond to higher concentrations of Fe and Mn due to complexation of Fe and Mn by organic matter (and perhaps these complexes stimulate increased biological activity causing NH_4^+ to rise as well).

TABLE 11—SUMMARY OF GEOCHEMICAL DATA BY AQUIFER TYPE.

Constituent, units	All Aquifers (50)		Alluvial (23)		Consolidated (14)		Unconsolidated (12)	
	Mean \pm SD	Median	Mean \pm SD	Median	Mean \pm SD	Median	Mean \pm SD	Median
Field pH, pH units	7.08 \pm 0.25	7.10	7.01 \pm 0.17	6.95	7.17 \pm 0.30	7.23	7.07 \pm 0.28	7.10
Field Spec. Cond., $\mu\text{mhos/cm}$	956 \pm 584	810	1130 \pm 677	950	826 \pm 447	690	777 \pm 495	668
Ca, mg/L	100 \pm 55	90	132 \pm 40	126	77 \pm 69	63	70 \pm 20	71
Mg, mg/L	21 \pm 11	19	25 \pm 10	26	21 \pm 13	20	16 \pm 8	14
Na, mg/L	72 \pm 105	34	75 \pm 129	35	67 \pm 80	27	69 \pm 90	29
K, mg/L	4.7 \pm 3.2	4.4	6.3 \pm 3.6	5.4	3.3 \pm 2.2	2.5	3.4 \pm 1.8	3.1
Sr, mg/L	1.0 \pm 0.8	0.8	1.1 \pm 0.7	0.9	1.0 \pm 1.3	0.7	0.8 \pm 0.4	0.6
HCO_3^- , mg/L	340 \pm 110	350	399 \pm 104	385	305 \pm 90	325	274 \pm 95	237
SO_4^{2-} , mg/L	97 \pm 118	68	124 \pm 102	95	92 \pm 174	40	51 \pm 44	35
Cl^- , mg/L	80 \pm 150	30	96 \pm 192	43	56 \pm 73	24	78 \pm 139	21
NO_3^- , mg/L	13.6 \pm 28.3	4.1	18 \pm 40	3.3	6.4 \pm 11.0	0.1	14 \pm 12	14
NH_4^+ , mg/L	0.3 \pm 0.3	0.1	0.4 \pm 0.4	0.1	0.3 \pm 0.3	0.2	0.1 \pm 0.1	0.05
Ba, $\mu\text{g/L}^*$	186 \pm 191	131	256 \pm 239	193	139 \pm 151	145	126 \pm 67	126
Fe, $\mu\text{g/L}^*$	1258 \pm 2887	122	2384 \pm 3972	464	499 \pm 1128	125	183 \pm 280	22
Mn, $\mu\text{g/L}^*$	240 \pm 495	14	489 \pm 658	276	13 \pm 15	5	66 \pm 123	2

* Excluding sample #20

TABLE 12—CORRELATION OF TOC AND INORGANIC CONSTITUENTS.

Constituent	Linear Regression Correlation Coefficient			
	All Aquifers (n=50)	Alluvial Aquifers (n=23)	Consolidated Aquifers (n=14)	Unconsolidated Aquifers (n=12)
pH	-0.175	0.178	0.121	-0.409
Specific Conductance	0.063	-0.294	0.457	0.008
Ca, mg/L	0.420**	0.061	0.337	-0.244
Mg, mg/L	0.290*	0.149	0.236	0.370
Hardness, mg/L as CaCO ₃	0.419**	0.101	0.327	0.007
Na, mg/L	-0.149	-0.328	0.263	0.012
K, mg/L	0.428**	0.203	-0.026	0.006
Sr, mg/L	0.131	-0.179	0.390	0.546*
HCO ₃ ⁻ , mg/L	0.565**	0.507*	0.520*	-0.196
SO ₄ ²⁻ , mg/L	0.057	-0.353	0.436	0.151
Cl ⁻ , mg/L	-0.116	-0.334	0.021	0.042
NO ₃ ⁻ , mg/L	0.150	0.013	0.184	0.594*
NH ₄ ⁺ , mg/L	0.500**	0.600**	0.183	0.395
NH ₄ ⁺ , mg/L ¹	0.736**	0.676*	0.594	—
Ba, µg/L ²	0.580**	0.681**	-0.132	-0.381
Fe, µg/L ²	0.648**	0.669**	0.049	-0.044
Mn, µg/L ²	0.449**	0.216	0.065	0.110
Fe + Mn, µg/L ³	0.966**	0.991**	—	—

* Statistically significant at the 5% level of significance

** Statistically significant at the 1% level of significance

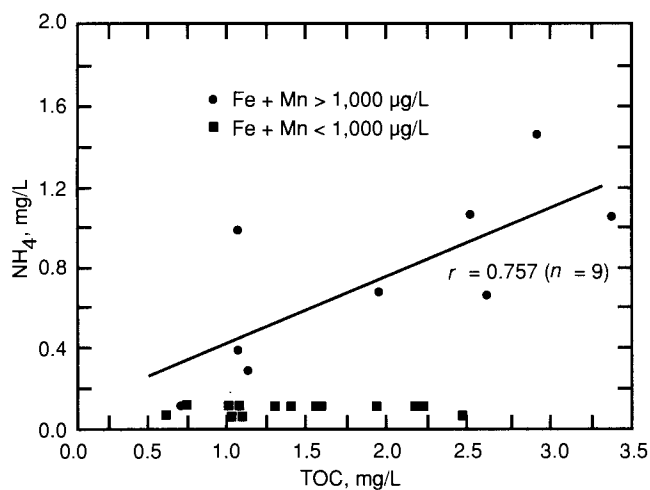
¹ With values ≤ 0.1 mg/L excluded (n = 19, 8, 9, and 2, respectively)² Excluding sample #20³ Excluding sample #20 and values < 1000 mg/L (n = 9, 8, 1, and 0, respectively)

FIGURE 7—AMMONIUM AS A FUNCTION OF TOC for alluvial aquifer samples.

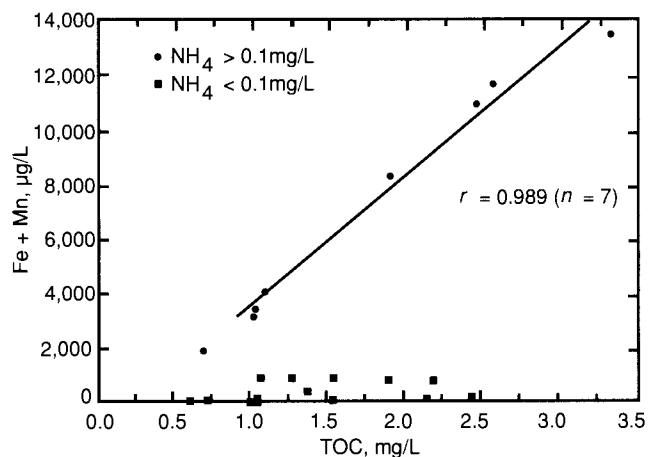


FIGURE 8—FE + MN AS A FUNCTION OF TOC FOR ALLUVIAL AQUIFER SAMPLES.

In any event, these relationships are strong enough and interesting enough to merit further investigation, especially in view of the fact that all of the constituents involved pose significant problems in regard to treatment of potable water supplies.

Implications for THM control in Kansas

The current federal MCL for THMs for utilities serving more than 10,000 persons is 100 µg/L. The Kansas Department of Health and Environment (KDHE) also has applied this requirement to all new supplies and to small systems (serving less than 10,000 people) undergoing plant modifications. The federal standard is expected to be lowered, perhaps substantially, when the new standards for disinfection byproducts are released in the near future. Approximately 8% of the study samples had TFPs greater than 100 µg/L (the present MCL for THMs), but 56% had TFPs greater than 25 µg/L and 90% had TFPs greater than 10 µg/L. Hence, many water-supply systems using ground waters in Kansas might have difficulty in meeting a substantially lower THM limit.

The highest TFP concentrations were found in samples from alluvial aquifers, so it is clear that utilities using waters from alluvial sources would be the most greatly affected by a lower THM limit. Since many communities in Kansas, especially eastern Kansas, are largely dependent on alluvial aquifers as sources for public water supplies, special attention should be given to monitoring and control of THM concentrations in drinking-water supplies derived from these aquifers.

The four major alternatives to controlling THMs include 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. 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, since the latter does not form THMs. In Kansas, a 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 chlorine is not as strong a disinfectant as free chlorine. There are several other advantages associated with combined chlorine: 1) it is 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 lower dosages of chlorine for waters already containing substantial concentrations of ammonium.

The use of combined chlorine in water supplies should only be implemented by those having adequate knowledge of the chemistry of chlorine and ammonium and the reactions between them, so that maximum disinfection can be achieved with minimum THM formation and a minimum of taste and odor problems. It also is important that any change in disinfection practice be carefully monitored to ensure that the microbial quality of the drinking water is not compromised.

The data also bear significant implications with regard to monitoring of water supplies for compliance with the THM regulations. Since TFP and TOC are very strongly correlated, TOC could be used as a surrogate measure of THM formation potential, and ground-water supplies having low concentrations of TOC could be exempted from monitoring for THMs. Also, because there was a strong correlation between the TFP and TTHM concentrations (with the former being generally higher), TFP analyses conducted in a centralized laboratory could be used as a substitute for TTHM analyses. The relationship between TOC and NH_4^+ , Fe, and Mn suggests that alluvial aquifers having high concentrations of Fe, Mn, and NH_4^+ should receive the most immediate attention and closer monitoring.

Summary and conclusions

Samples were collected from 50 different wells, each associated with a particular major aquifer system in Kansas, including a number of alluvial sources. The samples were analyzed for TOC, TFP, and an array of inorganic chemical constituents. In addition, the 31 samples from public water supplies were analyzed to determine their ITHM and TTHM concentrations.

The mean and median TOC concentrations were 1.03 and 0.84 mg/L, while the mean and median TFP concentrations were 46.7 and 30.6 µg/L, respectively. The mean TFP yield was 0.242 ± 0.07 µmol/mg of TOC, and the TFP concentration in micromoles per liter was very strongly correlated ($r = 0.953$) with TOC. Only 8% of the samples had a TFP concentration exceeding the present MCL for THMs of 100 µg/L, but 56% exceeded 25 µg/L

and 90% exceeded 10 µg/L, suggesting that many Kansas water supply systems using ground water might have difficulty meeting a substantially lower THM standard.

The average ITHM concentration was only 6.95 µg/L, while the average TTHM concentration was 35.6 µg/L. Hence, only a small fraction of the THM concentration to which consumers might be exposed is formed prior to distribution. For the 21 TTHM samples having a free chlorine residual at the end of the incubation period, TTHM was strongly correlated to both TOC ($r = 0.819$) and TFP ($r = 0.926$), suggesting that either of these might be a good surrogate measure for TTHM.

TOC (and TFP) appeared to be unrelated to aquifer (well-screen) depth, but both were clearly much higher in the alluvial aquifers, all of which were located at relatively

shallow depths. TOC also appeared to be unrelated to the inorganic constituents present in the samples, with the exception of a subset of samples from alluvial aquifers having high concentrations of NH_4^+ (>0.1 mg/L) and Fe + Mn ($>1,000$ $\mu\text{g/L}$). For these samples, TOC was strongly correlated with both NH_4^+ ($r = 0.676$) and Fe + Mn ($r = 0.991$). These relationships merit further investigation, since all of the constituents involved pose problems for water-treatment plants.

In Kansas, efforts to control THMs in public water supplies from ground-water sources should focus primarily

on alluvial aquifers, especially those having high concentrations of TOC, NH_4^+ , Fe, and Mn. TOC and TFP may be useful surrogates for TTHM and could be used as a basis for exemptions from monitoring requirements. Use of combined chlorine appears to be the simplest and most effective means of limiting THM formation, but the necessary precautions must be taken to ensure that the microbial quality of the drinking-water supply is not compromised.

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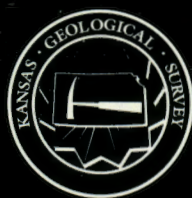
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McCauley, James R., *geologist*
McClain, Thomas J., *geohydrologist; special assistant to Director*
McElwee, Carl D., *hydrologist/geophysicist*
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Cunningham, Chris
Cunningham, Kevin
Deephungton, Kai
Feng, Zhaodong
Fillmore, Rob
French, John, Jr.
Garth, Frenchette
Givens, Walter
Gress, Karen
Hegde, Amita
Hudnall, Bill
Huffman, Daniel
Huynh, Derek
Jian, Xiaodong
Johnson, Ganay M.
Kau, Chee Yee (Gerald)

Kay, Stephen
Keiswetter, Dean
Kirshen, Deborah S.
Koillipillai, Andrew
Kollmeyer, Barbara
Kumarajeeva, Dinesh
Lambert, Michael W.
Lee, Siew P.
Liu, Wenzhi
Magana, Sara
Mason, Larry
Mayne, John F.
McDanel, Scott
Meehan, Terry
Michnick, Steven M.
Neal, Patrice
O'Keefe, Valerie P.
Park, Choon
Pourtakdoust, Seid
Roth, Steven
Roumas, Steve
Rowlands, Beth
Ruby, Jennifer
Schreifels, Michael
Schroff, Scott

Shamsnia, Saeed
Sommerville, Samuel
Sun, Hao
Valinske, Karen L.
Wade, Alan
Westlake, Courtney
Whitmore, John
Wong, Racky K.
Wong, Kwok
Woods, John J.
Xia, Jianghai
Yilmaz, Yahya
Young, David



Kansas Geological Survey
The University of Kansas
1930 Constant Avenue
Campus West
Lawrence, Kansas 66047